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RESEARCH ARTICLE

STUDYING THE RHEOLOGICAL PROPERTIES OF SOME POLYMERIC ADDITIVES BASED ON ACRYLATE ESTER WITH VINYL ACETATE

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ABSTRACT

In the present work, three esters were prepared by esterification of acrylic acid with alcohols having long different alkyl chain length. The structures of the prepared compounds were confirmed by Infra Red Spectroscopy. Three polymeric compounds were prepared by free radical polymerization of the different acrylate ester with vinyl acetate. All the prepared copolymers were soluble in lube oil. The molecular weights of the prepared compounds were determined by Gel Permeation Chromatography. The prepared copolymers were evaluated as viscosity index improvers and study the rheological properties of lube oil upon addition.

INTRODUCTION

Tribology comprises the study of: The characteristics of films of intervening material between contacting bodies and; the consequences of either film failure or absence of a film which is usually manifested by severe friction and wears (Stachowiak and Andrew 2005). Tribology plays an important role in manufacturing. In metal-forming operations. The engine tribologist is required to achieve effective lubrication of all moving engine components. The lubricant is designed to act to prevent direct contact between surfaces in relative mutual motion, and thus reduces both the frictional force between these surfaces and wears (Vaclav and Vesely 1992). Additives can radically change the properties of a lubricant and are essential to its overall performance. Rheology is probably the most important property of any lubricating oil base fluid. The viscosity behavior of a lubricant, depending on oil temperature, pressure, and shear rate, is crucial for its ability to form oil films that reduce friction and wear (Rudnick 1999). The viscosity index (VI) is a useful tool for lubricant users and refiners, since it is a measure of the effect of temperature changes on the viscosity of the oil (Sylvain *et al.*, 2009). The VI increases with increasing the concentration of the copolymer in the solution (Abdel –Azim and Rasha 2001). Large molecules with little branching have a high viscosity index (Sylvain *et al.*, 2009).

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MATERIALS AND METHODS

Esterification of Acrylic Acid with different types of Alcohols

The esters were prepared by reacting 1 mole of acrylic acid with 1 mole of different types of alcohols (1-hexadecanol &1-octadecanol or 1-docosanol). The reactions were carried out in a resin kettle in presence of 0.5% p-toluene sulfonic acid as a catalyst and 0.25% hydroquinone as inhibitor for the polymerization of acrylic acid and xylene as a solvent (to aid water removal). The esterification reactions were carried out under a slow stream of deoxygenated nitrogen; the reaction mixture was agitated using mechanical stirrer at 500 rpm. The reactants which were mixed with an equal weight of xylene were gradually heated from room temperature to 130° C ± 5°C using a well-controlledthermostat (Amal *et al.*, 2011). The extent of reaction was followed by monitoring the amount of liberated water to give products: (hexadecyl acrylate (D) or octadecyl acrylate (E) or docosanyl acrylate (F)).

Purification of Prepared Esters

The prepared esters were purified according to the following procedures:

Suitable amount of charcoal was added to the esters and allowed to reflux for 4 hours and filtered. Unreacted acid was neutralized by 0.5 N sodium hydroxide in separating funnel to

removal of unreacted acid, then washed several times with distilled water to remove any traces of sodium hydroxide then the ester was left overnight on calcium chloride anhydrous to absorb the excess of water. It was then removed by filtration and xylene was removed by distillation. The ester is ready to use in the copolymerization.

Infra-Red Spectroscopic Analysis

I.R Spectra of the synthesized esters were measured by using F.T.I.R. Spectrometer Model Type Mattson- Infinity Series Bench top 961 for the purified esters.

Synthesis of Polymeric Additives Based on Alkylacrylate

Polymericadditives were prepared by free radical copolymerization of vinyl acetate monomer with the prepared esters, the polymerization was carried out in a 4- necked round bottom flask equipped with a stirrer, efficient condenser, thermometer, and an inlet for the introduction of nitrogen, the nitrogen was dried by passing it through silica gel. In the flask was placed 1 mole of the prepared esters and 1 mole of vinyl acetate monomer, the desired weight of initiator (benzoyl peroxide), then heated for 8 hours at 60°C ± 5°C in the presence of toluene as a solvent. When the reaction was completed, the temperature was allowed to reduce to room temperature, then the reaction mixture was poured drop by drop in cooled methanol with continues stirring, filtered off and dried.

