

Synthesis, Characterization and Performance Evaluation of Poly Octadecyl Methacrylate and Poly Octadecyl Methacrylate-Co-Methylmethacrylate as an Additive for Lubricating Oil

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Abstract: Methacrylate polymers are widely used as additives in lubricating oils, as pour point depressants and viscosity index improvers. In this study, homopolymer of Octadecyl methacrylate and Octadecyl methacrylate_co_methylmethacrylate with molar ratios of 30:70, 50:50 and 70:30 were synthesized and characterized. The free radical polymerization was carried out at 70 °C in toluene solvent and 2, 2'-azobisisobutyronitrile (AIBN) as initiator. All products were characterized by FTIR, ¹H-NMR and gel permeation chromatography (GPC). The obtained results showed the efficacy of the additives as viscosity index improvers, pour point depressants. The pour points of most base oils containing each polymer decreased compared to that of the pure base oil. 70% octadecyl methacrylate units showed a 15C° reduction in their pour points, thus establishing the large efficiency of the products synthesized in this work. The efficiencies of the prepared compounds as viscosity index improvers were investigated. It was found that the efficiency of the prepared compound as viscosity index improvers increases with increasing the concentration of additives.

Keywords: Lubricant oil, Additives, Poly alkyl methacrylate, pour point, Viscosity Index Improvers

I. Introduction

Lubricant base oils are formed by (350C° and 500C°) petroleum fractions obtained by crude oil distillation under atmospheric pressure; it contains saturate hydrocarbons and lower amounts of aromatic and naphthenic compounds [1,2]. The majority of crude oils contain a large amount of oil waxes called paraffin. The base oil also has substantial amounts of paraffin because it is produced in the refining process of crude oil. Paraffins are mixtures of hydrocarbons with linear chains that contain mainly 20–40 carbon atoms in addition to alkanes with branched and cyclic [3]. Additives are synthetic chemicals that can improve or add performances to lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life.

Most of the important types of additive are Viscosity Index Improvers (VII) commonly known as viscosity modifier [4] and pour point depressant (PPD) [5]. Viscosity index improvers are long chain, high molecular weight polymers that function by causing the relative viscosity of an oil to increase more at high temperatures than at low temperatures [6], this result is due to a change in the polymer's physical configuration with increasing temperature of the mixture. It is postulated that in cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect [7]. Viscosity index (VI) is an arbitrary number which indicates the resistance of a lubricant to viscosity change with temperature [8], Performance of viscosity index improvers depends on the behavior of the polymer molecules in the oil, Polymer solubility, molecular weight, and resistance to shear degradation are the most important parameters [9].

The pour point (PP) of lubricating oil is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions [10]. The paraffin crystals grow as the temperature decreases, creating a crystalline net which begins to trap the molecules of liquid hydrocarbon until the oil cannot flow. The temperature at which this happens is called pour point [11].

In order to improve this pour point, (PPD_s) are suitably added to the oil [12]. Various theories have been suggested for the mechanism of action of PPDs, among them adsorption, co crystallization, nucleation, and improved wax solubility are widely accepted [13]. Copolymers containing alkyl methacrylate structural units are some of the most widely used additives for lubricating mineral oils they improve the viscosity temperature behavior and at the same time, lower significantly the pour point of base oils [14].

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. ¹HNMR spectrum (solvent DMSO) was recorded on a 300 MHz spectrometer with TMS as internal standard in chemistry department, Al-Albayat University, Jordan.
3. The molecular weights of the prepared compounds were determined by using gel permeation chromatography (GPC; Waters 600 E). polystyrene calibration in HPLC grade THF (0.4% w/v) at 40c°.
4. Rotary evaporator Yamato RE 510 was used for evaporating solutions.

2.2 Materials.

Octadecanol alcohol was purchased from Aldrich. MMA was used in the synthesis of the methacrylate monomer and polymethacrylate polymer, 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. a,a-0-Azobisisobutyronitrile (AIBN) 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 Octadecyl methacrylate monomer (ODMA).

Octadecyl methacrylate monomer was prepared by the esterification of MMA with Octadecyl alcohol in the presence of sulfuric acid as the catalyst and hydroquinone as the inhibitor. Octadecanol 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 90C° for 18 h with constant stirring to react with each other. Afterward, the unreacted MMA was removed from the product under reduced pressure through a gradual increase in the temperature until distillation was complete. The synthesized product was purified to remove the unreacted octadecanol and hydroquinone. The purification process were Performed by pouring the product 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 monomer, octadecyl methacrylate (ODMA), was obtained through this procedure.

