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Synthesis and Development of Novel Copolymer Additives for Enhancing Viscosity Index and Pour Point of Medium Viscosity Iraqi Lubricating Oil

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ABSTRACT

Four novel copolymers (HT, TT, OT, and DT) were synthesized through free radical polymerization by reacting various alkyl chain-length acrylate with 1-tetradecene. The structural characterization of these copolymers was achieved by determining their molecular weights using Gel Permeation Chromatography (GPC), analyzing their chemical structure with Fourier Transform Infrared spectroscopy (FTIR), and examining their composition through Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy. thermogravimetric analysis (TGA) was also employed to assess thermal stability. The copolymers were evaluated for their effectiveness as additives to enhance the viscosity index and pour point of medium viscosity Iraqi lubricating oil (base oils 60). The results indicated that the efficiency of new copolymers as viscosity index improvers increased by an increase in concentration and alkyl chain lengths in the acrylate components. All new copolymers achieved good results compared to free additives lubricating oil, but the copolymer (DT) achieved the best efficiency (VI= 170) at (5% wt.) concentration compared to free additives lubricating oil (VI = 98). On the other hand, the efficiency of copolymers as a pour point depressant increased by decreasing the concentration and alkyl chain length; the copolymer (HT) achieved the best efficiency (PPD = -20^{o}C) compared to free additives lubricating oil (PPD = -5 ^{o}C).

Keywords: Viscosity index improvers; alkyl acrylate; pour point depressant; copolymer

Introduction

"Lubricating oils" is conventionally employed to encompass various substances exhibiting lubricating properties. This category includes a wide spectrum of lubricating components utilized in fluid form. Lubricating oil is derived from crude oil's residual, highly viscous component, which persists after distilling gas oil and lighter fractions [1, 2]. Meeting the demanding performance criteria of lubricants often necessitates incorporating advanced technology, as reliance just on the essential liquid mineral oil is typically insufficient. In contemporary formulations, lubricants are systematically engineered with a combination of crucial liquids and chemical additives to ensure compliance with the stringent standards established by original equipment manufacturers[3]. Lubricating oil additives introduced variations in both quantity and quality contingent upon their intended purposes. When incorporated into lubricating fluids, these additives include compounds or mixtures that boost their inherent properties and optimize their operational efficacy in established applications. Several categories of additives can be used in diverse applications to amplify the performance of lubricants. These additives encompass viscosity index improvers (VIIs)[4], pour point depressants (PPD)[5], dispersants, antioxidants[6], corrosion inhibitors, and detergents.. In this study, we focus on viscosity index improvers (VIIs) and pour point depressants (PPD), sometimes called viscosity modifiers, which are among the most important additives to add to lubricants[5]. Most of these additives are polymers with elongated hydrocarbon chains and high molecular weights that heighten oil viscosity to a greater extent at elevated temperatures or lower the viscosity at low temperatures. This phenomenon arises due to the alteration in the physical arrangement of the polymer as the temperature of the mixture increases. According to a theory, the polymer molecules tend to assume a coiled shape when the oil is cold, minimizing their impact on viscosity[7]. The effectiveness of the viscosity index improvers and pour point depressants relies on the characteristics of the polymer additive in the oil, including polymer solubility, molecular weight, and shear resistance[8–10]. The polymer's solubility typically increases as the temperature increases due to the polymer chains shifting from a condensed conformation to a more stretched one, resulting in an overall increase in volume. This observed increase in volume leads to a corresponding elevation in the oil viscosity, consequently attenuating the expected viscosity decrease that would normally occur with increasing temperatures[4, 11]. Efficient lubricant design involves carefully selecting additives, their dosages, and the base oil to achieve optimal performance. Due to the chemical nature of additives, careful selection of compatible molecules is essential to avoid undesirable outcomes resulting from potential chemical and physical interactions between additives [7]. In this study, we develop alkyl acrylate copolymer, which is one of the most famous Lubricating oil additives, to detect the most convenient copolymer structure as a viscosity index improver and pour point depressant for medium viscosity Iraqi lubricating oil and detect the most efficient concentration of copolymer additives with this type of lubricating oil.

Experimental

Materials

The following chemicals were used: Hexyl acrylate $C_9H_{16}O_2$ (≥95% purity Merck, Germany), Docosyl acrylate $C_{25}H_{48}O_2$ (97% purity Merck, Germany), benzyl peroxide as initiator $C_{14}H_{10}O_4$ (25%H_2O purity Merck, Germany), Tetradecyl acrylate $C_{17}H_{32}O_2$ (97% purity Merck, Germany), Octadecyl acrylate $C_{21}H_{40}O_2$ (97% purity Merck, Germany), 1-Tetradecene (97% purity Merck, Germany), and toluene (≥99% purity Merck, Germany). The free additives medium viscosity lube oil (Base oil 60) from the Al-Daura Refinery was used in this study. Table 1 shows the physicochemical properties of Iraqi lubricating oil.

Table 1. The physicochemical characteristics of lube oil.

Specification Base oil 60	
Kinematic viscosity at 40°C, cSt	66.5
Kinematic viscosity at 100°C, cSt	8.84
Viscosity Index	105
Specific Gravity at 15.6°C	0.8857
Pour Point, °C	-5

Instruments

Spectroscopic analysis for the purified copolymers, the FTIR Spectrometer Model Type (FT-IR Affinity-1shimadzu) SHIMADZU (model Japan), was used to measure the IR spectra. The structure of the prepared copolymers was investigated using (^{1}H-NMR) spectra obtained with a BRUKER 400MHz (Germany) equipment using (DMSO-d6) or ($CDCl_3$) as a solvent, while ^{13}C-NMR spectra used 125 MHZ for device JEOI-JNN-EX type advance ultra-shield instrument (Japan), The Thermal analysis (TGA) technique were conducted using TGA Q500 V6.7 (Germany) at 10°C min^{-1} heating rate of 25 to 800°C under (25 ml min^{-1}) nitrogen atmosphere. Gel Permeation Chromatography (GPC) was used to determine the molecular weights distribution of variously produced copolymers. The analysis was conducted at 25° C with 1 ml/min flow rate.

General procedure

Free radical polymerization was used to prepare copolymer additives, each alkyl acrylate polymerized separately, with 1-tetradecene with molar ratios, as shown in Table 2. The mixture and (1% w/w) of initiator benzoyl peroxide was dissolved in 25 mL of anhydrous toluene and charged into a 250 mL three-neck round bottom flask equipped with a condenser, mechanical stirrer, and glass tube as inlet section. For 15 minutes, the mixture was flushed with argon. The argon flow rate was then regulated and progressively heated to reflux temperature. The reaction was controlled for 8 hours[12, 13]. The reaction was then cooled to room temperature, and the polymer was pricipate by add methanol to reaction mixture, filtering, and washing with 20 mL of dried acetone, followed by vacuum drying at room temperature for 24 hours Figure (1).