Determination of the Mean Molecular Weight of the Prepared Copolymers

Molecular weights of the prepared copolymers were determined by using Gel Permeation Chromatography (GPC), Water 600E.

The solubility test

The solubility of the prepared copolymers was investigated by dissolving the polymer in free additive base oil (SAE 30). In a conical flask, 2 g of the copolymer were added to previously weighed base oil (100g) and the mixture was allowed to stand overnight. This time was enough to procure the required swelling for the polymer. The conical flask was immersed in an oil bath placed on a thermostated hot plate fixed over a magnetic stirrer. The temperature of the oil bath was then raised to 60°C and at this point the mixture was agitated by a Teflon covered magnet for 20 minutes.

Evaluation of the Prepared Copolymers as Lube Oil Additives

The soluble copolymers were evaluated as viscosity index improver for lube oil and rheology using base oil (SAE 30) through the viscosity index test (V.I.) according to the ASTM D-2270-87.The kinematic viscosity of the oil containing the tested copolymer was determined at 40°C and 100°C. Different quantities ranging between 0.00 and $30.00x10^3$ ppm were used to study the effect of copolymer concentration on V.I (Abdel-Azim *et al.,* 2009).

Investigation of Rheological Properties of Lube Oil

Rheological studies were performed on an oil samples using Brookfield Rheometer (Model DV-III+). The following are the specifications of this rheometer:

- Shear Rate (Sec^{-1})
- Shear Stress (N/m^2)
- Viscosity (mPa.s)

Also the effect of temperature increase on the rheological properties of the oil was investigated by using controlled oil path unit attached to the Brookfield Apparatus. Then series of experimental was performed to determine the effect of prepared additives on the rheological properties of the engine oil. To study the effect of additive concentration another series of the experimental was performed using different concentrations starting from (0.25-3.00) % by weight. To illustrate the effect of temperature on the performance of different additives, one fixed concentration was used and the rheological properties were measured at different temperatures (40^oC, 60^oC and 100^oC).

RESULTS AND DISCUSSION

Three esters were prepared via esterification reactions of acrylic acid with C_{16}, C_{18}, and C_{22}alkanols. The IR spectroscopy was used to elucidate the completion of the esterification reactions. All esters (D, E, and F) afford similar I.R spectrum. Figure (1) represented IR spectrum of ester (D) which shows that: No sign for the presence of strong absorption band at 3200 $cm^{-1}$of aliphatic(-OH) group or the characteristic absorption bands of the carboxylic acids. These bands are broad peak extending from 3300 cm^{-1} to 2500 cm^{-1} due to hydrogen bonded (-OH) and the (-CH) stretching vibrations. Appearance of the ester group bands at 1720±10 cm^{-1} and 1250±100 cm^{-1} due to (C=O) and (C – O – C) stretching respectively. The band for methylene group (CH = CH) appear near 1465 cm^{-1}. The bands for methyl group, which appear, near 1370 $cm^{-1}$to 1465 cm^{-1}. The band for (-C– H) aliphatic appears near 2840 cm^{-1}& 2950 cm^{-1}. Disappearance of the strong band at 3200 cm^{-1} and the characteristic bands of (-COOH) group indicate that all hydroxyl and carboxyl groups of alcohols and acids, respectively, were consumed in the esterification reactions. On the other hand, the formation of the bands, which represents the ester group, i.e., (C=O) and (C – O – C) vibration reveals that the esterification reaction is complete. The polymeric additives were prepared by addition polymerization of vinyl acetate and prepared alkyl acrylate. The mean molecular weight of copolymers is given in Table (1) which indicates that the molecular weight of copolymer D is the biggest and the molecular weight of copolymer F is the smallest one.

