

Synthesis, Characterization and Evaluation of two Copolymer of Alkyl methacrylate and Styrene as Viscosity index improvers for Lubricating Oil

Abdul Halim A-K Mohammed¹, Mohammad.R.Ahmed², Maysoun.A.hamad³

1(Cheical Engineering department, College of Engineering / Baghdad University, Iraq Country)

2(Department of Chemistry, College of science / Baghdad University, Iraq)

3(Department of Chemistry, College of science / Baghdad University, Iraq)

Abstract : Dodecylmethacrylate and Octadecylmethacrylate and copolymers of each of them with styrene were synthesized and characterized. All products were characterized by FTIR, ¹H-NMR and gel permeation chromatography (GPC). Viscosity index improver (VII) properties were tested with additive doped base oil in terms of viscosity index (VI) of the base oil – additive blends. VI values of the additive doped base oils depend on the concentration and the alkyl chain length of VI improvers and it was found that the efficiency of the prepared compound as viscosity index improvers increases with increasing the concentration of additives and with the alkyl chain length increasing.

Keywords - Viscosity index, base oils, blended oils, viscosity index improvers.

I. INTRODUCTION

Lubricant base oil is the basic building block of a lubricant. The performance of lubricant base oils is often governed by their rheological properties such as low temperature fluidity, viscosity and viscosity temperature relationship. For example, to provide an effective performance at low as well as at high temperatures, an engine lubricant should have good low temperature fluidity and minimal variations of its viscosity with temperature [1, 2].

In order to obtain commercial lubricant oils, base oils are mixed with additives which particularize them or enhance some of their characteristics. The role of these products is to minimize wearing caused by physical friction, by separating moving surfaces with the formation of a thin resistant layer. This gives them a wide range of applications on a variety of mechanical equipments, namely industrial, automotive, marine, railroads and hydraulic systems [3- 5].

For example, Pour point depressants (PPDs) are a chemical additive that lowers the pour point of the base oil so that the performance of the base oil at low temperatures can be improved, oxidation inhibitors reduce the oxidation of the lubricants, and antiwear agents impart abrasion-proof properties to the lubricants. viscosity index improvers (VIIs) are a kind of chemical additive that optimize the viscosity of the lubricants under high and low-temperature conditions,

The most frequently used method for comparing the variation of viscosity with temperature between different oils by calculation of dimensionless numbers, known as the viscosity index (VI). So VI is an indicator of the change in viscosity as the temperature is changed [6].

The oils whose viscosities have a high sensitivity to temperature have a low VI and those whose viscosities have low sensitivity to temperature have a high VI [7]. High VI oils are generally preferred for

use in most lubricants. The viscosity of any fluid changes with temperature, increasing as the temperature is decreased, and decreasing as the temperature is increased.

VIIIs can be blended into oils to increase VI. VIIIs are long-chain, high molecular weight polymers that are added to lubricating oils to make them conform more closely to the ideal by increasing the relative viscosity of them more at high temperatures than they do at low temperatures [8-13]. Although a few non-polymeric substances such as metallic soaps exhibit VI improving properties [14, 15].

II. MATERIALS AND METHODS

2.1 Instruments.

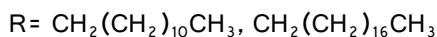
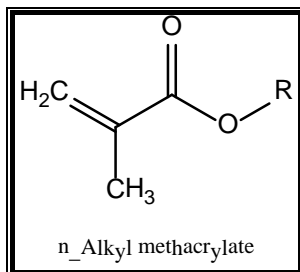
1. The FTIR spectra in the range (4000–400) cm^{-1} were recorded on a Shimadzu FTIR-8400S Spectrophotometer as KBr disc.
2. ^1H NMR spectrum (solvent DMSO) was recorded on a 300 MHz spectrometer with TMS as internal standard.
3. The molecular weights of the prepared compounds were determined by using gel permeation chromatography. Polystyrene calibration in High performance liquid chromatography (HPLC), Model: Smart Line System, Made in Holland by KNOUER Company.
4. Rotary evaporator Yamato RE 510 was used for evaporating solutions.

2.2 Materials.

Alcohols were purchased from Aldrich. MMA was used in the synthesis of the methacrylate monomers, it was purchased from Aldrich and It was washed several times with an aqueous solution of NaOH (5% m/V) then washed by distilled water. It was dried with anhydrous magnesium sulfate and distilled. Sulfuric acid and hydroquinone were also purchased from Aldrich and were used as the catalyst and inhibitor, respectively, in the synthesis of the methacrylate monomers. Benzoyl peroxide (BZP) was the initiator and was purchased from Aldrich .