Table 2. The copolymer composition

symbol	Polymer designation	Monomers ratio
HT	Poly (Hexyl acrylate -co- Tetradecene)	0.5 mole:0.5mole
TT	Poly (Tetradecyl acrylate -co- Tetradecene)	
OT	Poly (Octadecyl acrylate -co- Tetradecene)	
DT	Poly (Docosyl acrylate -co-Tetradecene)	

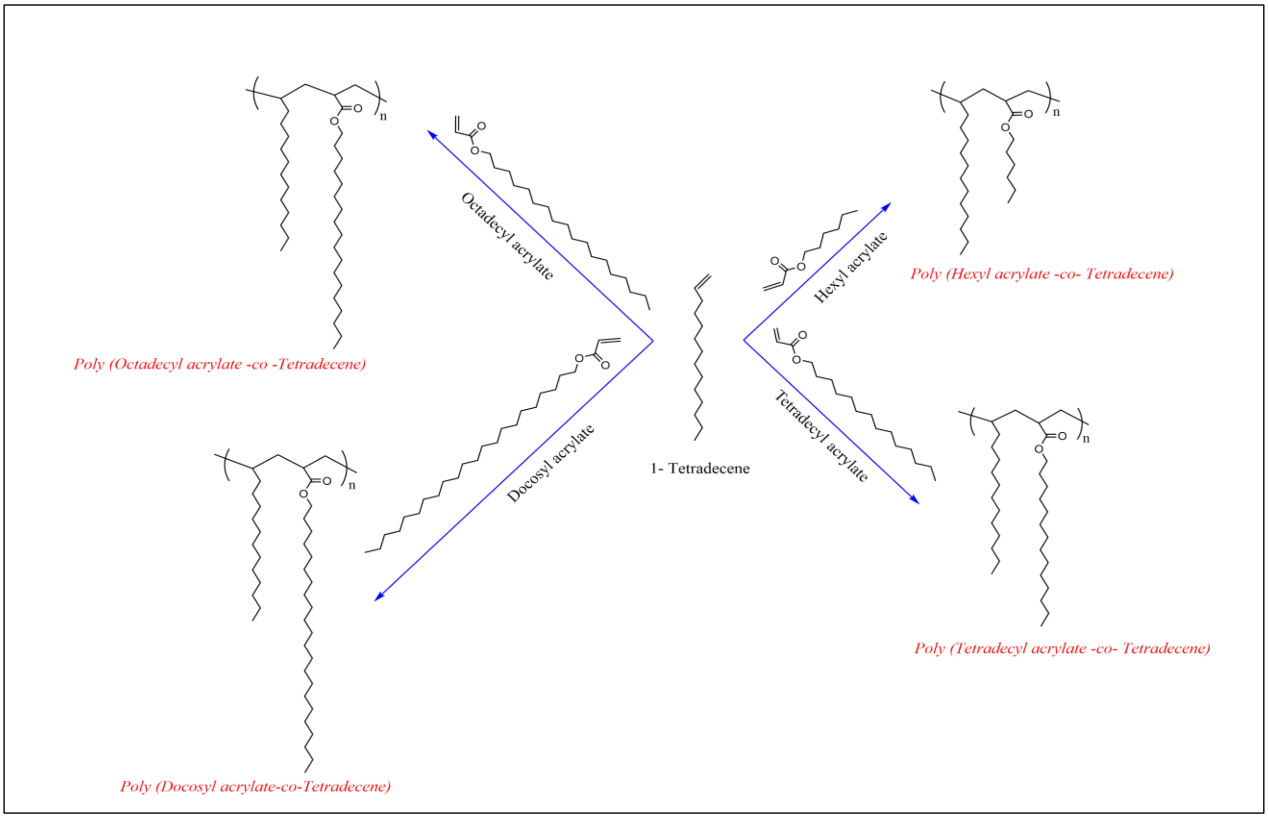

Figure 1. (Tetradecene-co-alkyl acrylate) copolymers structures.

Results and discussion

FTIR analysis showed similar pattern spectrums for all four copolymers with different absorption band intensities. Figure (2-5) shows the FTIR spectra of the prepared copolymer. The absorption bands at 2988 cm^{-1} and 2862 cm^{-1} were attributed to the asymmetric stretching and symmetric stretching of $-CH_2$, respectively, where an increase in intensity is observed due to an increase in the acrylate hydrocarbon chain length in the composition of the prepared copolymers. The absorption bands at 1442 and 1490 cm^{-1} represented to bending vibration of -CH [14]. A strong peak at 1732 cm^{-1} is assigned to the carbonyl (C=O) group of acrylate, and two peaks at 1149 cm^{-1} and 1250 cm^{-1} represent (C-O) bond stretching of ester groups [15]. The absence of the C=C peak at (1680-1600) cm^{-1}, which is characteristic of monomers, confirms the copolymer formation, and polymerization was accomplished [16].

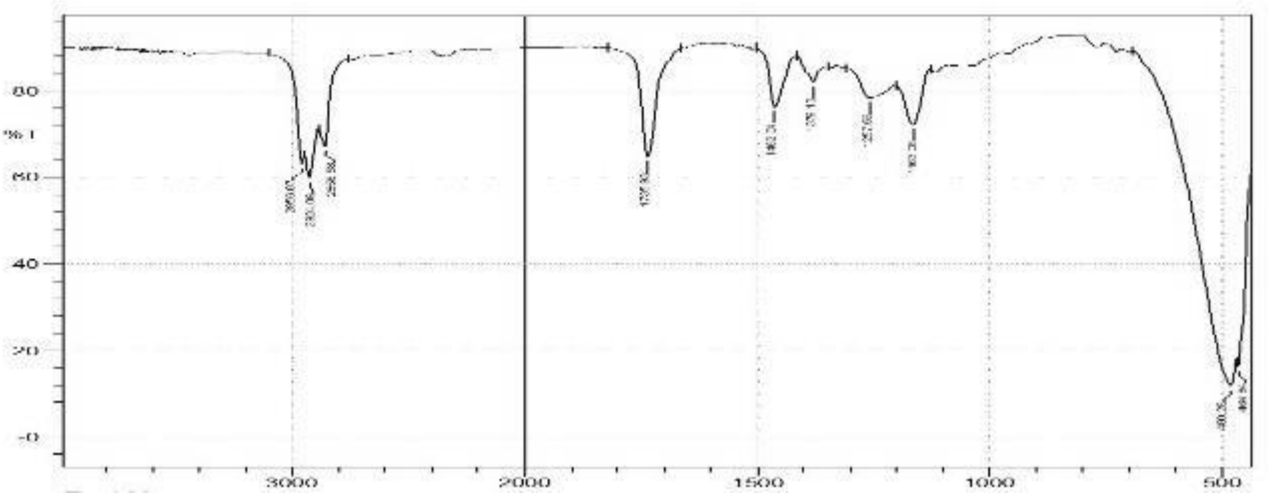

Figure 2. FTIR spectrum of copolymer (HT).