2.4 Preparation of homopolymer of Octadecyl methacrylate (PODMA).

Homopolymer of Octadecyl methacrylate (PODMA) was prepared by free-radical polymerization of the synthesized monomer. The polymerization was carried out in a two-necked round flask equipped with a cooling condenser, controlled heating mantle, and inlet for nitrogen gas. In the flask, desired mass of Octadecyl methacrylate (ODMA) in toluene and the initiator AIBN (1 mol %) was placed. The reaction was carried out at 70C° for 5 h under constant stirring and a nitrogen atmosphere. After completion of the reaction, the reaction mixture was poured into cold methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its chloroform solution by methanol followed by drying under vacuum at 70C° until the weight was constant.

2.5 Preparation of Poly Octadecyl methacrylate-co-methylmethacrylate (PODMMA).

The polymer was prepared by free-radical polymerization of the synthesized monomer ODMA with MMA. ODMA and MMA in toluene were added (at a 7: 3 molar ratio) to a three-necked round flask equipped with a cooling condenser, controlled heating mantle, and inlet for nitrogen gas. AIBN (1 mol %) was used as the initiator. The reaction was carried out at 70C° for 5 h under constant stirring and a nitrogen atmosphere. After completion of the reaction, the toluene was distilled off under reduced pressure. The remaining product was purified in chloroform/ methanol and vacuum-dried at 70C° until the weight was constant. Poly (octadecyl methacrylate-co-methylmethacrylate) (PODMMA) was obtained through this procedure. The different kinds of PODMMA were also obtained by the reaction of ODMA and MMA at 5: 5 and 3: 7 molar ratios.

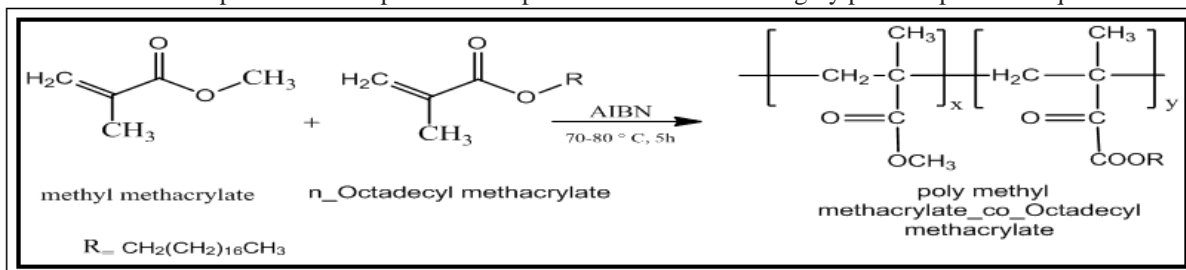
2.6 Measurements.

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 (GPC; Waters 600 E). Polystyrene calibration in HPLC grade THF (0.4% w/v) at 40c°

3.1.3 Synthesis of Poly Octadecyl methacrylate-co-methylmethacrylate (PODMMA)

The copolymerization reaction was performed to produce the poly (octadecyl methacrylate- co-methyl methacrylate) (PODMMA) using an ODMA:MMA feed ratio of 7:3 . Different reactions were performed in order to evaluate the reproducibility of the method. Copolymerization was performed using two other molar feed ratios 3:7 and 5:5 for ODMA: MMA. The copolymerization reaction was performed with AIBN as the initiator of the free-radical reaction in the toluene solvent. After copolymerization for 5 h, the highly viscous liquid dissolved in toluene. The toluene was removed under a reduced pressure, and the product was purified. Because the product was very viscous and solidified easily at room temperature, it was first dissolved in chloroform. Various purification steps were then performed to achieve a highly purified product. Equation 3



Equation 3

3.2 Spectroscopic analysis.

FT-IR spectrum of the (ODMA) exhibited absorption at 1728 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1321 and at 1163 cm^{-1} can be explained owing to the C-O (ester bond) stretching. The peak ranging from $2852\text{-}2922\text{ cm}^{-1}$ was due to the presence of stretching vibration (C-H), and the stretching vibration band for the C=C bond at 1640 cm^{-1} . Figure1

FT-IR spectrum of the (PODMA) exhibited absorption at 1726 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1240 and at 1168 cm^{-1} can be explained owing to the C-O (ester bond) stretching. The peak ranging from $2850\text{-}2920\text{ cm}^{-1}$ was due to the presence of stretching vibration (C-H) with the absence of the stretching vibration band for the C=C bond of the monomer in the 1640 cm^{-1} indicated the formation of polymer. Figure2.

