Synthesis and characterization of multifunctional polymer additives for lubricating oils based on 2-ethylhexyl acrylate and *N*-isopropylmethacrylamide

Ghofran Qasem Siwan[1)], **Ameen Hadi Mohammed**[1), *)] (ORCID ID: 0000-0003-2323-198X)

Abstract: The long-chain acrylate monomer, 2-ethylhexyl acrylate (EHA), was obtained by esterification of acrylic acid with 2-ethylhexanol, and the copolymer by free radical polymerization with *N*-isopropylmethacrylamide (PMA) in various proportions using azobisisobutyronitrile (AIBN) as the initiator in a benzene solvent. High conversion polymers were obtained: polyEHM, polyPMA, 3EHM/1PMA, 1EHM/1PMA and 1EHM/3PMA, which were named P1, P2, P3, P4 and P5, respectively. The chemical structure was confirmed by Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR). The percentage of nitrogen was used to determine the reactivity coefficient of EHA-*co*-PMA using the Kelin-Todosa method, r_{EHA} = 1.14 and r_{PMA} = 0.321. Based on the reactivity and solubility coefficients in the virgin SN 500 base oil, the performance of polymers, except P2, as additives to lubricating oils was assessed. Polymers with a high content of hydrophobic EHA monomer (P1 and P3) showed good performance as viscosity increasing and freezing point lowering agents, while P4 had the best anti-corrosion properties.

Keywords: long chain acrylate monomers, copolymerization, reactivity ratios, lubricant additives.

Synteza i charakterystyka wielofunkcyjnych dodatków polimerowych do olejów smarowych na bazie akrylanu 2-etyloheksylu i *N*-izopropylometakryloamidu

Streszczenie: Długołańcuchowy monomer akrylanowy, akrylan 2-etyloheksylu (EHA), otrzymano poprzez estryfikację kwasu akrylowego 2-etyloheksanolem, a kopolimer poprzez polimeryzację wolnorodnikową z *N*-izopropylometakryloamidem (PMA) w różnych proporcjach z użyciem azobisizobutyronitrylu (AIBN) jako inicjatora w rozpuszczalniku benzenowym. Otrzymano polimery o wysokiej konwersji: polyEHM, polyPMA, 3EHM/1PMA, 1EHM/1PMA i 1EHM/3PMA, które nazwano odpowiednio P1, P2, P3, P4 i P5. Strukturę chemiczną potwierdzono metodą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) i protonowego jądrowego rezonansu magnetycznego (^{1}H-NMR). Zawartość procentową azotu zastosowano do określenia współczynnika reaktywności EHA-*co*-PMA metodą Kelina-Todosa, r_{EHA} = 1,14 i r_{PMA} = 0,321. Na podstawie współczynników reaktywności i rozpuszczalności w surowym oleju bazowym SN 500, oceniono działanie polimerów, z wyjątkiem P2, jako dodatków do olejów smarowych. Polimery o dużej zawartości hydrofobowego monomeru EHA (P1 i P3) wykazały dobre działanie jako środki zwiększające lepkość i obniżające temperaturę krzepnięcia, natomiast P4 miał najlepsze właściwości antykorozyjne.

Słowa kluczowe: długołańcuchowe monomery akrylanowe, kopolimeryzacja, współczynniki reaktywności, dodatki smarne.

In the last two decades, the interest in the synthesis of multifunction polymers derived from acrylate monomers, having long aliphatic alkyl chain, gained more attention because of their extended usage in different medical and industrial fields [1-4]. This type of polymers has remarkably diverse, characteristic, sought-after properties, from hardness and strength, transparency, elasticity to super-absorbency [5-7]. Therefore, acrylic polymers have found wide use in biomedical applications such as bone cements and contact lenses, as well as in other applications such as cosmetics, textiles, orthopedics, coatings, diapers, lubricant additives, paints, and adhesives [8, 9]. Many methods can be used to overcome the disadvantages of polymers made from long-chain acrylate monomers. One of

[1)] Department of Chemistry, College of Science for Women, University of Baghdad, 10071 Baghdad, Iraq.