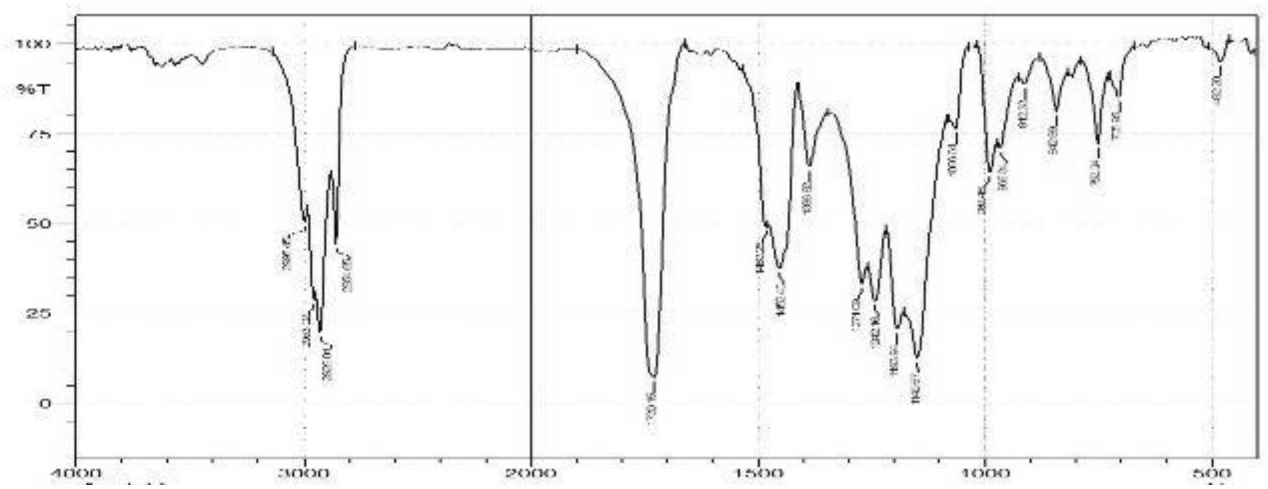

Figure 3. FTIR spectrum of copolymer (TT).

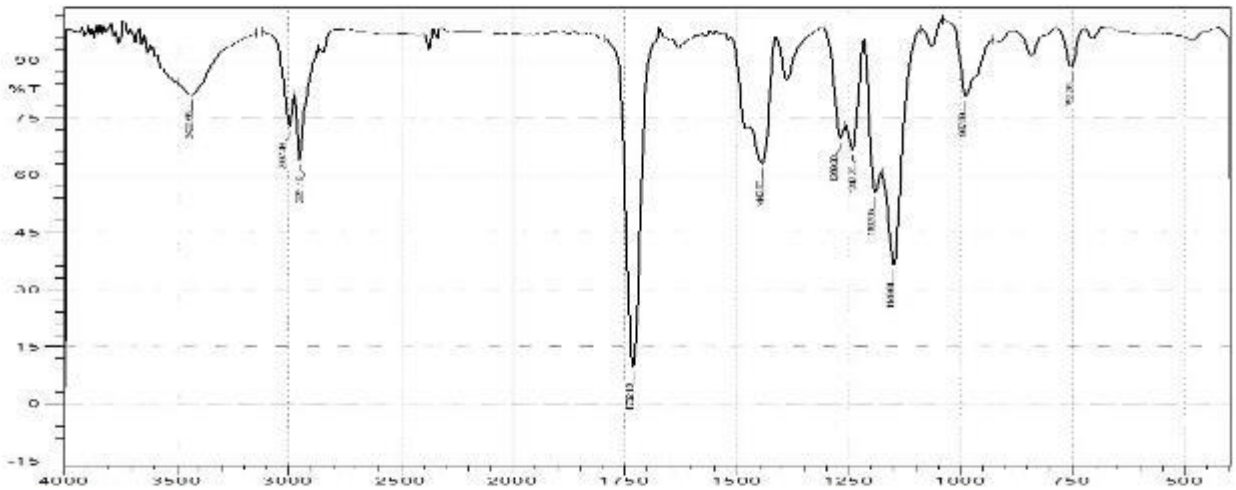

Figure 4. FT-IR spectrum of copolymer (OT).

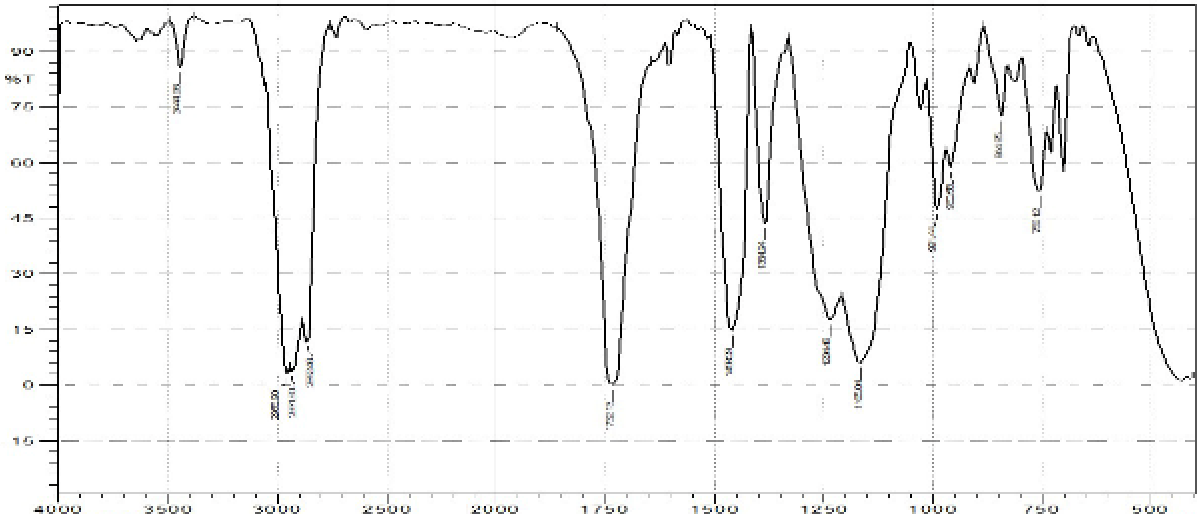

Figure 5. FT-IR spectrum of copolymer (DT).

^{1}H-NMR was used to confirm the copolymer's structure., as in Fig. (6 - 9). A signal in δ 3.99 belonging to (COO – CH_2–) of the alkyl acrylate was found, as well as typical peak signals that correspond to δ- 0.860 for (–CH_3) of alkyl acrylate and tetradecene, δ-1.29 for (–CH_2-) of alkyl chain in tetradecene and alkyl acrylate, and δ-2.54 for (CO–CH) of alkyl acrylate. The copolymer's successful synthesis is qualitatively confirmed by the ^{1}H-NMR and FT-IR spectra. ^{13}C-NMR was also used to confirm the polymer's structure; it gave an identical spectrum for all prepared copolymers, as shown in Figure (10) for copolymer (HT).