FT-IR spectrum of the (PODMMA) exhibited absorption at 1730 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1269 and at 1151 cm^{-1} can be explained owing to the C-O (ester bond) stretching. The peak ranging from $2850\text{-}2920\text{ cm}^{-1}$ was due to the presence of stretching vibration (C-H) with the absence of the stretching vibration band for the C=C bond of the monomer in the 1640 cm^{-1} indicated the formation of polymer. Figure3.

$^1\text{H-NMR}$ spectra of the (ODMA) showed a broad singlet centered at 1.2 ppm due to the proton of -OCH₂- group; a broad singlet at 0.8 ppm was due to methyl groups of octadecyl chain, a broad singlet centered at 5.5 & 6.1 ppm due to the protons of CH=CH₂ group. Figure4

$^1\text{H-NMR}$ spectra of the (PODMA) showed a broad singlet at 0.9 ppm was due to methyl groups of octadecyl chain, a broad singlet centered at 1.26 ppm , which was caused by the protons attached to carbon atoms on the side chain (CH₂)_n, broad singlet at 3.6 ppm due to the proton of C-CH₃ group, a broad singlet at 4.4 ppm due to the proton of -OCH₂ group. Figure5.

$^1\text{H-NMR}$ spectra of the (PODMMA) showed a broad singlet at 0.89 ppm was due to methyl groups of octadecyl chain, a broad singlet centered at 1.26 ppm , which was caused by the protons attached to carbon atoms on the side chain (CH₂)_n, a broad singlet centered at 3.9 ppm due to the proton of -OCH₂- group, a broad singlet centered at 3.6 ppm due to the proton of -OCH₃ group. Figure6.

3.3 Effect of additive concentration on viscosity index of lube oil.

Different concentrations of the prepared additives ranging from 0.25, 0.5, 1.00, 2.00, and 3.00 % by weight were used to study the effect of the additive concentration on VI; the data are tabulated in Table 3, which indicates that the VI increases with increasing the concentration of the prepared additives in solution. The viscosity of a particular fluid is not constant, however, but varies with temperature. As oil is heated, its viscosity decreases, and becomes thinner. The polymer-oil interaction at low temperature is minimal but increases as the temperature rises. This interaction of the polymer with the base oil at elevated temperatures increases the effective hydrodynamic volume of the polymer, thereby increasing the effective volume fraction of the viscosity modifier. This, in turn, leads to an increase in lubricant viscosity. The increase in the 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 polymer.

3.4 Effect of additive concentration on the pour point of lube oil.

Different concentrations of prepared additives (P_1P_4) ranging from (0.25 to 3.00 %) by weight were tested as pour point depressants and experimental data are tabulated in Table 3, which indicates that the prepared compounds are efficient as pour point depressants and the efficiency increases by decreasing the concentration of the prepared additives. This is explained by that solvation power of any solvent decreases with decreasing temperature and vice versa. This reduction in solvation power becomes more obvious when the molecular weight of the solute and its concentration increases.