[*)] Author for correspondence: ameenhadi80@yahoo.com

them is copolymerization with other monomers, which can improve their thermal and mechanical properties [10, 11]. Due to their direct impact on the properties of the produced copolymers, the values of the reactivity coefficients of comonomers should be considered and determined using accurate methods [12, 13].

There are several methods that have been employed to improve the performance of lubricant oils. The main problems caused by their usage are corrosion, heating, high energy coast, damage in the joints, and/or chemical degradation. Polymeric additives for lubricant oils are among the best methods used for improving lubricant oils properties. The potential use of polymers, based on long-chain acrylate monomers, as lubricant additives has gained more attention due to their excellent performance as pour point depressants (PPD) and Viscosity Index Improvers (VII) for base oils [14]. The long-chain acrylate polymers and base oils can easily form homogenous component because of the similarity in their chemical structures which contain the aliphatic alkyl chains. Based on this fact, a lot of research has been done in the field of lubricating oils. Ghosh and Das have synthesized homopolymer of decyl acrylate and its copolymer with styrene. The synthesized polymers were evaluated for using as PPD of base oil where the copolymer was more effective than homopolymer [15]. Al-Sabagh *et al.* studied the effect of alkyl chain length of poly(*n*-alkyl itaconate-*co*-vinyl acetate) on its efficiency as viscosity improver. The polymers showed superior performance when the length of alkyl chain decreased [16]. In another research performed by Du *et al.*, different methacrylic acid ester monomers were synthesized then copolymerized with maleic anhydride; solidification point (SP) of the lubricant oils was reduced by adding different amounts of the prepared polymers [17].

The aims of this research are to synthesize long chain acrylate monomer, 2-ethyl hexyl acrylate, to homopolymerized and copolymerized the prepared monomer with *N*-isopropylmethacrylamide at low and high conversion, and to determine the reactivity ratios values of the comonomers. This work also evaluates the performance of the prepared polymers as lubricant additives.

EXPERIMENTAL PART

Materials

Acrylic acid, 2-ethyl hexanol, *N*-isopropylmethacrylamide, azobisisobutyronitrile, paratoluenesulfonic acid, hydroquinone, stannous chloride, aluminum oxide, hydrochloric acid, xylene, isopropanol, toluene, ethanol, and benzene were purchased from Sigma-Aldrich (Saint Louis, MO, USA). To purify the monomer *N*-isopropylmethacrylamide, it was passed through Al_2O_3 column several times. The initiator azobisisobutyronitrile was purified by recrystallization from ethanol. The virgin base oil SN 500 was collected from Middle Refineries Company (Baghdad, Iraq).

Methods

The synthesized monomer, homopolymer and copolymer were characterized by employing the spectrophotometer PerkinElmer 1650 (Waltham, MA, USA) at 400 to 4000 cm^{-1} using KBr disk method. JEOL JMTC-500/54/SS (Akishima, Tokyo, Japan) spectrometer was used to record the ^{1}H-NMR of the monomer and copolymers, dimethyl sulfoxide was used as a solvent and tetramethylsilane as an internal standard. The compositions and reactivity ratios of the copolymer were determined based on the results of Nitrogen % collected from LECO CHNS-932 (LECO Corp., Saint Joseph, MI, USA) elemental analyzer. Viscosity index and kinematic viscosity of base oil at 40 and 100°C were determined by following ASTM D 2270-10 and ASTM D445 standard, respectively. Pour point temperatures of base oil, before and after polymers addition, were determined according to the ASTM D-97 standard.

To evaluate the anti-corrosion performance of the synthesized polymers, standard corrosion tests according to ASTM A1008 were used. Polished and weighed small pieces of carbon steel metals were degreased using an equal mixture of xylene-isopropanol. The pieces were immersed in 100 ml of virgin and formulated base oil for 180 hours at 95°C. A mixture of 35% HC and 4% SnCl$_2$ was then used to de-rust the metals and the pieces were reweighed to calculate weight loss.