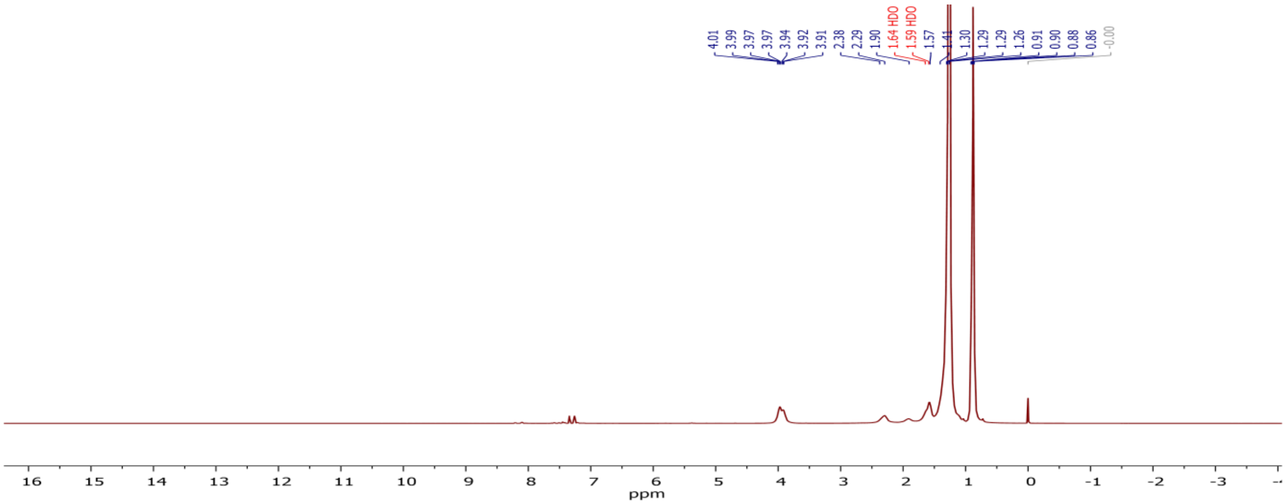

Figure 6. ^{1}H-NMR spectra of (HT) copolymer.

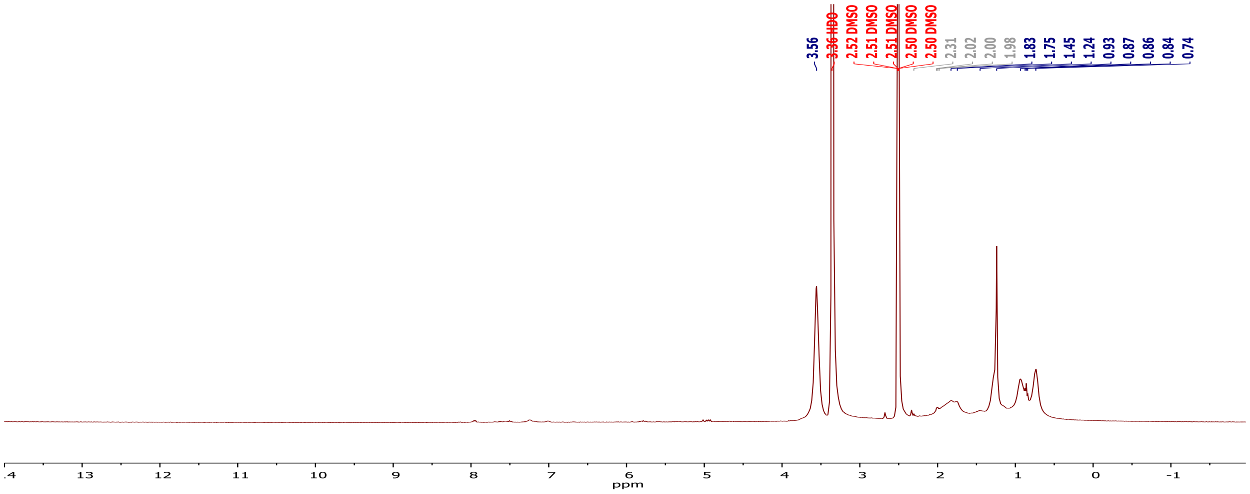

Figure 7. ^{1}H-NMR spectra of (TT)copolymer.

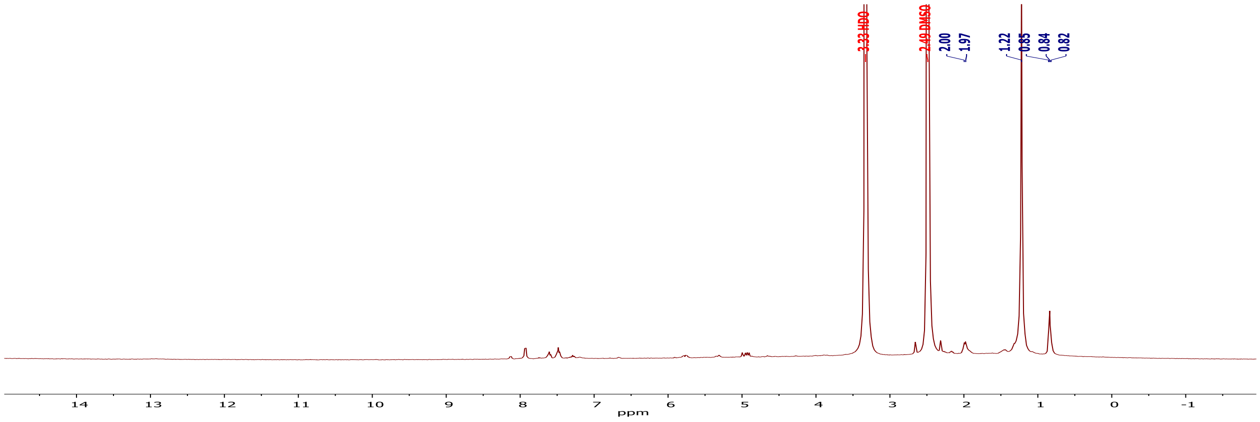

Figure 8. ^{1}H-NMR spectra of (OT) copolymer.