IV. Figures And Tables

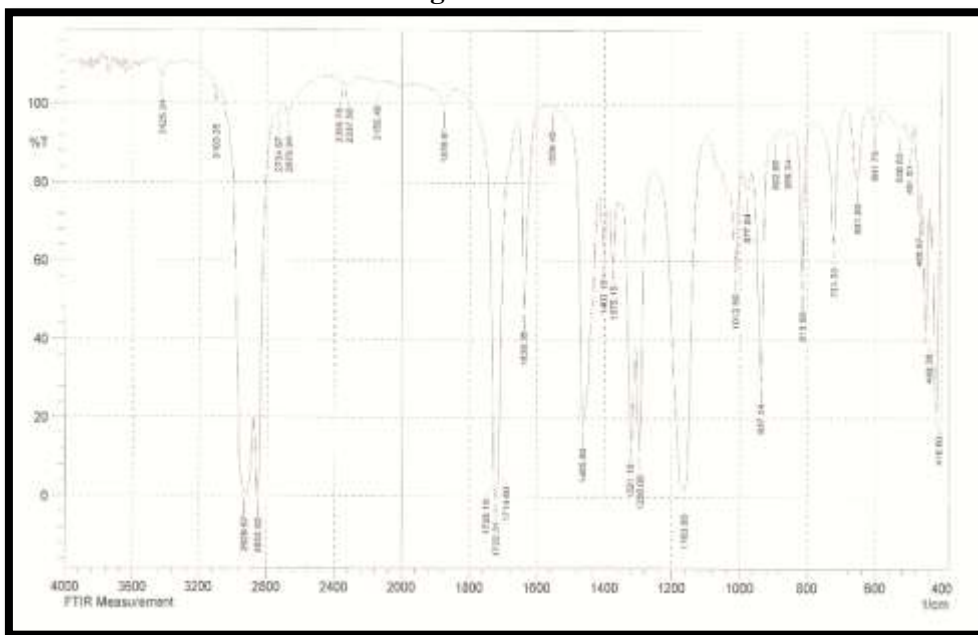


Fig. 1. FTIR spectra for octadecyl methacrylate (ODMA).

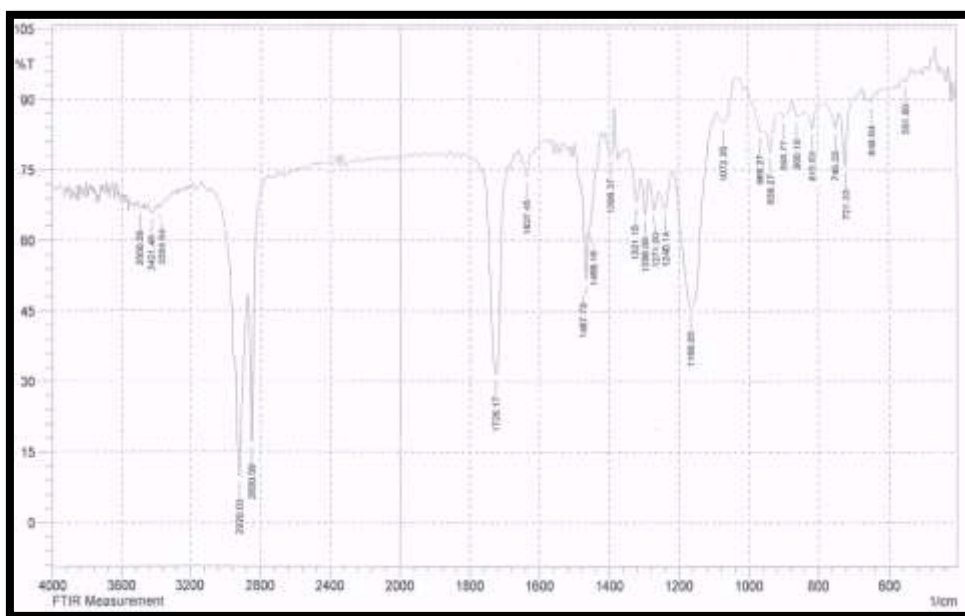


Fig. 2. FTIR spectra (PODMA) polymer.

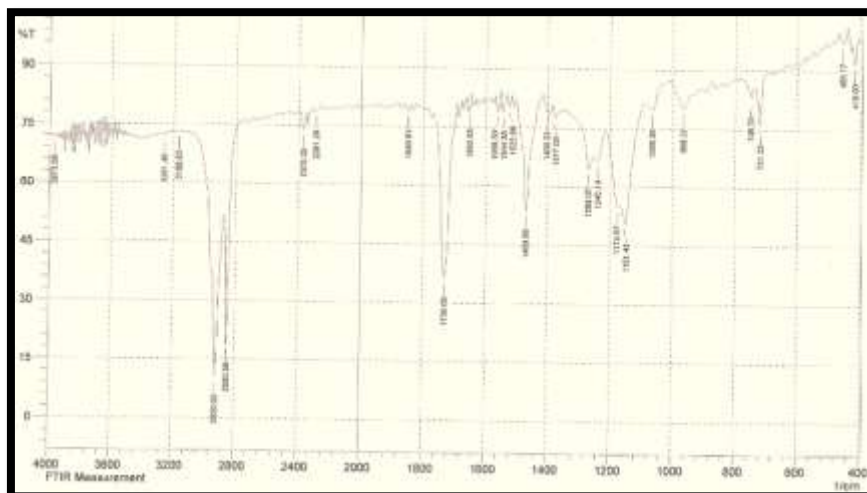


Fig. 3. FTIR spectra (PODMA) polymer.