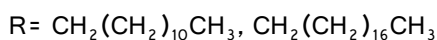
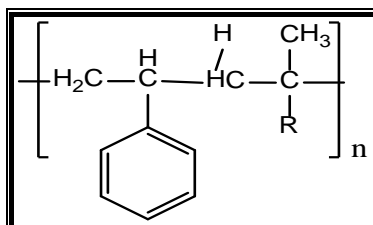
The base oil was obtained from Midland Refineries Company .The properties of base lubricating oil (60 stocks) were listed in Table 1.

2.3 Synthesis of the n-alkyl methacrylate monomer (M1 and M2).



n-alkyl methacrylate monomers were prepared by the esterification of MMA with dodecyl and octadecyl alcohol in the presence of sulfuric acid as the catalyst and hydroquinone as the inhibitor. alcohol and MMA were added (1: 2 molar ratio) in addition to sulfuric acid (0.5 mol %) and hydroquinone (3 wt % compared with MMA) in a round flask connected to a cooling condenser and fitted in a controlled heating mantle. These materials were heated to 90°C for 24 h with constant stirring to react with each other. Afterward, the unreacted MMA was removed from the product under reduced pressure until distillation was complete. The synthesized products were purified to remove the unreacted alcohol and hydroquinone. The purification process were Performed by pouring the products into an excess volume of methanol, which was about two times as much as the synthesized product, and separating the product from the methanol. The desired monomers, dodecyl methacrylate and octadecyl methacrylate (M1 and M2), was obtained through this procedure.

2.4 Synthesis of poly n_alkyl (metha)acrylate _co_ styrene (P1 and P2).



The polymerization was taken place in a three necked round bottom flask equipped with a stirrer, condenser, thermometer, inlet for the introduction of nitrogen gas and a dropping funnel. In the flask, a desired mass of M1 was placed and initiator (BZP) followed by the desired mass of styrene which was added drop wise for 1h in the presence of toluene as solvent. The reaction carried out at 80°C for 6 h. After the complete reaction, the reaction mixture was poured into cold methanol with stirring to precipitate the polymer. The polymer was purified by precipitation of its chloroform solution by

methanol to produce (P1). Polymer (P2) was prepared and purified under the same conditions using M2 instead of M1. The physical properties of the polymers (P1 and P2) are recorded in the table 2.

2.5 Formulation of oil blends.

Blends of the prepared (P1 and P2) were prepared by dissolving each polymer in (60 stock) base oil with continuous stirring at 60°C for 1 hour. The prepared 60 stock oil blends contain different dosages (0.5, 1%, 2%, and 3% wt) of each of synthesized additives. The Blends were evaluated as viscosity index improvers.

2.6 Measurements.

2.6.1 Spectroscopic measurements

Spectroscopic IR spectra were recorded on a Shimadzu FT-IR 8400s spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm^{-1} . HNMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer. DMSO was used as solvent and TMS as reference material. Gel Permeation Chromatography, Model: Smart Line System, Made in Holland by KNOUER Company.

2.6.2 Evaluation of the prepared additives as Viscosity Index Improver in lube oil.

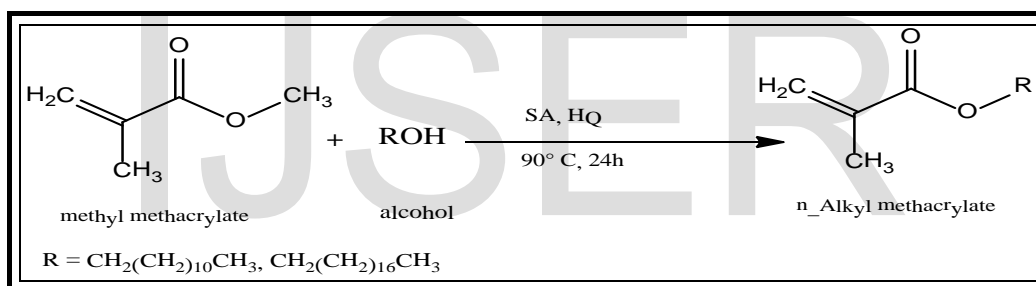
The various blends were prepared by using one type of lubricating oil (60 stock). Viscosities and the viscosity index (VI) of this oil were calculated according to ASTM D2270. The kinematic viscosity of the oil containing the tested polymer was determined at (40°C and 100°C). Different concentrations between (0.5 to 3 wt%) were used to study the effect of concentration on VI of the additive-doped lube oil. All of the experimental data as mentioned above were noted by taking an average of three experimental results under identical conditions.