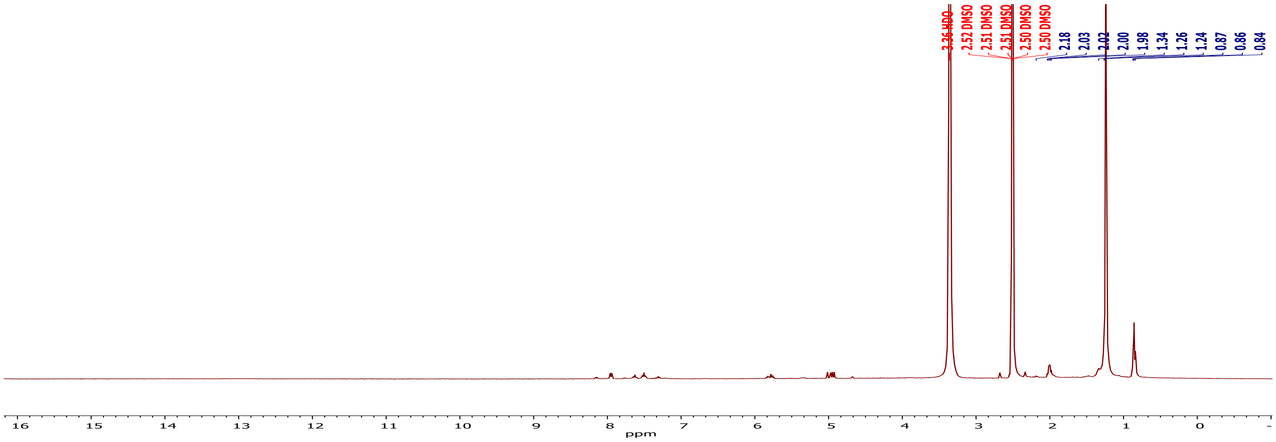

Figure 9. ^{1}H-NMR spectra of (DT) copolymer.

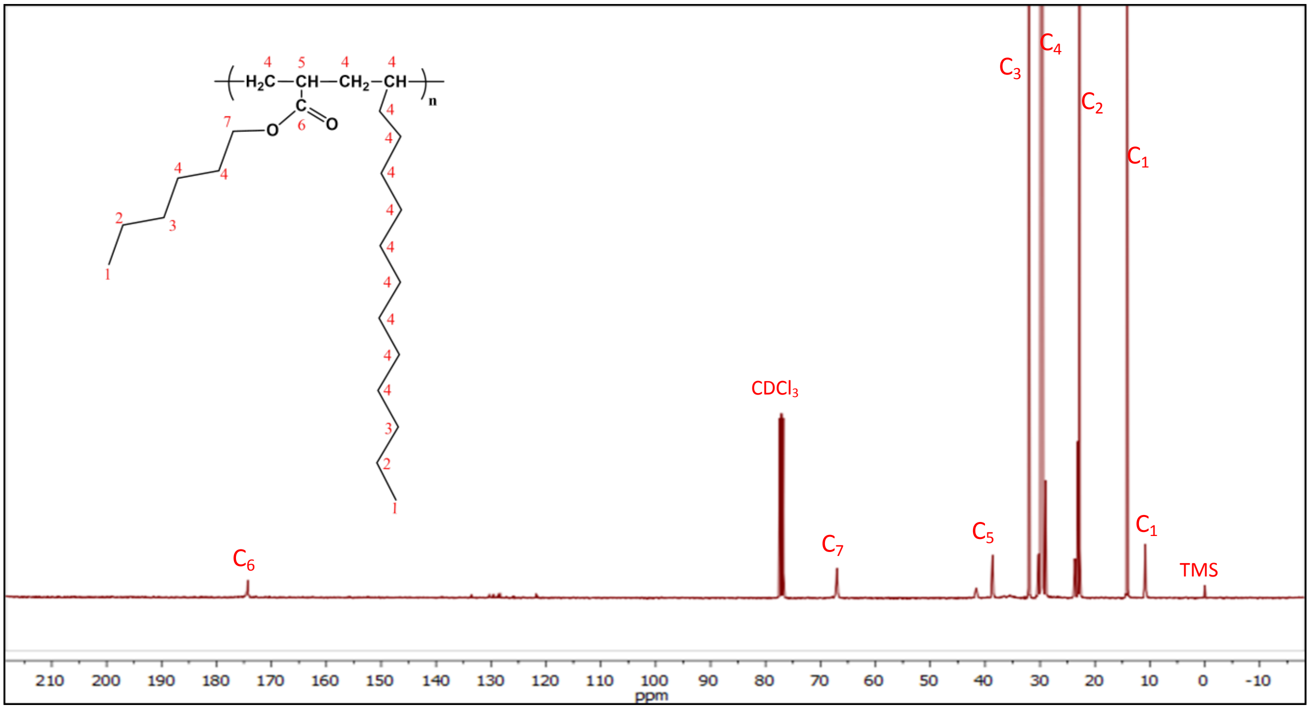

Figure 10. ^{13}C-NMR spectra of (HT) copolymer.

The thermal stability of the copolymers (HT, TT, OT, and DT) was investigated using (TGA-DTG). Figure (11) shows that all copolymer's primary degradation was above 100°C (HT occurs at 240°C with 2.5% weight loss, TT at 252°C with 7% weight loss, OT at 254°C with 13.4% weight loss, and at 285°C with 17% weight loss), and they degrade completely at temperatures (383-446) °C with (86.5%-89%) weight loss. The first degradation can be attributed to the cleavage of the ester group and corresponding to the evaporation of intra and intermolecular moisture. In contrast, the second degradation corresponds to the polymer backbone[17]. Indicating that prepared copolymers have high thermal stability confirms the prepared copolymers' suitability as viscosity index improvers additives for lubricating oil [15, 18].

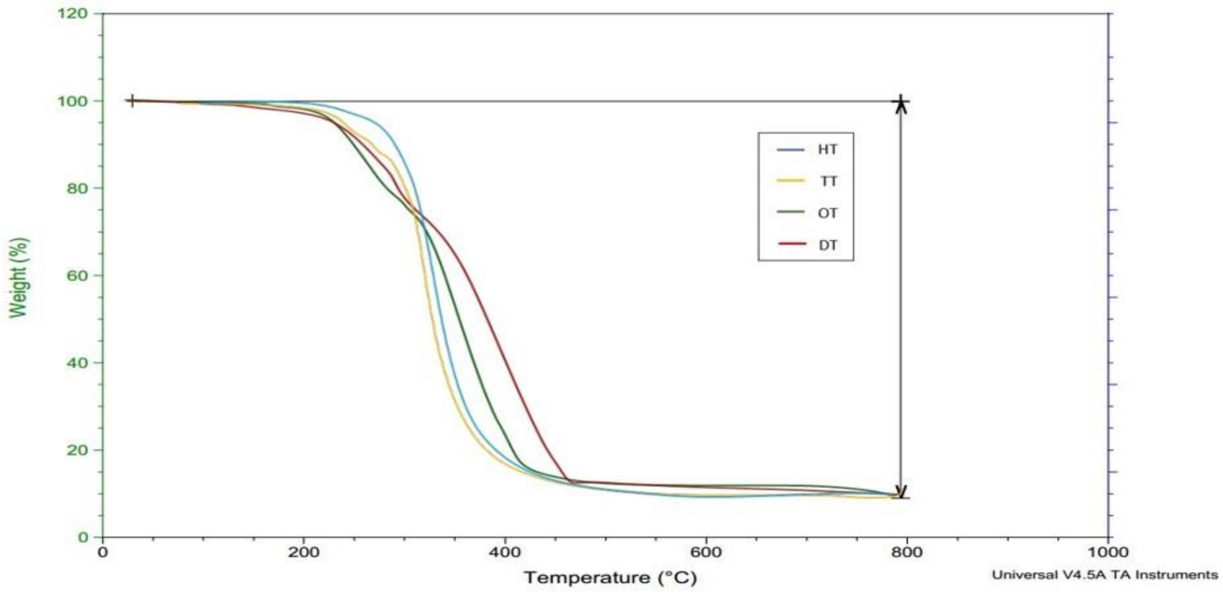

Figure 11. TGA thermogram of copolymer additives.