Synthesis of 2-ethyl hexyl acrylate EHA monomer

Direct esterification method was followed to synthesize the monomer 2-ethyl hexyl acrylate EHA. In a 250 mL round bottom flask, 1 mole of 2-ethyl hexanol, 1 mole of acrylic acid, 0.5 wt% of hydroquinone as polymerization inhibitor, and 0.8 wt% of paratoluenesulfonic acid as catalyst were dissolved in 100 mL of toluene, the mixture was then refluxed at 60°C for 12 hours. After removal of water (which was done by Dean-Stark apparatus), a rotary evaporator was used to remove the solvent from the reaction mixture. To remove the catalyst and any unreacted acrylic acid, the crude product was washed with ethanol and distilled water several times, and then dried in a vacuum oven at 45°C for 10 hours.

Copolymerization of EHA with PMA

EHA/PMA copolymers, at low and high conversion, were synthesized by following the procedure mentioned in the literature [18, 19]. By changing the mole fraction of the two monomers in the feed mixture (f_1=0.1–0.9), five different compositions were prepared. In a quick fit test tube, the polymerization mixture including the two monomers and AIBN as initiator were dissolved in 10 mL of benzene. After reducing the effect of oxygen inhibition by bubbling the solution with nitrogen gas for 15 min, the tubes with reagents were placed in a thermostat water
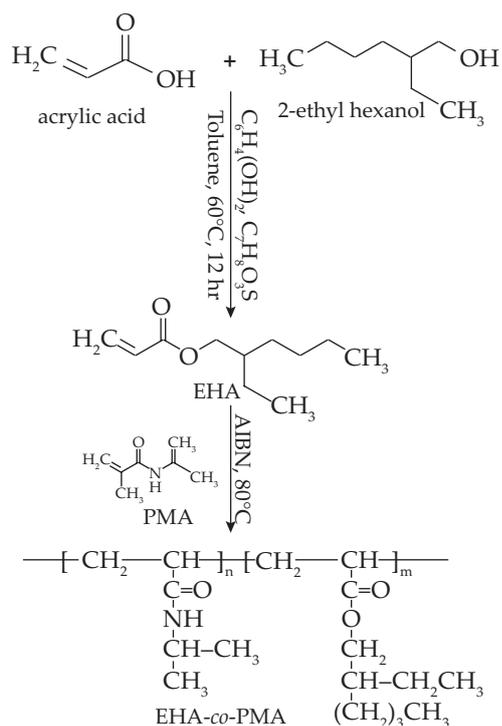
Scheme 1. Synthesis of EHM and its copolymer with PMA

bath at 80°C. Conversion percentage was controlled by changing the polymerization time, 10–20 min for low conversion polymerization and 2–4 hours for high conversion polymerization. After the completion of polymerization process, obtained polymers were subsequently precipitated and washed with ethanol to remove any unreacted monomers, and then dried in a vacuum oven at 35°C for 24 hours. Similar procedure was followed to prepare poly-EHM and polyPMA. Scheme 1 shows the preparation process of EHM and its copolymer with PMA.

RESULTS AND DISCUSSION

Characterization

Figures 1 and 2 show the FT-IR spectrum of synthesized 2-ethyl hexyl acrylate and its copolymer with 2-(dimethylamine) ethyl acrylate, respectively. The absorption bands of EHM are as follow: 2959 cm^{-1} (alkane C-H stretching), 1736 cm^{-1} (ester C=O), 1616 cm^{-1} (aliphatic C=C), 1408 cm^{-1} (alkane C-H bending), and 1057 cm^{-1} (ester C-O). The success of copolymerization was confirm by presence the absorption bands which belong to the stretching vibration in different functional groups of corresponding monomers, EHM and PMA: 3456 cm^{-1} (amide N-H), 1717 cm^{-1} (ester C=O), 1632 cm^{-1} (amide C=O), and 1057 cm^{-1} (ester C-O). In addition, absence of aliphatic C=C absorption band at 1616 cm^{-1} proves the completion of polymerization process.