III. RESULTS AND DISCUSSION

3.1 Synthesis.

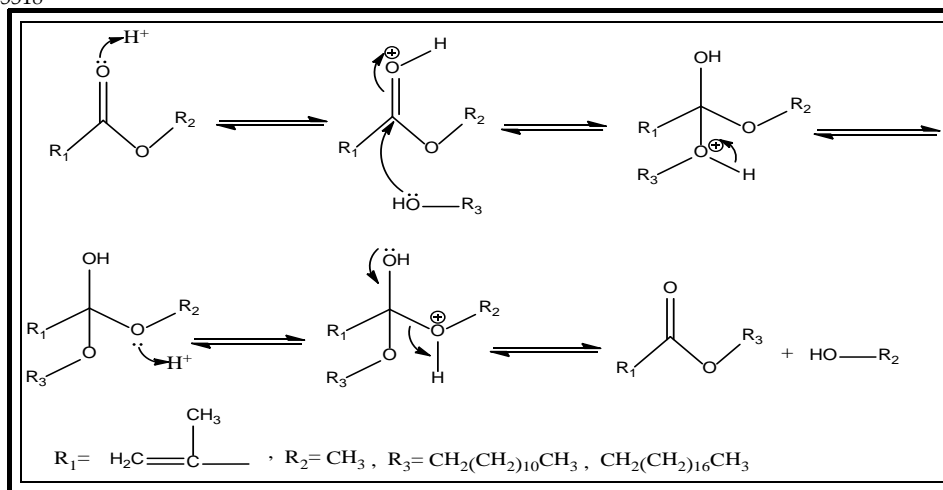
3.1.1 Synthesis of the n-alkyl methacrylate monomer (M1 and M2).

The synthesis of n-alkyl methacrylate monomer (M1 and M2) was performed following an experimental procedure had previously studied according to which the product was obtained using a large excess of MMA and of hydroquinone, in order to avoid the polymerization of the monomers. The first synthesis of M1 was carried out by the esterification of MMA with dodecyl alcohol, as described in the experimental section. After synthesis for 24 h, a light yellow liquid was obtained, which contained a mixture of M1, residual MMA, and hydroquinone. The residual MMA was distilled off under reduced pressure through a gradual increase in the temperature until the distillation was completed. The presence of MMA with the produced monomer hindered the purification of it; therefore the complete removal of MMA was essential before the purification step. The purification of M1 was performed with methanol to remove hydroquinone. Pure M1, which was a light yellow liquid, was obtained through several purification steps. The other monomer M2 was obtained and purified by the same procedures used for M1. The purification of M2 was more efficient because of its high melting point which was around room temperature. The molten product was submitted to various extractions with small portions of methanol to remove the inhibitor and the unreacted octadecyl alcohol. A pure waxy white solid product of M2 was obtained. The reaction synthesis of methacrylate monomers M1 and M2 is shown in the Equation 1.



Equation 1

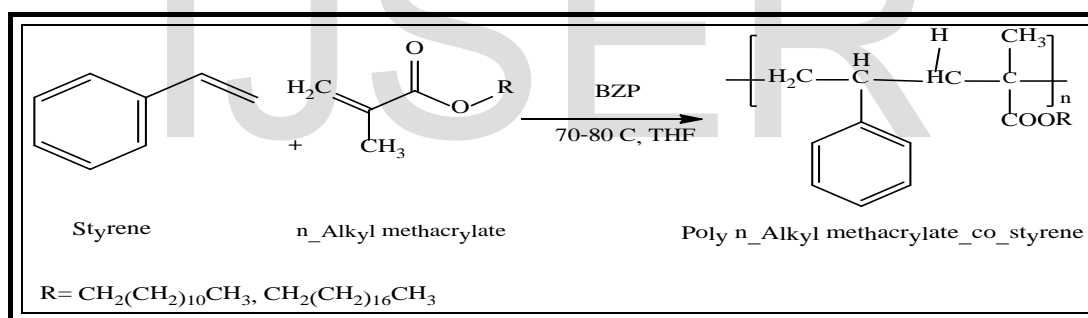
Transesterification mechanism involves a protonation of the carbonyl by the acid which makes it more activated toward a nucleophilic attack by the incoming alkoxide (R_3O^-) to give a tetrahedral intermediate, followed by proton transfer then removal of the leaving group step to produce the transesterified product (R_1COOR_3). Scheme 1 describes a general mechanism for the formation of these monomers (M1 and M2)



Scheme 1 General mechanism of transesterification reaction to synthesis monomers (M1 and M2).