The weight average molecular weight (M_w) of the prepared copolymers is shown in Figures (12)-(15) and Table (3). The data indicates that increasing the hydrocarbon chain length of alkyl acrylate causes increases in molecular weight[18].

Table 3. Copolymer compositions and weight average molecular weight (Mw).

Copolymer		M_w
HT	Poly (Hexyl acrylate-co-Tetradecene)	16351
TT	Poly (Tetradecyl acrylate-co-Tetradecene)	19150
OT	Poly (Octadecyl acrylate-co-Tetradecene)	29454
DT	Poly (Docosyl acrylate-co-Tetradecene)	35417

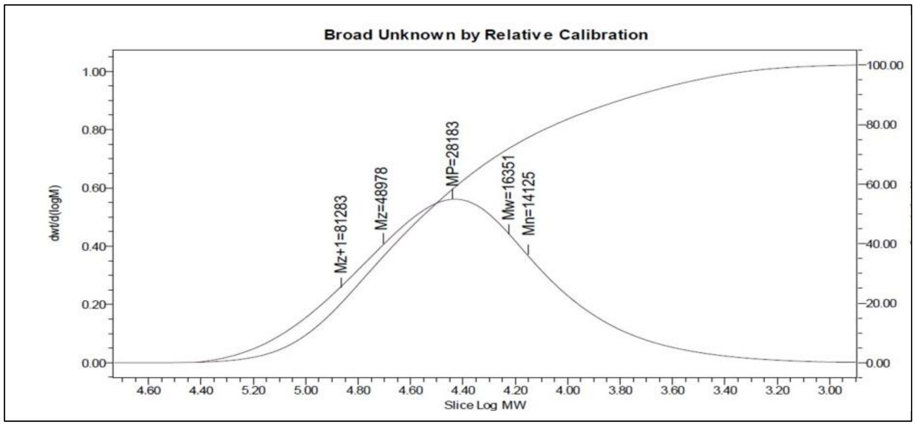

Figure 12. GPC spectra of copolymer HT.

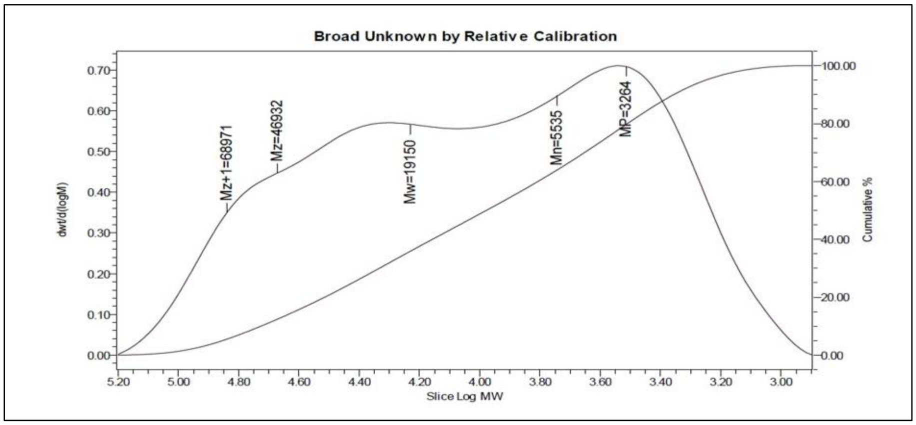

Figure 13. GPC spectra of copolymer TT.

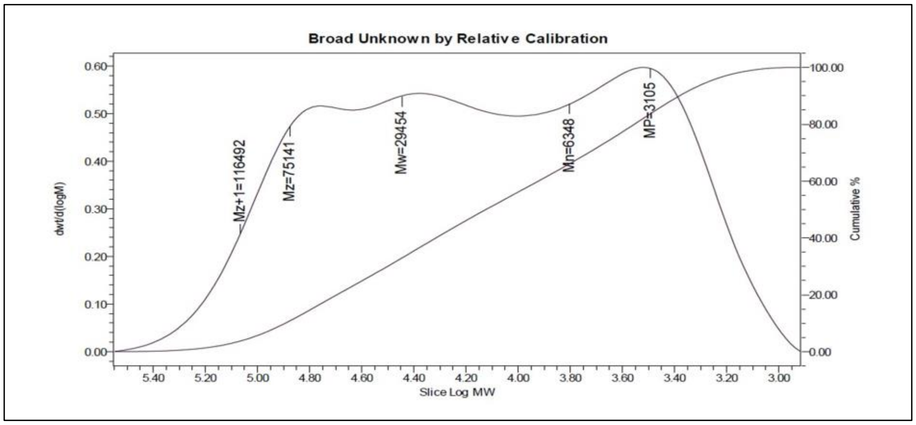

Figure 14. GPC spectra of copolymer OT.

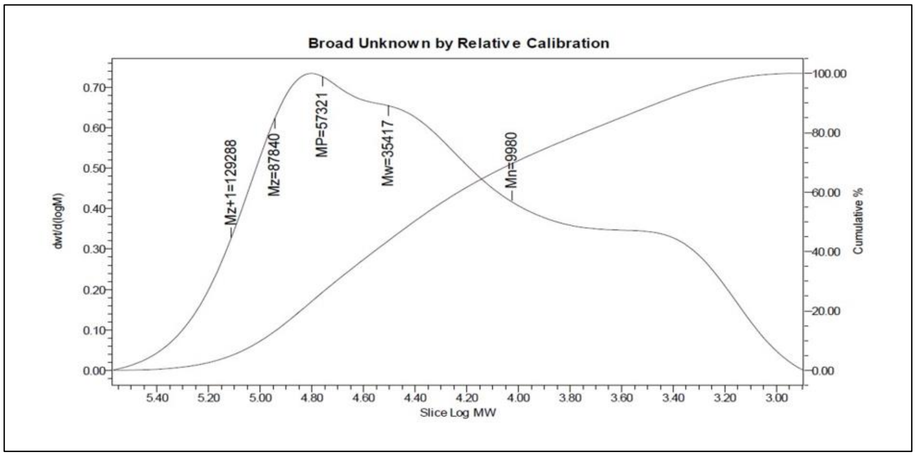

Figure 15. GPC spectra of copolymer DT.