Figure 3 shows ^{1}H-NMR data for the synthesized monomer. The signals at about 2.7 ppm and 4 ppm could be assigned to the protons of CH in the hexyl group and the protons of O-CH$_2$, respectively. The protons of terminal CH$_3$ in the hexyl chain and CH$_3$ of the ethyl group resonate at 0.8 ppm, while protons of CH$_3$ attached to the main chain backbone resonate at 1.8 ppm. The signals at 5.7 ppm and 6.3 ppm are assigned to the methylene group of the main chain backbone. The protons of CH$_2$ of the ethyl and the hexyl groups resonate at about 1.3 ppm and 1.5 ppm, respectively.

Copolymer composition

The mole fraction of PMA was determined based on N% results obtained from elemental analysis [20] using Equation 1.
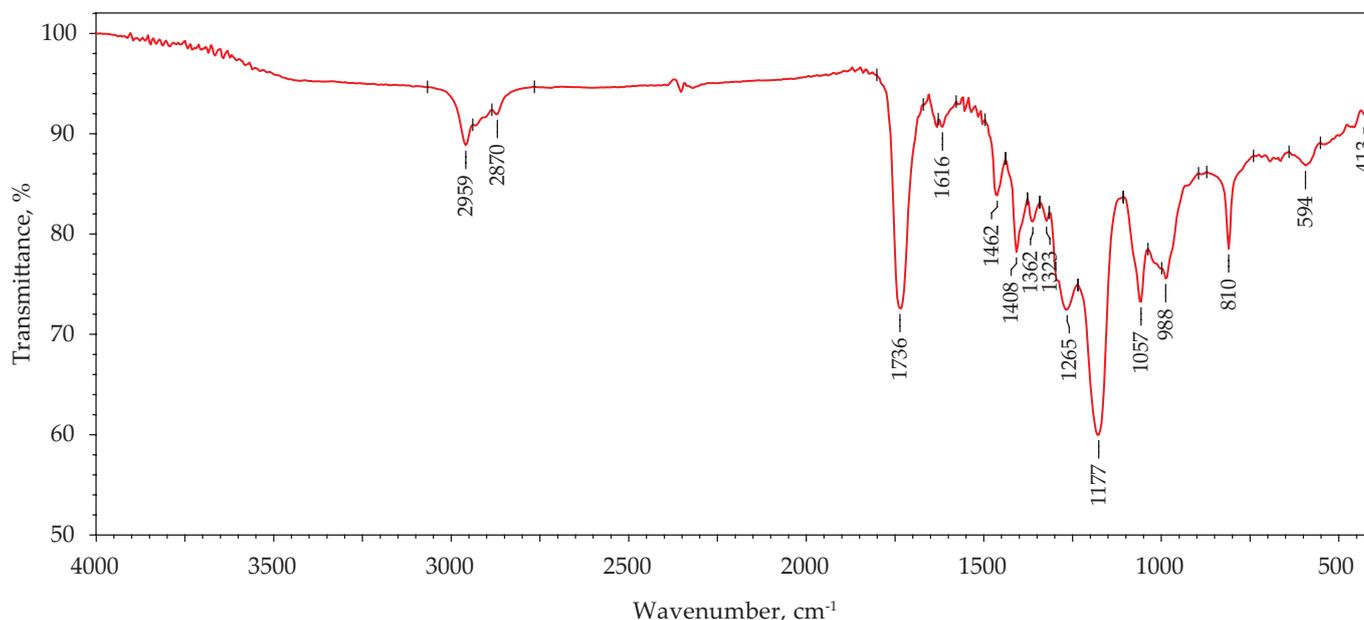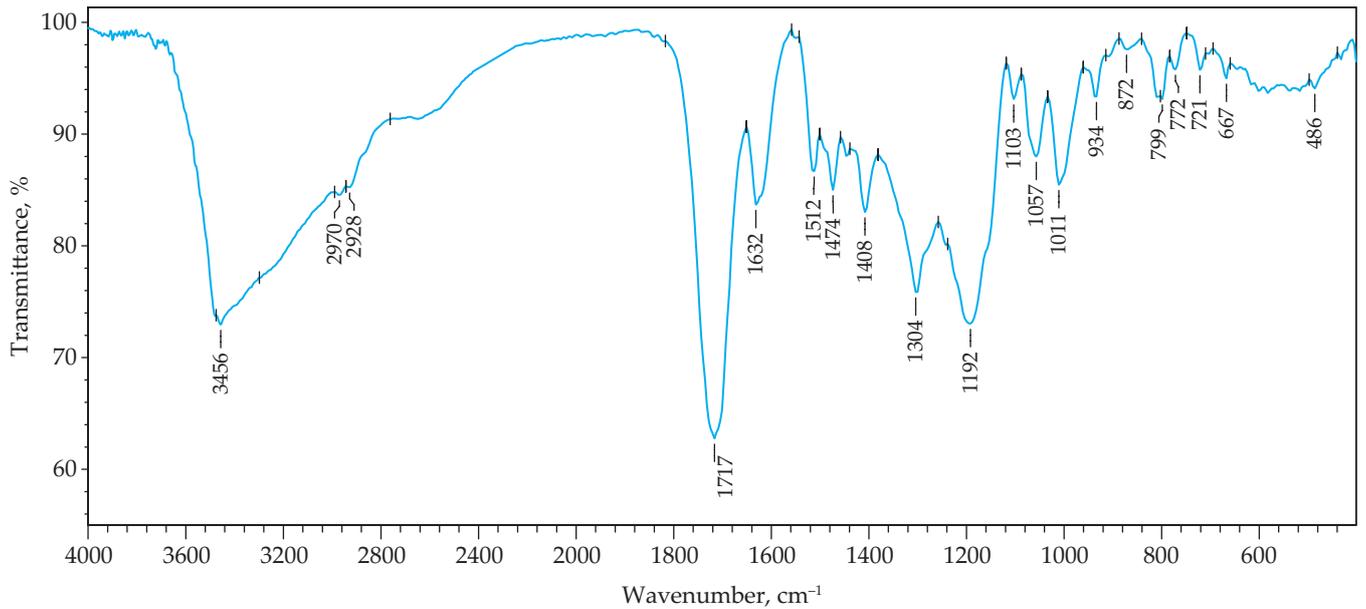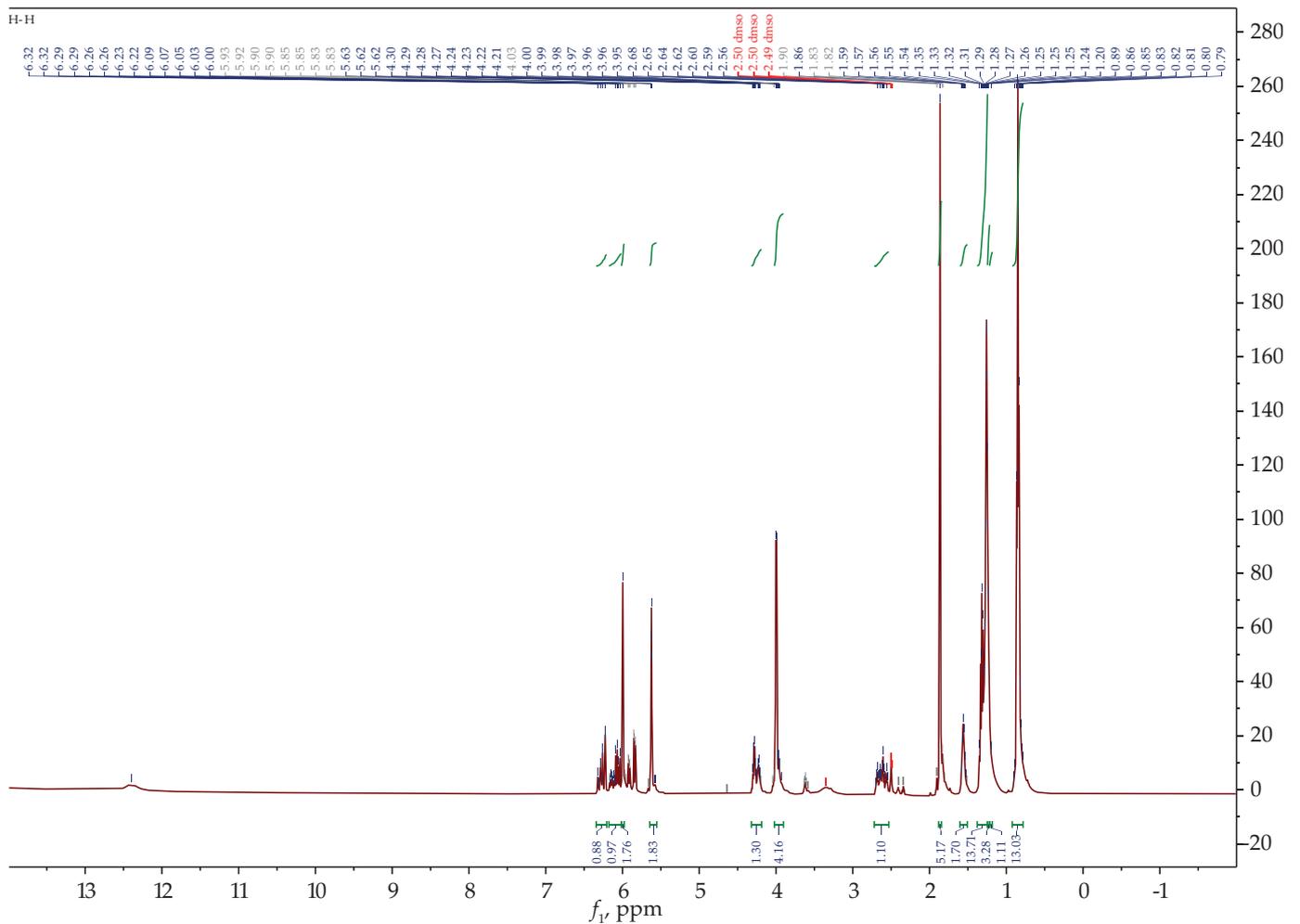