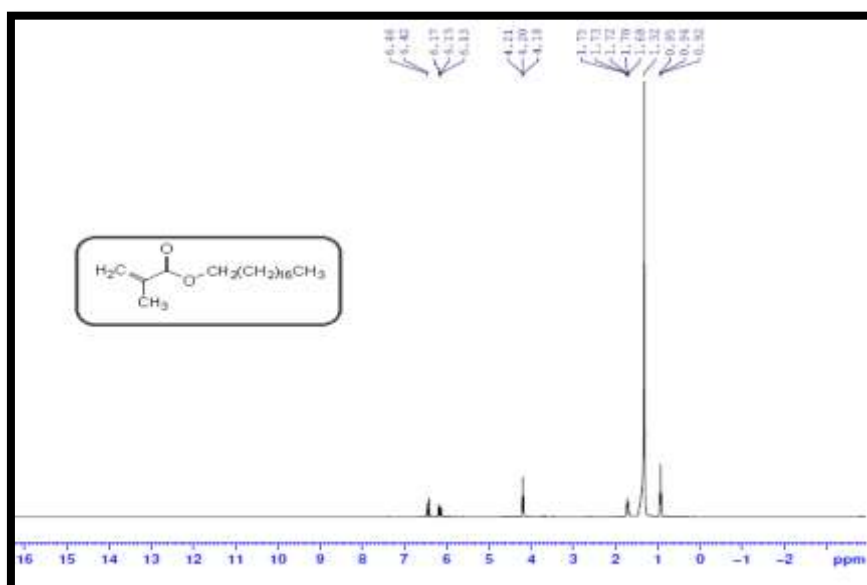


Fig.4 H^1 NMR spectrum for octadecyl methacrylate monomer (ODMA)