3.1.2 Synthesis of poly n_alkyl (metha)acrylate _co_ styrene (P1 and P2).

Copolymers P1 and P2 were synthesized by free-radical polymerization of synthesized monomers M1 and M2 with styrene. The chemical structures of the synthesized copolymers were studied by infrared spectrometry and ¹HNMR. The reaction Synthesis of copolymers P1 and P2 is shown in the Equation 1.



Equation 2

3.2 Spectroscopic analysis.

For the two monomers M1 and M2 (figures 1 and 2), the stretching bands for the ester groups C=O and C-O-C appeared at 1730-1735 cm⁻¹ and 1150-1275 cm⁻¹, respectively. Methylene group (-CH = CH-) band appear near 1465 cm⁻¹, while, -C-H aliphatic bands appear near 2843 cm⁻¹ and 2955 cm⁻¹. The peak of methyl group appears at range 1371-1466 cm⁻¹.

IR spectra of the Copolymers P1 and P2 (figures 3 and 4) showed absorption band near 1733-1730 cm⁻¹ due to the ester carbonyl group stretching vibration. The broad peak ranging from 1262 to

1120cm^{-1} appeared owing to the ester C-O-C stretching vibration with the absorption bands at 977 and 713 cm^{-1} were due to the bending of C-H bond and band on region $(3200\text{ to }2900)\text{ cm}^{-1}$ due to the stretching vibrations of aromatic C-H. The major FTIR absorptions (cm^{-1}) of synthesized monomers and copolymers were listed in table 3.

$^1\text{H-NMR}$ spectra of the monomers presented in figures 5 and 6 showed a broad singlet near 0.89 ppm was due to methyl groups of alkyl chain. A broad singlet centered at $1.26\text{-}1.35$ ppm due to the proton of $(\text{CH}_2)_n$. A broad singlet centered at $4.01\text{-}4.1$ ppm due to the proton of $-(\text{OCH}_2-)$ group. A singlet between 5.1 and 6 ppm due to vinylic proton in the monomers.

$^1\text{H-NMR}$ spectra of the copolymers P1 and P2 (figures 7 and 8) showed a multiplet centered near 8.1 ppm indicated the presence of aromatic protons of phenyl group. A broad singlet near 4.1 ppm was belonging to the protons of the $-\text{OCH}_2-$ group. The absence of singlet between 5.1 and 6 ppm which indicated the absence of vinylic proton in the copolymer.

3.3 Evaluation of the prepared additives as viscosity index improvers.

3.3.1 The effect of additive Concentration on VI of Lube Oil.

Different concentrations of the prepared additives ranging from 0.5 , 1.00 , 2.00 , and 3.00% by weight were blend with basic lubricant for evaluation viscosity index improver. The result of viscosity at 40°C and 100°C and VI of the blends were presented in table 4.

Figure 9 shows the change in VI of the blends with different prepared additives indifferent concentration. These tables and figures show that the VI increase with percentage of additives increase. The lube oil viscosity decreases as the temperature increased; meanwhile the polymer molecule expands due to the increase in the solvation power, and the size of the micelle increases. This increase in the micelle size counterbalances the reduction of the viscosity of the lube oil and, hence, decreases the changes of viscosity with the temperature of the mixture. The increase of concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution.

Consequently, a high concentration of polymer will impart a higher viscosity index than a low concentration of the same polymer.

3.3.2 The effect of alkyl chains length of the Prepared Additives on viscosity of the oil blends

Figure 10 shows the effect of alkyl chain length of the prepared additives as viscosity index improves on blends at constant percentage of additive. These figures show that the viscosity index of oil blends increases with the alkyl chain length increasing.

IV. Figures and Tables

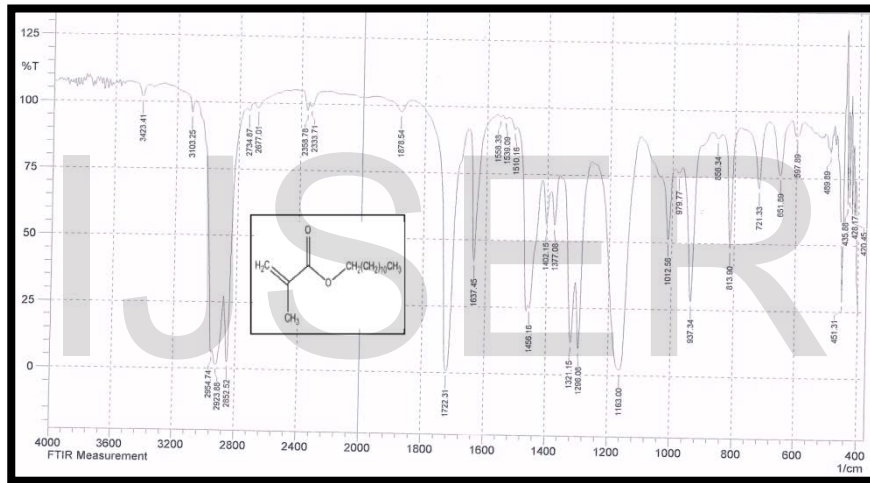


Fig. 1. FTIR spectra for dodecylmethacrylate (M1)

