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# *Synthesis of alkyl sulfur-functionalized oleic acid-based polymethacrylates and their application as viscosity index improvers in a mineral paraffinic lube oil*

**Juliette Lomège, Claire Negrell, Jean-Jacques Robin, Vincent Lapinte, Sylvain Caillol\***

Institut Charles Gerhardt Montpellier UMR 5253, Univ Montpellier, CNRS, ENSCM, Université de Montpellier, CC1702, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

\* Correspondence to: S. Caillol (E - mail: sylvain.caillol@enscm.fr)

**Keywords:** Oleic acid; Thiol-ene coupling; Methacrylate; Radical polymerization; Viscosity Index Improver; Lubricant application

## **Abstract**

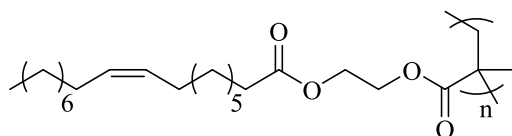
This work describes the synthesis of alkyl sulfur-functionalized polymethacrylate-based Viscosity Index Improvers (VII)s derived from oleic acid for mineral paraffinic lubricating oils. In this strategy, oleic acid was firstly quantitatively ramified by alkyl thiols containing long aliphatic chains through thiol-ene coupling as demonstrated by  $^1\text{H}$  NMR spectroscopy with the complete consumption of oleic acid internal double bonds. The resulting alkyl sulfur-functionalized oleic acid-based derivatives were methacrylated through Steglich esterification in order to afford highly suitable hydrophobic oleic acid-based monomers which, as far as we know, have not been described yet in the current literature. High polymethacrylate molecular weights were reached through radical polymerization despite the long alkyl pendant chains contained in their backbones. Finally, the resulting alkyl sulfur-functionalized oleic acid-based polymethacrylates have been blended in a mineral paraffinic oil (MPO) of reference at 5 wt. % and evaluated as VIIs. Rheological measurements revealed that polymer thickening powers were significantly improved in oil with temperature and promoted by increasing the pendant alkyl thiol contained in polymer backbones. Moreover, the viscosity index of MPO was significantly improved with the addition of both synthesized homopolymers which confirmed their efficiency as VIIs. In the meantime, these results have been compared to a previously reported polymer, the poly(2-(methacryloyloxy)ethyl oleate) (PMAEO) which demonstrated a lower VII efficiency compared to its analogous polymethacrylates containing an additional alkyl chain in their pendant chains.

# Introduction

The viscosity is one of the main important characteristics of lubricating oils (Neveu et al., 2012; Bartz et al., 1978). In mechanical systems, fluid viscosity leads to the formation and strength of lubricating films that protect the metal parts from friction and wear. Therefore, it is essential that the viscosity of a lubricant change minimally with fluctuating operating conditions (Eskici et al., 2008). In the industry, the viscosity-temperature dependency of a lubricant is evaluated by the measurement of the viscosity index (VI) which defines the quality of a lubricant and its application temperature range (Stanciu, 2012). According to the calculation method of the VI, lubricants with a high VI exhibit a low viscosity variation with temperature and are generally preferred in most machines. Therefore, in order to provide performant lubricant, base oils are generally formulated with specific high molecular weight polymer additives known as Viscosity Index Improvers (VIIs) (Martini et al., 2018; Almeida et al., 2014; Rattan et al., 2017). The addition of these polymers, which display viscosity thickening power as a result of their high molecular weight, are able to minimize viscosity variation in temperature, increase the VI, and thus, widen the application temperature range of lubricants. Commonly used VIIs for mineral lubricating oils are poly(alkylmethacrylates) (PMA)s (Ahmed et al., 2017; Akhmedov et al., 1993; Mohamad et al., 2012; Horne et al., 1949). The mechanism of action of such additives is based on their difference of solubility at low and high temperatures, resulting in an improvement of the additive thickening power in temperature (Selby, 1958; Ramasamy et al., 2016; Covitch et al., 2015; Müller, 1978). Indeed, as PMAs show only poor solubility in mineral oil at low temperatures (coil polymer contraction), it induces a relatively low viscosity contribution. However, PMAs show improved solubility as temperature increases (coil polymer expansion) inducing higher thickening power which thus limits the loss of viscosity of the fluid at elevated temperatures.