Fig. 1. FT-IR spectrum of EHM monomer

Fig. 2. FT-IR spectrum of EHM/PMA copolymer

Fig. 3. ¹H-NMR of EHM monomer
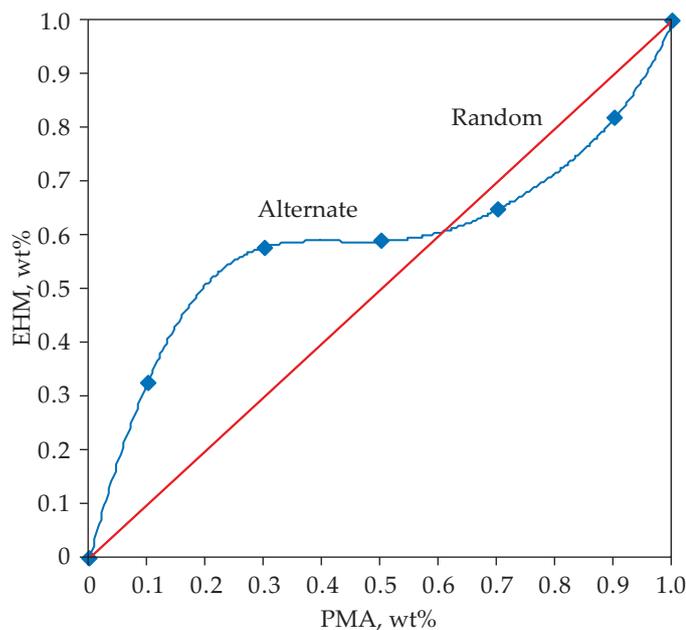
Fig. 4. Composition of EHM/PMA copolymer, alternative behavior

Fig. 5. Effect of amount and type of polymer on viscosity index of base oil

$$\frac{N\% \text{ Copolymer}}{N\% M_2} = \frac{M_{wt} \text{ of } M_2}{M_{wt} \text{ of } M_2 + \dfrac{M_{wt} \text{ of } M_1}{F}} \quad (1)$$

where: M_1 and M_2 are EHM and PMA, respectively; $F=F_1/F_2$.

From the copolymer composition behavior described in Figure 4 and the reactivity ratios values (r_{EHM}, r_{PMA}) determined by Kelen-Todos method, it can be concluded that EHM formed alternative copolymer with PMA. The stabilization of EHM and PMA macroradicals can be explained by the presence of carbonyl and amide groups. Mohammed *et al.* [21] discussed the effect of macroradicals stabilization on reactivity ratios when 2-benzothiazoylacrylamide was copolymerized with α-methyl styrene and methyl acrylate.