Evaluation of viscosity index copolymers to improve the Iraqi lubricating oil

The efficiency of the copolymer additives (HT, TT, OT, and DT) as viscosity index improvers (VII) for Iraqi lubricating oil (base oil 60) was investigated by calculating the kinematic viscosity of the lubricating oil with the prepared copolymers was tested at temperatures of (40°C) and (100°C) and the viscosity index (VI) according to the ASTM D-2270-87 standard[19]. Table 4 shows the viscosity index for prepared copolymers for a series of concentrations, 0%,1%, 2%, 3%, 4%, and 5% by weight, were selected to examine the impact of copolymer additives [20, 21].

Table 4. shows the viscosity index values for the alkyl acrylates copolymers and (base oil 60) lubricant.

Conc. % by weight	Viscosity index			
	HT	DT	TT	DT
0%	98.2	98.2	98.2	98.2
1%	116.7	116.3	130.1	133.6
2%	123.4	125.0	139.1	140.5
3%	131.1	130.9	148.3	157.3
4%	134.4	143.3	153.3	165.3
5%	141.4	147.7	155.9	170.8

Table 4 and Figures (16) show that the VI increases as the copolymer additives concentration in the lubricating oil increases. The lubricating oil viscosity reduces as the temperature rises; however, the polymer chain expands due to the rise in solvation power, and the polymer volume grows. This increase in polymer size counterbalances the loss in lubricating oil viscosity and, as a result, reduces the viscosity fluctuations with temperature of the mixture. [22, 23]. The oil solution's total volume of polymer increases as polymer concentration increases. As a result, a polymer with a high concentration gives a higher viscosity index value than a low polymer concentration. [15, 24].

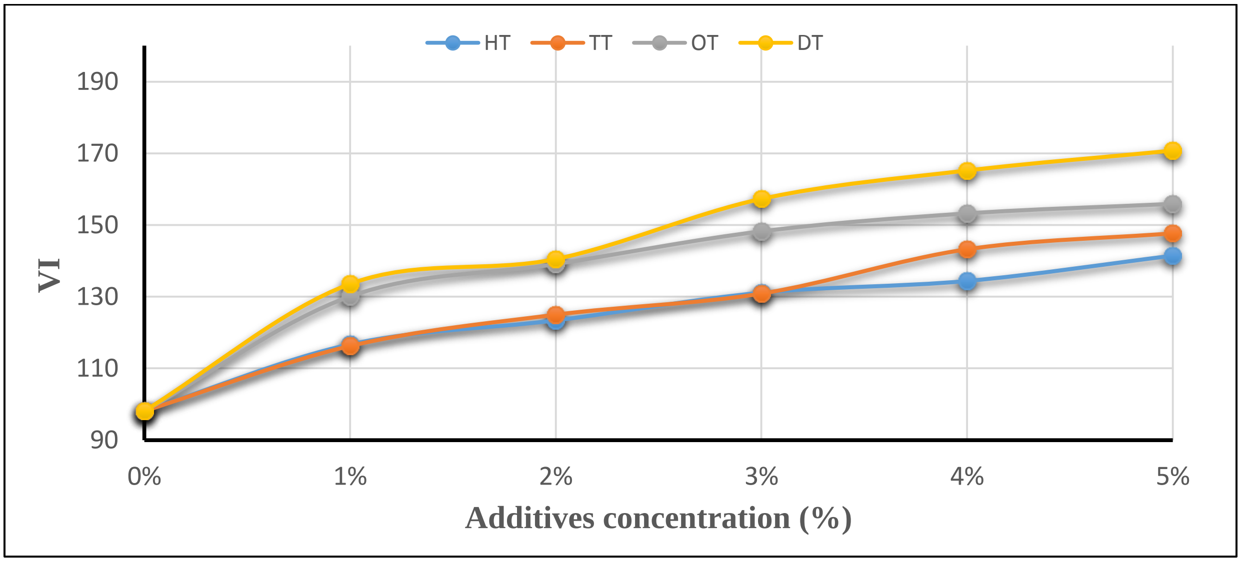

Figure 16. Influence of copolymer additives' concentration on lubricating oil's viscosity index.

The alkyl acrylate chain length also shows an impact on the efficacy of copolymer additives as viscosity index improvers for lubricant oil, Figures (17) show that increasing the alkyl chain length of alkyl acrylates increases the efficiency of the additive by increasing the VI. This could be due to the effect of molecular weight on the effective coil radius of the copolymer and, as a result, the viscosity index. [25, 26].

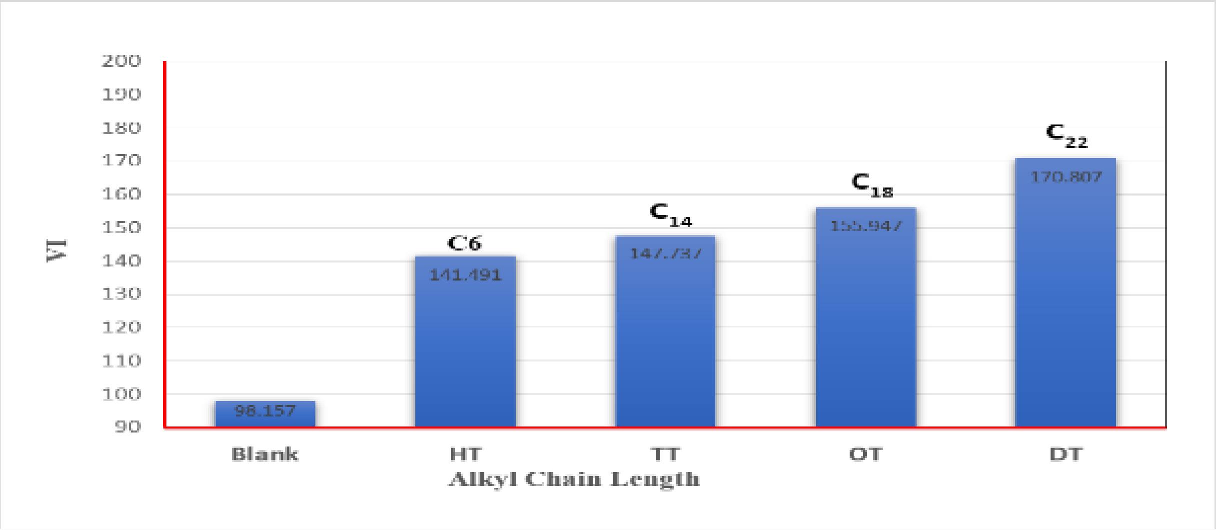

Figure 17. Influence of the alkyl chain length of copolymer additives at a concentration of (5%) by weight concentration on the viscosity index of lubricating oil.

Copolymers evaluation as pour point depressant for Iraqi lubricating oil

Copolymers were evaluated as pour point depressants with Various concentrations, including 1%, 2%, 3%, 4%, and 5% by weight according to the ASTM D 97 method [19].