Efficiency of the prepared compounds as viscosity index improvers

The prepared copolymers were tested for their effectiveness as viscosity index improvers for base oil (SAE-30) according to

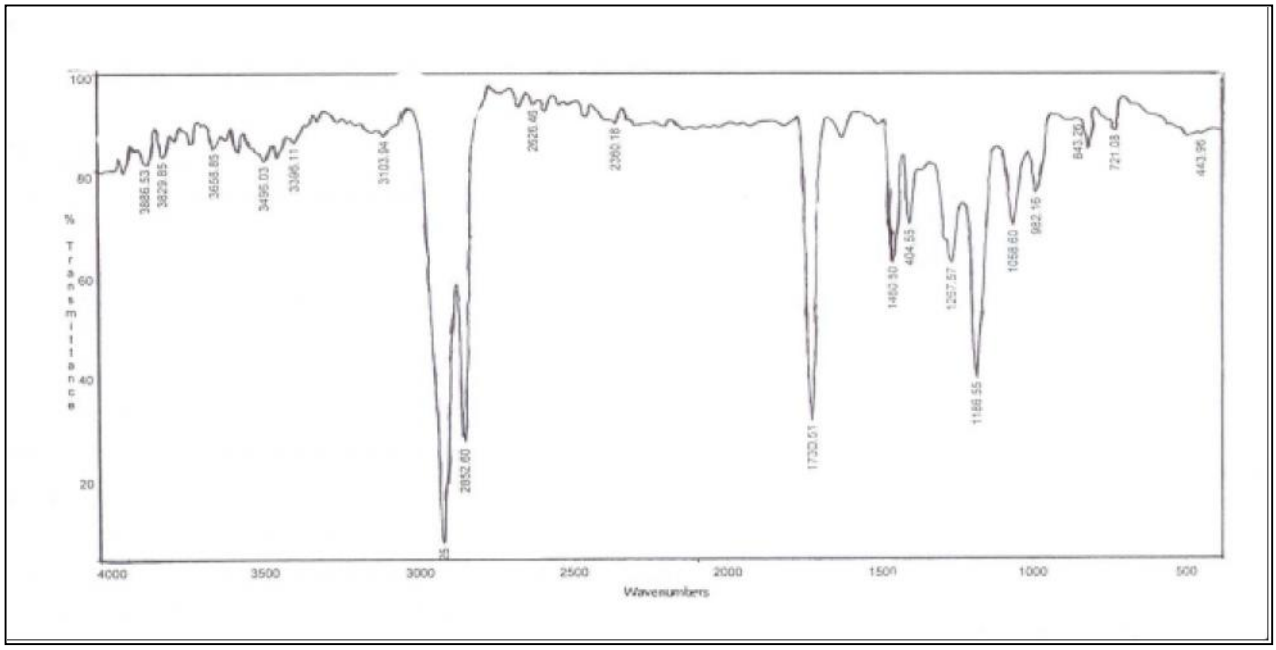

Figure 1. I.R. Spectrum of (D)

ASTMD-2270. In this respect, the kinematic viscosity of the oil doped with different concentrations of the tested additives was determined at 40°C and 100°C.The concentrations were ranging from 0.0 to $3x10^{-3}$ ppm which is used to study the effect of the additives concentration on VI of lube oil. The VI increases with increasing the concentration of the prepared additives in solution as in Table (1) and increases with increasing the mean molecular weight of prepared copolymers as in Figure (2).

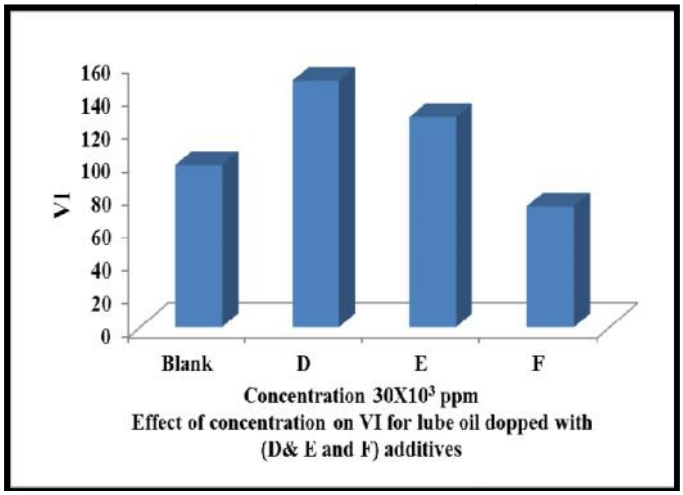

Figure 2. Effect of concentration on VI for Lube oil doped with esters (D, E and F) additives

Table 1.The mean Molecular Weight of the prepared Copolymers

Components	Mean M. wt.
D	283,309
E	251,693
F	220,480

Table 2. Dependence of VI on the concentration of (D, E and F) Additives

Conc. **P**pm ⇦10^{-3}	D	E	F
0.00	98	98	98
2.50	106	103	98
5.00	108	108	100
10.00	121	109	103
20.00	134	120	106
30.00	149	127	108

As the temperature is raised the lube oil viscosity decreases meanwhile the polymer molecule expands, due to the increase in the solvation power and the size of the micelle increases. This increase in micelle size counterbalances the reduction of the viscosity of the lube oil and hence decreases the change of viscosity with temperature of the mixture (Abdel-Azim *et al.*, 2009). The increasing in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution.