Formulation of polymers in base oil

The solubility of synthesized polymers in virgin base oil was also tested by mixing different concentrations of them (1–3 wt%/wt%) with virgin base oil at 30°C by using mechanical stirrer. The obtained results are presented in Table 1. Polymers with high content of EHM such as P1 and P3 have a good solubility in base oil due to the similarity of EHM structure with base oil structure. On the other hand, when the concentration of PMA was increased in the reaction feed, the solubility of polymers in base oil lowers due to increase the hydrophilicity of the polymers. Because EHM is more reactive than PMA (r_{EHA}= 1.14 and r_{PMA}=0.321), by the end of polymerization, the polymers will compose of only polyPMA. Thus, P1, P3 and P4 were successfully used as lubricant additives
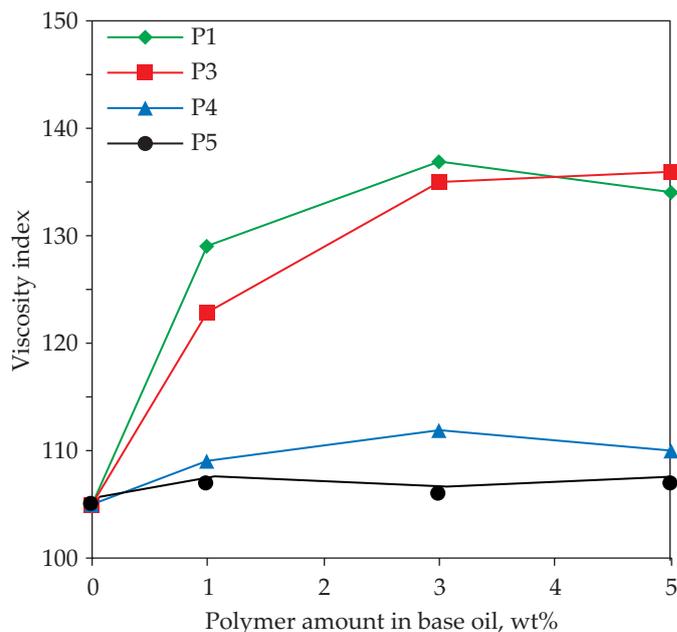
T a b l e 1. Solubility of the synthesized polymers in base oil

Polymeric additives	Symbol	Level of solubility in base oil
polyEHM	P1	+ + +
polyPMA	P2	– – – –
3EHM/1PMA	P3	+ + +
1EHM/1PMA	P4	+ +
1EHM/3PMA	P5	+

whereas P2 was set aside and has not been used in the current study.

Viscosity index assessment

Figure 5 shows diverse types and concentrations of polymers, as base oil additives, plotted versus viscosity index values of formulated oil calculated from kinematic viscosity at 40 and 100°C. The results revealed that P1 and P3 showed superior performance as viscosity index improver compared with P4. This may be explained by the increase of hydrophobicity of the polymers and the presence of the long alkyl chain of EHM. The high molecular weight of P1 and P3 compared to P4 and P5 can be another explanation of the obtained results. In addition, by increasing the concentration of polymers blended with base oil, the viscosity index increases especially when 4 wt/wt% of polymers were added. Thus, P1 at 3 wt/wt% concentration showed the best performance by increasing the viscosity index value of base oil from 105 to 137. Similar behavior has been observed by when the performance of *N,N*-dimethylacrylamide-*co*-alkyl acrylates as viscosity index improvers was studied [22].
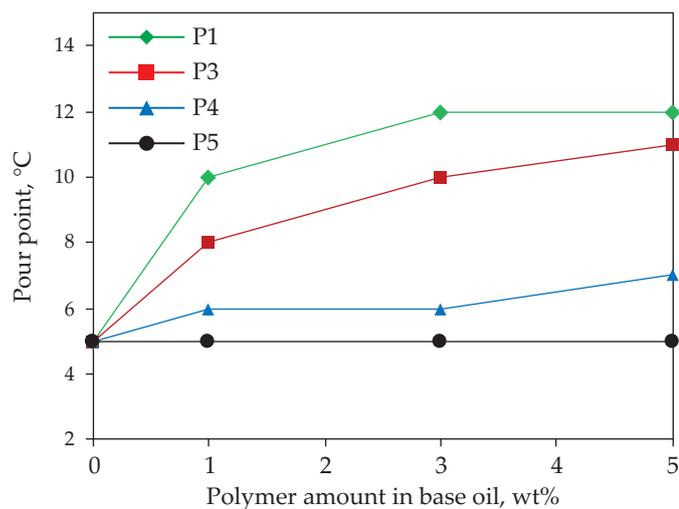
Fig. 6. Effect of amount and type of polymer on pour point of base oil