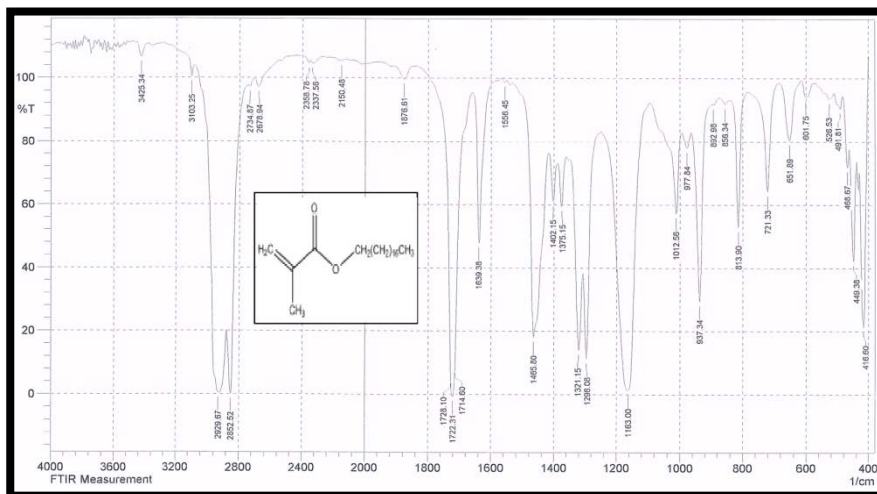


Fig. 2 FTIR spectra for octadecylmethacrylate (M2)

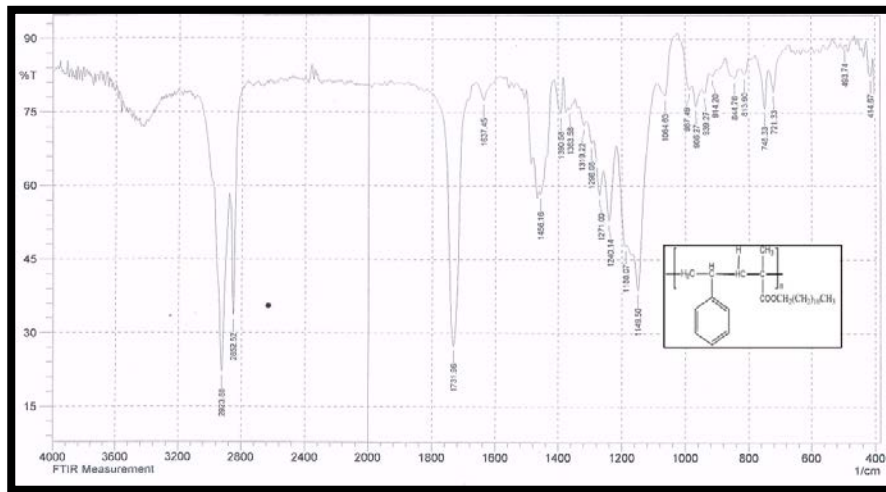


Fig. 3 FTIR spectra for copolymer (P1)

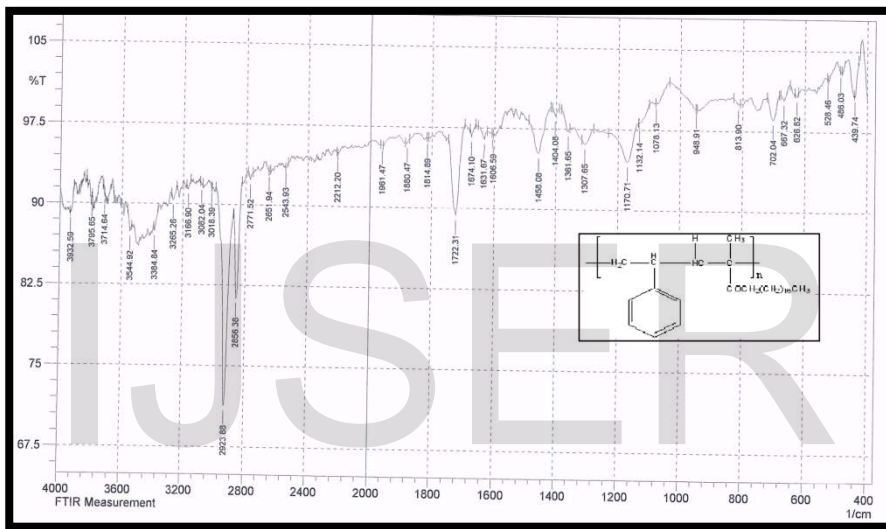


Fig.4 FTIR spectra for for copolymer (P2)