Sensitivity of the prepared viscosity modifiers to mechanical stresses

The sensitivity of viscosity index (VI) improvers to clarify this point the sensitivity of VI to addition was calculated in each case from the following equation:

$$S = \frac{C\, d(VI)}{VI\, d(C)} = \frac{d\ ln(VI)}{d\ ln(C)} \qquad (1)$$

Where C……..is the concentration of the polymer, (ppm).

Plots of (ln VI) against (ln C), are given the slopes of the fitted straight lines represent the sensitivity of VI to addition in each case. By studying these figures it is clear that VI is directly proportional with the molecular weight of additives. Physically

this can be attributed to the increase of the friction between oil layers by the increase of the molecular weight. Figures"2, 3"the additive (D) displays the highest sensitivity.

Study of the flow curve of the oil samples

A list of experiments was done using the Brookfield rheometer to examine the flow characteristics of the used oil samples. These oil samples prepared by adding different concentrations (0.25 % up to 3.0 %) of each type of polymer additives to the blank oil (SAE 30) at temperatures (40, 60 and 100^{o}C). The rheological results for E as example were plotted on Figures ″4 - 6" By studying these data were drawn to fit the linear Bingham model in the form:

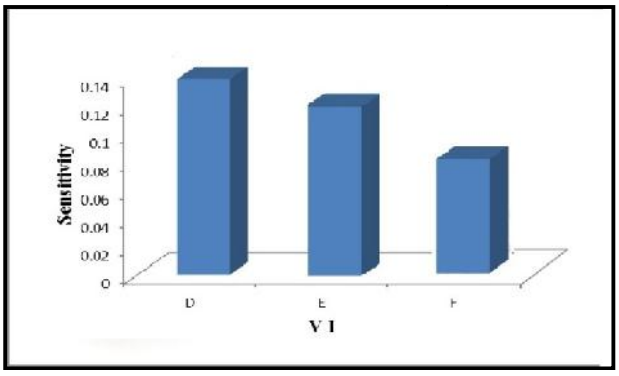

Figure 3. Sensitivity against V.I. for esters (D, E and F) Additives

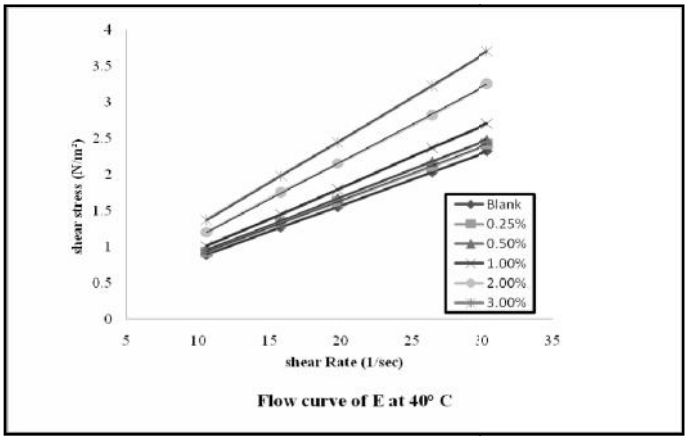

Figure 4. Flow curve of E additive at 40^{o}C

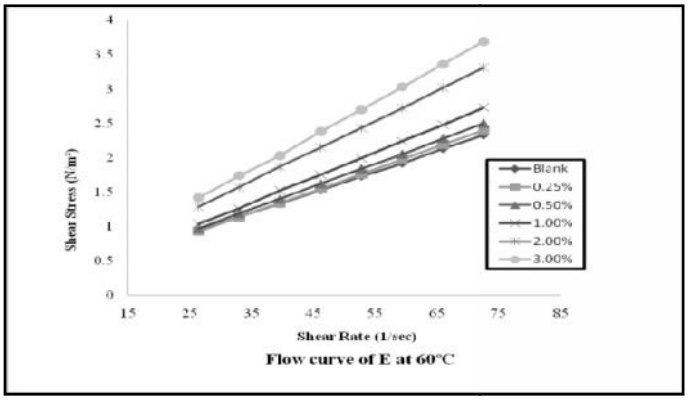

Figure 5. Flow curve of E additive at 60^{o}C

$\tau = \tau_o + K\gamma^{\bullet}$ (2)