All prepared copolymer additives (HT, TT, OT, and DT) had a good effect as pour point depressants at the lowest concentration (1%) by weight[5]. As shown in the experimental data in Table 5 and Figure 18, the copolymers are effective as pour point depressants, and the efficiency increases by decreasing the additive concentration. The solvation power of the lubricating oil explains this. It is well understood that the solvation power of any solvent decreases with a decrease in temperature and vice versa. This reduction in solvation power becomes clearer when the molecular weight and concentration of the solute increase[27].

The alkyl chain length also influences the efficiency of copolymers as pour point depressants. Figure 18 shows that as the alkyl chain length decreases, the effectiveness of these additives as pour point depressants improves. This observation may be attributed to reducing additives molecular weight, which reduces oil solubility by decreasing temperature[27, 28].

Table 5. The pour point and the concentration of copolymer additives.

Conc. % by weight	Pour Point (^oC)			
	HT	TT	OT	DT
0 %	-5	-5	-5	-5
1 %	-20	-16	-14	-11
2 %	-17	-14	-12	-12
3 %	-14	-12	-10	-9
4 %	-12	-12	-10	-7
5%	-12	-9	-9	-7

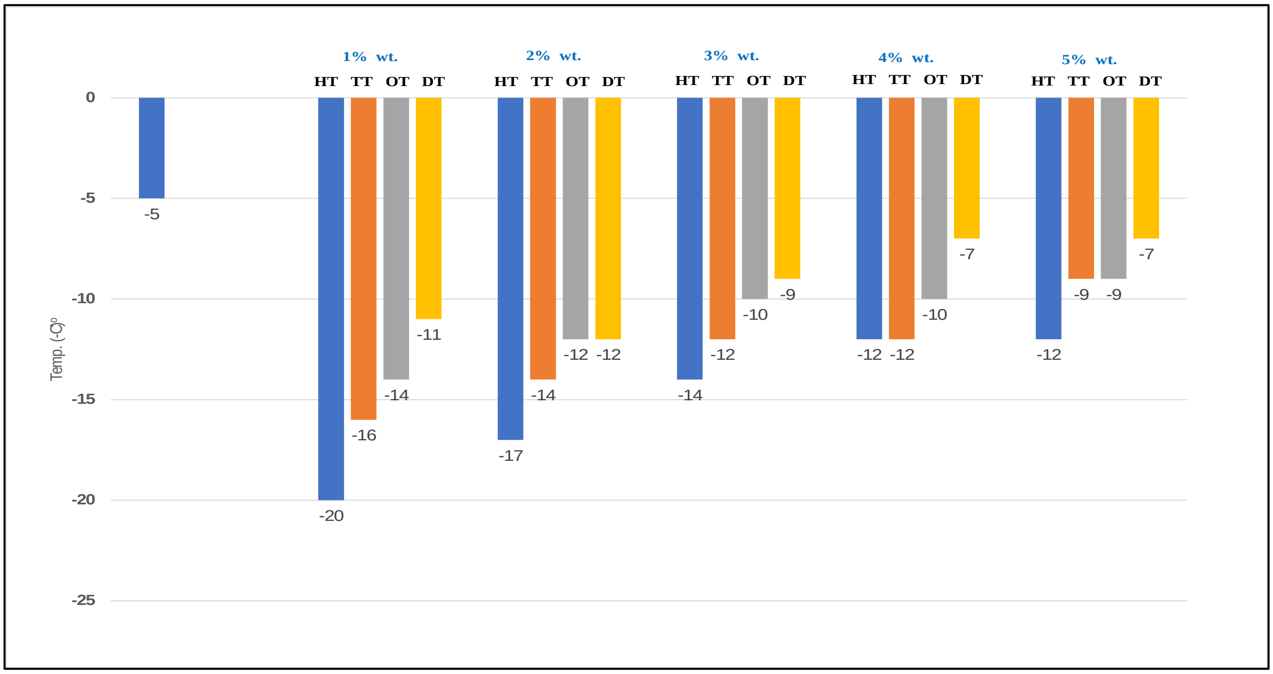

Figure 18. Influence of the concentration and alkyl chain length of copolymer additives (HT, TT, OT, and DT) on the pour point of lubricating oil.

Conclusions

The results demonstrated that the efficiency of the prepared copolymers as VI improvers increased with increasing concentration and alkyl chain lengths in the acrylate components. The copolymer DT exhibited the highest VI enhancement, achieving a VI of 170 at a concentration of 5 wt.% compared to the base oil VI of 98. Conversely, the effectiveness of copolymers as PPDs increased with decreasing concentration and alkyl chain lengths. The copolymer HT exhibited the best PPD performance, achieving a PPD of (-20 °C) compared to the base oil's PPD of (-5 °C). These results suggest that optimizing copolymer composition can tailor the multifunctional properties of additives to address specific requirements of lubricating oils, and this study highlights the potential of novel copolymers as promising VI improvers and PPDs for lubricating oil applications.

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الخلاصة

تم في هذه الدراسة تحضير أربعة بوليمرات مشتركة جديدة هي (HT,TT,OT,DT) عن طريق البلمرة بالجذور الحرة من خلال تفاعل مشتقات اكريلات الاكيل ذات اطوال سلاسل هيدروكاربونية مختلفة مع 1-تترادیسین. شخصت البوليمرات المشتركة من خلال تحديد أوزانها الجزيئية باستخدام تقنية (GPC) ، وتحليل بنيتها الكيميائية باستخدام مطيافية الأشعة تحت الحمراء (FTIR) و مطيافية الرنين النووي المغناطيسي للبروتون والكاربون (^{1}H-NMR) (^{13}C-HNMR) تم أيضًا استخدام تقنية التحليل الوزني الحراري (TGA) لتقييم الاستقرار الحراري لها . قيمت فعالية الكوبوليمرات الجديدة كمضافات لتحسين مؤشر اللزوجة ونقطة الانسكاب لزيت التشحيم العراقي متوسط اللزوجة (الزيت الأساسي 60) ، وأشارت النتائج إلى أن كفاءة الكوبوليمرات الجديدة كمحسّنات لمؤشر اللزوجة تزداد مع زيادة التركيز وطول سلسلة الألكيل في الأكريليت. حققت جميع الكوبوليمرات الجديدة نتائج جيدة مقارنة بزيت التشحيم الخالي من المضافات ، أظهر الكوبوليمر (DT) أفضل كفاءة (VI = 170) عند تركيز 5٪ مقارنة بزيت التشحيم الخالي من المضافات (VI = 98) ، من ناحية أخرى ، أرتفعت كفاءة الكوبوليمرات كمحسنات لدرجة الانسكاب مع انخفاض التركيز وطول السلسلة الألكيلية ؛ حيث أظهر البوليمر (HT) أفضل كفاءة (PPD = -20) درجة مئوية (مقارنة بزيت التشحيم الخالي من المضافات (PPD = -5) درجة مئوية.