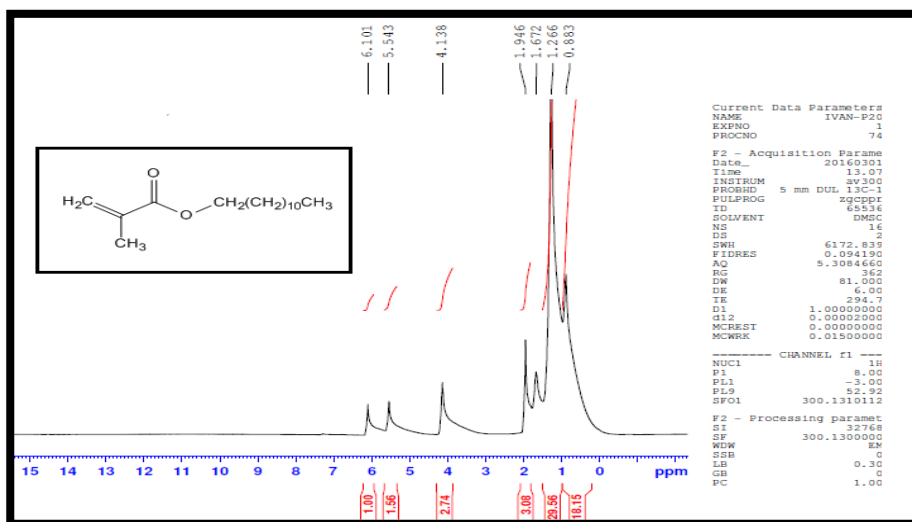


Fig. 5 H^{-1} NMR spectrum for dodecylmethacrylate (M1)

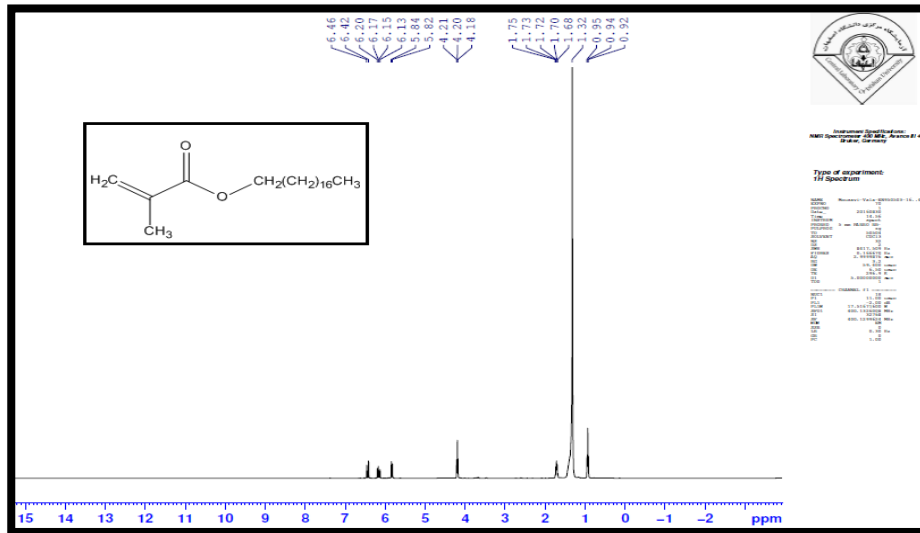


Fig. 6 H^{-1} NMR spectrum for octadecylmethacrylate (M2)