Where**τ**……...is the shear stress acting on the fluid (Pa)

τ_o……..is the yield value or yield stress.

K……..is the Consistency Index

$\gamma^{\bullet}$……...is the shear rate (s^{-1}).

The degree of regression was very close to unity. This means that this formula describes the rheological properties of the tested oil samples: Namely, each one of these samples are simple-Bingham fluid with yield values and consistency indices.

Viscosity-shear rate dependence

The apparent viscosity of each oil sample was measured by the same rheometer Brookfield at different temperatures. The data of Eforexample were plotted on Figures ″7-9". The curve shows that the viscosity slightly decreases with the increase of shear rate. This confirms the last rheological relation eq.(2), which was concluded by calculating of μ_{app} **as** $= \tau / \gamma^{\bullet}$ from which the fallowing equation was obtained:

$$\mu_{app} = \tau / \gamma^{\bullet} = \tau o / \gamma^{\bullet} + K \quad (3)$$

Where

μ …....is the apparent viscosity.

Which show the last relation between μ_{app} and γ• (Mongkol and Chatchai 2010).

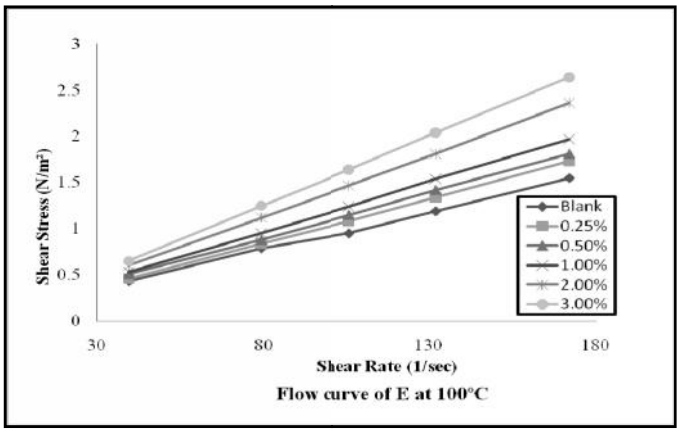

Figure 6. Flow curve of E additive at 100^{o}C

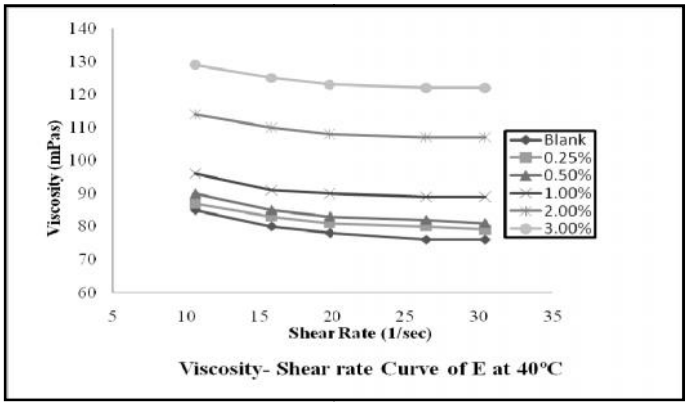

Figure 7. Viscosity-Shear rate curve of E additive at 40^{o}C