Fig 7. Effect of amount and type of polymer on metal weight loss

Pour point assessment

The behavior of the prepared polymers as pour point depressants, as shown in Figure 6, is like their behavior as viscosity index improvers. Thus, P1 and P3 at 3 wt/wt% concentration lowered the pour point of base oil from -5 to -12 and -10, respectively, whereas no change in the pour point of base oil was observed for P4 and P5. Moreover, it is found that the pour point of base oil decreased with increasing the concentration of polymers blended with the base oil. The best value of pour point temperature was recorded as -12 with using P1 additive at 5 wt/wt% concentration. These findings could be explained in term of the rigid network of crystalized wax in base oil was distracted by the effect of the high molecular weight of the polymer additives [23, 24].

Anticorrosive activity

The anticorrosive activity of synthesized polymers was examined by following the weight loss of the metal put in base oil, before and after polymers addition. The results shown in Figure 7 reveal that polymers with high content of PMA, such as P4 and P5, showed high anticorrosive activity compared to P1 and P3. Thus, the value of metal weight loss decreased to 0.37 mg from the original value of 1.05 mg for the base oil when P4 and P5 were used as additives for base oil. However, the minimum value of metal weight loss (-0.39 mg) was recorded to the base oil blended with 5 (wt/wt%) of P5 because this polymer has the highest amount of PMA. The enhancement in the anticorrosive activity with increasing the concentration of PMA could be attributed to the higher polarity in this monomer which leads to increase the interacting with the metallic surface and then formation a protective layer [25, 26].
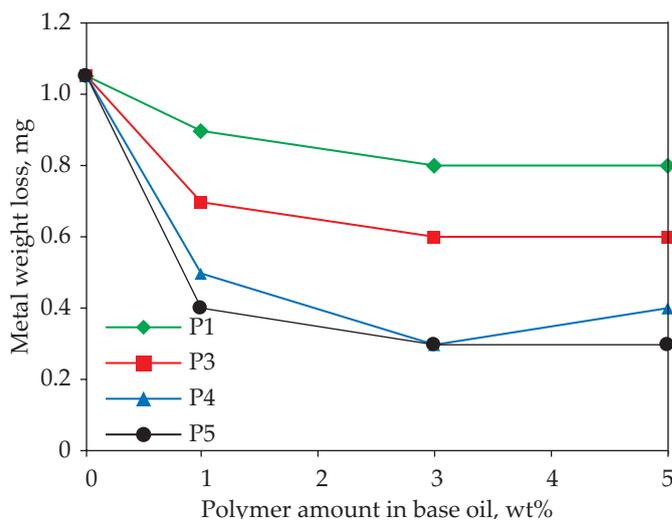
CONCLUSIONS

The long chain monomer, 2-ethyl hexyl acrylate, have been successfully synthesized and then copolymerized with *N*-isopropylmethacrylamide at low and high conversion. Based on solubility test of prepared polymers in base oil and reactivity ratios of copolymer calculated by Kelin-Todos method, some compositions were selected to examine their performance as lubricant additives. The presence of long alkyl chain of EHM explains the superior performance of P1 and P3 as viscosity index improvers and pour point depressants for base oil whereas the anticorrosive activity of P4 and P5 was attributed to the higher polarity of PMA monomer which provided the metallic surface with protective layer and decreased the metal weight loss.

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