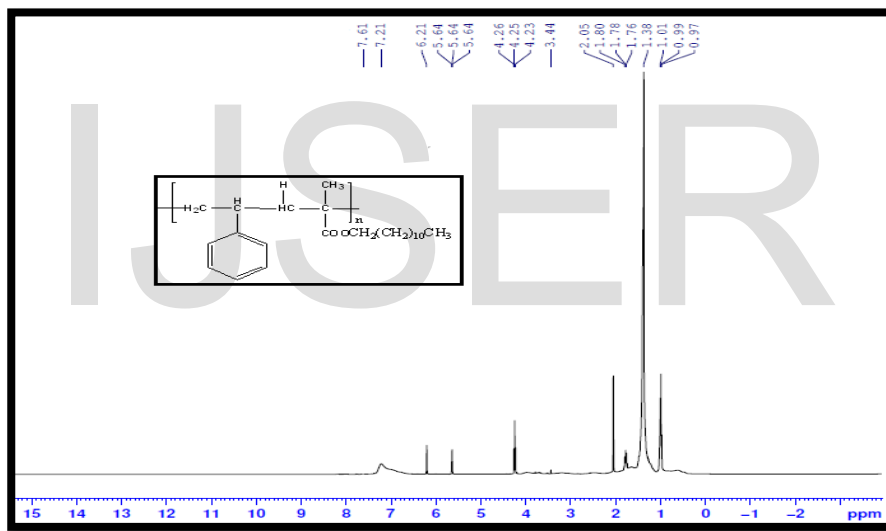


Fig. 7 H^{-1} NMR spectrum for copolymer (P1)

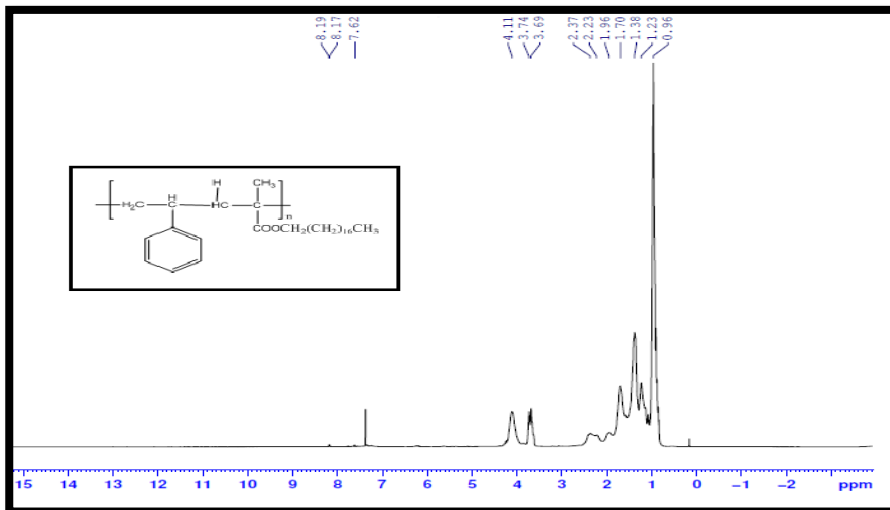


Fig. 8 ¹H NMR spectrum for copolymer (P2)