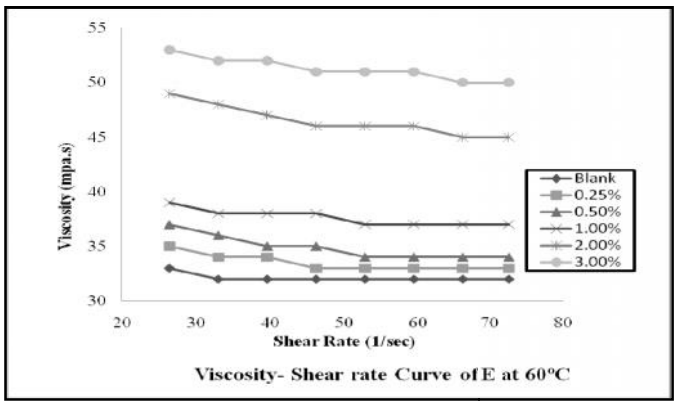

Figure 8. Viscosity-Shear rate curve of E additive at 60°C

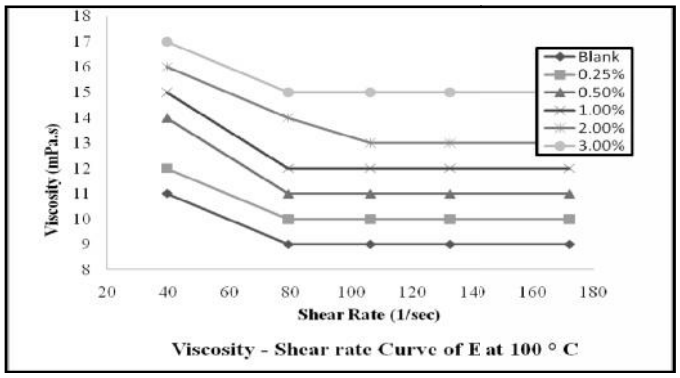

Figure 9. Viscosity-Shear rate curve of E additive at 100°C

EFFECT OFTEMPERATURE ON THE CONSISTENCY INDEX OF OIL SAMPLE

The viscosity of fluids largely depends upon temperature. The viscosity is a decreasing function of temperature; this drop is important at low temperature and is smaller at high temperature. The assumed relation is of the form:

$$K=be^{-aT} \quad (5)$$

Where a & b are two specific parameters that were obtained and represented in the Figures ″10,11".

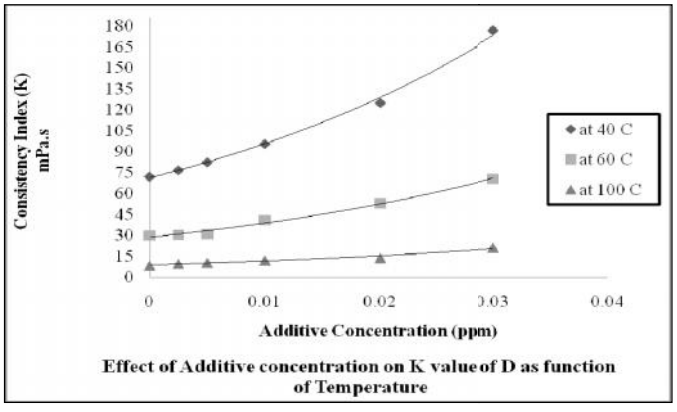

Figure 10. Effect of additive concentration on K value of D as function of Temperature

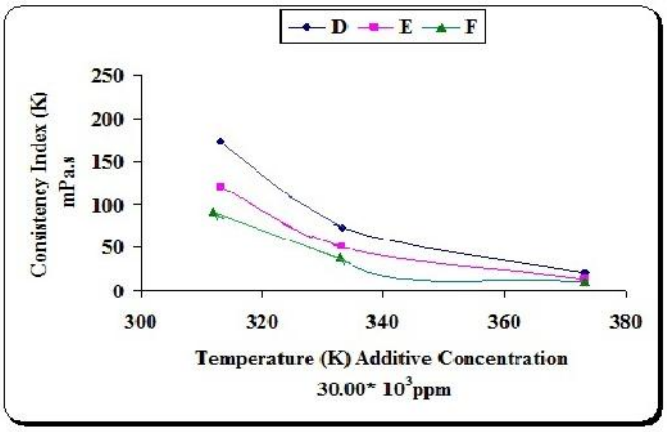

Figure 11. Effect of Temperature on K value for (D, E and F) Additives

Conclusion

- Three additives were prepared via free radical chain addition polymerization.
- All the prepared polymers were found to be soluble at lube oil SAE-30 free of additives.
- The structures of the prepared polymers were elucidated by Fourier Transform Infrared Spectroscopy (F.T.I.R.), and Gel Permeation Chromatography (GPC).
- The rheological behavior of lube oil (SAE-30) was studied with and without additives.

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