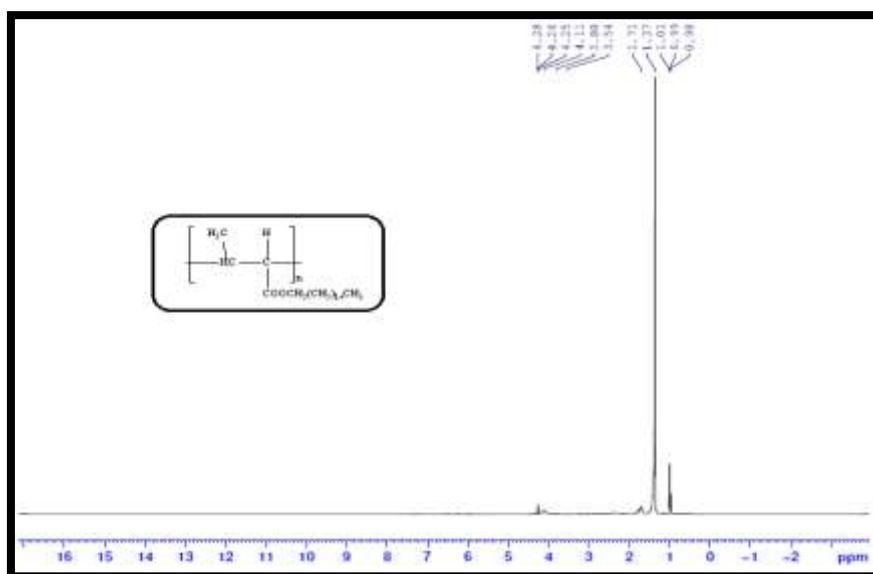


Fig.5. H^1 NMR spectrum for (PODMA) Polymer

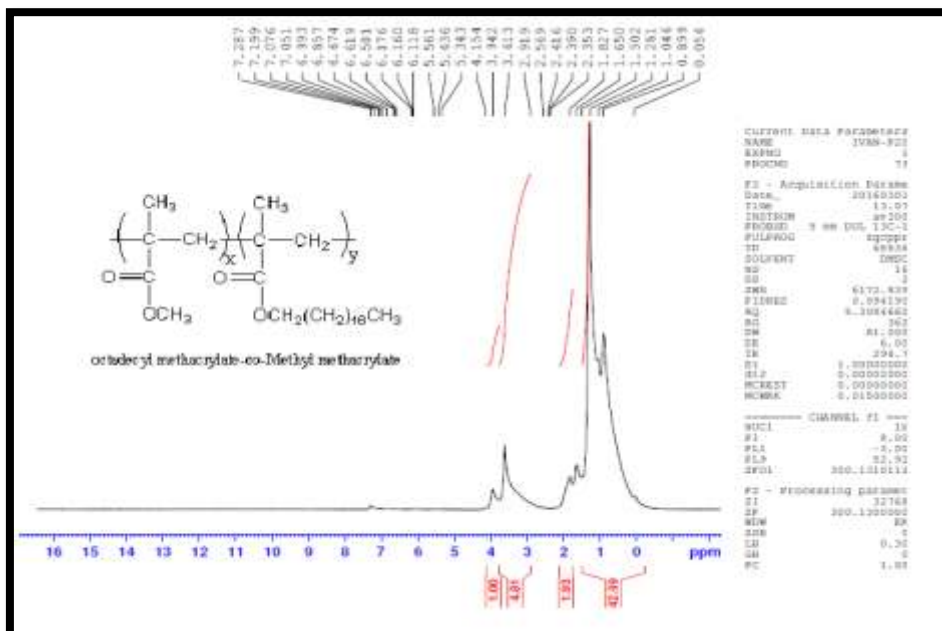


Fig.6. ¹H NMR spectrum for (PODMA) Polymer

Table1. 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 Molar Weight Data and the Average Yield of the Copolymers

Polymers code	Composition (ODMA : MMA)	Molar weight		PDI (M _w /M _n)	Yield (%)
		M _w	M _n		
P ₁	10.0	11,655	14,732	1,264	92
P ₂	7:3	106,446	47,921	2,221	85
P ₃	5:5	75,000	37,000	2.00	80
P ₄	3:7	48,811	23,956	2.038	93

Table 3 Viscosity index and pour point of lube oil treated with the prepared polymers

Polymers code	Viscosity Index (VI)					Pour Point (C°)				
	0.25%	0.5%	1.00%	2.00%	3.00%	0.25%	0.5%	1.00%	2.00%	3.00%
P ₁	100	102.4	106	114	124	-9	-9	-6	-6	-6
P ₂	102.2	104.3	110	130	136.4	-12	-9	-9	-6	-6
P ₃	102.2	102.9	105.3	114	116	-12	-9	-9	-6	-6
P ₄	106	112.4	113.8	130	134.2	-12	-12	-21	-9	-6

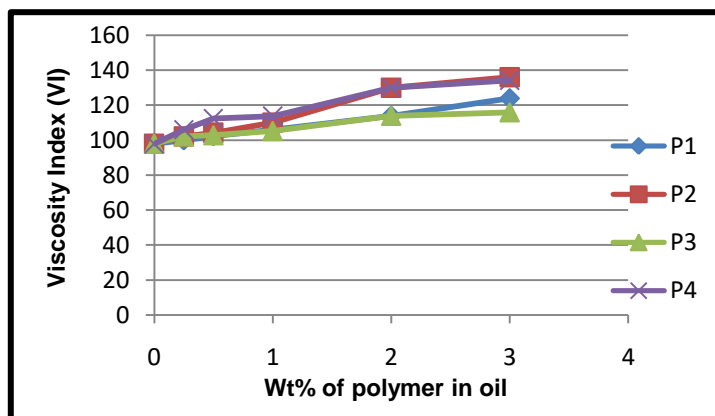


Fig.5. Dependence of Viscosity Index on the concentration of additives in base oil.

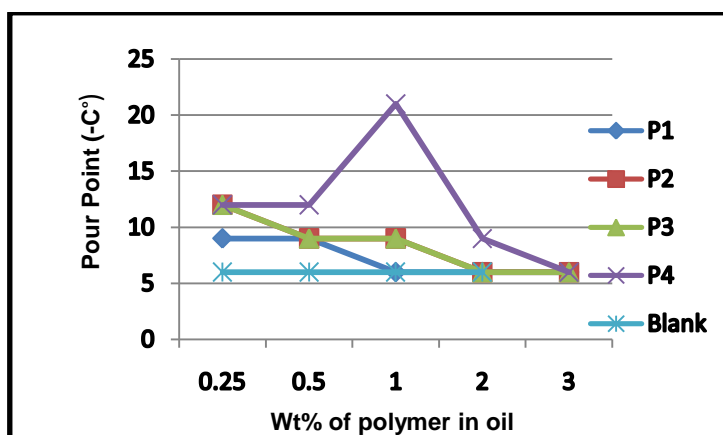


Fig.6. Dependence of our point on the concentration of additives in base oil.

V. Conclusion

1. Polymers were synthesized and elucidated by using FTIR, 1H-NMR and GPC.
2. The prepared polymers were evaluated as lubricating oil additives (pour point depressants and 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 prepared polymers are efficient as pour point depressants and the efficiency increases by decreasing the concentration of the prepared additives, but the polymer P₄ with 1.00%w concentration show high value.

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