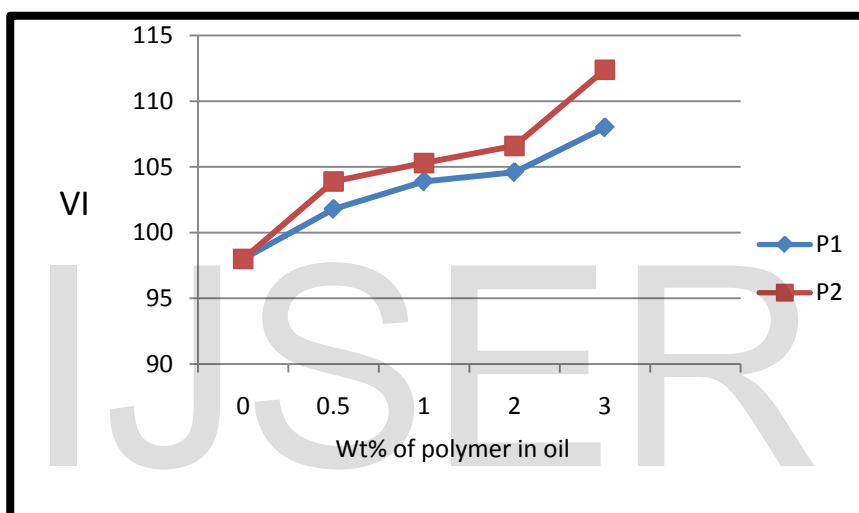


Fig. 9 The effect of concentration of additives (P1 and P2) on VI of base oil

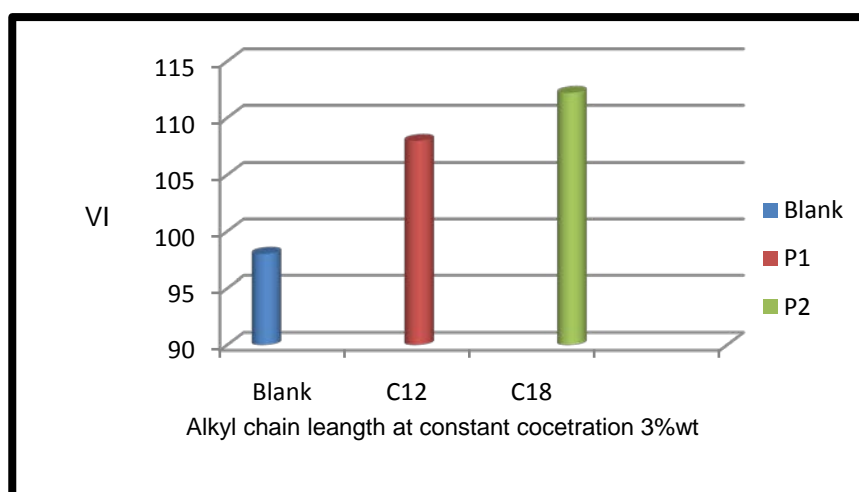


Fig. 10 Effect of alkyl chain length of (P1 and P2) additives on VI of lube oil

Table 1 Properties of base lubricating oil 60 stock

No.	Specification	Value	Standard Test
			Method
1.	Kinematic viscosity at 40 °C, cSt (mm ² /s)	70.34	ASTM-D 445
2.	Kinematic viscosity at 100 °C, cSt (mm ² /s)	8.86	ASTM-D 445
3.	Viscosity index	98	ASTM D- 2270
4.	Specific gravity at 60/60°F	0.884	ASTM D-4052
5.	Pour point , C°	-6	ASTM D-97
6.	Flash Point, C°	246	ASTM D-92
7.	Color	3.5	ASTM D-1500

Table 2 physical properties of the polymers (P1 and P2)

Comp. No.	Common name	Molar weight		PDI (M _w /M _n)	Colour	Yield (%)
		M _w	M _n			
P1	Poly dodecyl methacrylate_co_ Styrene	48,810	23,95	2.03	white	77
P2	Poly octadecyl methacrylate_co_ Styrene	104,44	53,33	2.00	white	68

Table 3 Major FTIR absorptions (cm⁻¹) of synthesized monomers and copolymers

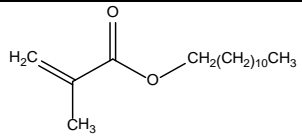
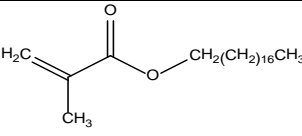
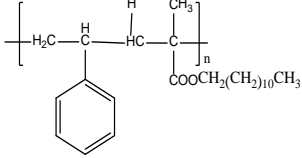
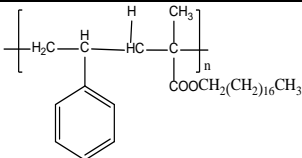
Comp. No.	Chemical structure	vCH ₃	vCH ₂ aliphatic	vCH ₂ aromatic	v(C=O)	v(C=C) aliph. arom.	v(C-O-C)
M1		as.2954	vas.2923 vs.2852	---	1722	aliph. 1456	sy.1012 as.1163
M2		as.2929	vas.2927 vs.2852	---	1722	aliph. 1465	sy. 1012 as. 1163
P1		as.2956	as.2927 sy.2854	3147	1728	arom. 1512	sy. 1254 as. 1154
P2		as.2958	as.2923 sy.2854	3283	1722	arom. 1550	sy. 1224 as. 1164

Table 4 Experimental kinematic viscosity in (cSt) at 40°C & 100°C and VI Values of Polymers (P1 and 2) Doped in Base Oil

Conc. (wt%)	P1			P2		
	40°C	100°C	VI	40°C	100°C	VI
0	70.34	8.86	98	70.34	8.86	98
0.5	71.658	9.1104	101.8	74.206	9.4429	103.9
1	74.206	9.4429	103.9	73.920	9.503	105.3
2	75.210	9.430	104.6	74.210	9.4430	106.6
3	76.810	9.8530	108	47.81	7.2637	112.2

V. CONCLUSION

1. Copolymers were synthesized and elucidated by using FTIR, 1H-NMR and GPC.

2. The prepared Copolymers were evaluated as lubricating oil additives (viscosity index improvers).
3. It was found that the viscosity index of lube oil increase by increasing the concentration of polymer.
4. It was found that the viscosity index of oil blends increases with the alkyl chain length increasing .

VI. References

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