Even if the afore-mentioned additives, essentially obtained from fossil feedstock (Neveu et al., 2012; Cai et al., 2015), fulfill the requirements in term of viscosity tailoring, there is a growing demand for additives originated from renewable feedstock (Ghosh et al., 2014; Ghosh, 2014; Ghosh et al., 2017; Ghosh et al., 2017). In this context, it is advantageous to investigate novel biobased polymers showing close chemical structures and/or comparable technical performances to the currently used fossil-based polymeric VII. Plant oils and their fatty acids (FA) derivatives represent a perfect feedstock to achieve this goal. Indeed, polymers originated from these renewable resources have many advantages including the

hydrophobicity required to this kind of additives that must be soluble in mineral oils, an important flexibility in chemical structures and properties (as seen from the large series of papers (Caillol et al., 2012; Stemmelen et al., 2011; Pelletier et al., 2006) and reviews (Lligadas et al., 2013; Montero de Espinosa et al., 2011), and the monomers needed for their synthesis are considered feasible on a large scale due to the wide availability of plant oils. In this environmental context, our previous works reported the synthesis of various polymers containing methacrylate FA moieties (C12-C18) through radical polymerization which proved to be promising VIIs for a reference mineral paraffinic oil (MPO) (Lomège et al., 2018). Moreover, the results of this study have shown that the thickening efficiency of the resulting VIIs can be promoted by using preferentially high molecular weight polymers as well as by using methacrylate monomers derived from long FA chain length such as oleic acid (C18:1) as described in Fig. 1.



**Fig. 1:** Chemical structure of the poly(2-(methacryloyloxy)ethyl oleate)-based VII (PMAEO)

Hence, in order to afford even more performant VIIs with improved thickening power in MPO, the chemical structure of PMAEO can be modified by grafting an additional pendant alkyl chain on its pendant chain *via* the available internal double bonds. Among many existing reactions involving these unsaturations, the addition of alkyl thiols to olefins is a promising strategy to achieve this goal since it is nowadays frequently employed for the synthesis and polymerization of renewable monomers from vegetable oils (Ionescu et al., 2015; Bantchev et al., 2009; Biresaw et al., 2011). For instance, Desroches *et al.* previously reported the successful quantitative thiol-ene coupling of mercaptoethanol on oleic acid unsaturations (Desroches et al., 2011). Alternatively to the modification of monomers, this reaction can also be employed in a post-polymerization functionalization approach, if the polymer still contain vinyl groups after polymerization (Bowman et al., 2010; Vidal et al., 2015; Vidal et al., 2016). Then, thiol-ene coupling of oleic acid with alkyl thiols containing long aliphatic chains could yield suitable highly hydrophobic monomers for providing high performant polymer-based VIIs for MPO.

The approach followed in this work consisted of synthesizing oleic acid-based monomer structures to afford polymeric VIIs with high thickening power efficiency in MPO. For this

purpose, oleic acid, which is widely available in most of the plant oils and therefore cost-effective, has been firstly functionalized by thiol-ene coupling with two alkyl thiols including either 1-dodecanethiol or 1-octadecanethiol. Then, the two resulting alkyl sulfur-functionalized derivatives were methacrylated by Steglich esterification to provide suitable monomers for radical polymerization. Finally, the oleic acid-based polymers containing pendant aliphatic chains with ramified alkyl sulfur were mixed in a mineral paraffinic oil and evaluated as VIIs by monitoring the tendency of their thickening power in temperature through rheological measurements. All monomer and polymer structures were determined by  $^1\text{H}$  NMR spectroscopy and characterized by TGA, DSC and SEC.

## Materials and methods

### Reagents

Oleic acid (OA, 98 %) was purchased from Fisher Scientific while dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP, 99 %), 2-hydroethyl methacrylate (HEMA, 99%), 1-dodecanethiol (98 %), 1-octadecanethiol (98 %), benzoyl peroxide (BPO, with 25 m. %  $\text{H}_2\text{O}$ ) and deuterated chloroform ( $\text{CDCl}_3$ ) were purchased from Sigma-Aldrich and used as received except azobis(isobutyronitrile) (AIBN, 98 %) which was recrystallized in methanol before being used. All solvents including tetrahydrofuran (THF, 99 %), toluene (99 %), methanol (MeOH, 99 %), cyclohexane (CY, 98 %) and ethyl acetate (EtOAc, 98 %) were obtained from VWR and were used without further purification. A mineral paraffinic oil (MPO) was kindly supplied by ITERG. The lubricating oil characteristics are detailed in Table 1.

**Table 1:** Mineral paraffinic oil (MPO) properties (Technical data)

Properties	
Density at 20 °C (g.cm <sup>-3</sup> )	0.8503
Kinematic viscosity at 40 °C (mm <sup>2</sup> .s <sup>-1</sup> )	26.92*
Kinematic viscosity at 100 °C (mm <sup>2</sup> .s <sup>-1</sup> )	4.87*
Viscosity Index	103
Pour Point (°C)	-15
Thermal stability (at 5 % weight loss, °C)	200

\*: calculated through rheological measurements (see instrumentation part below).

## Instrumentations

### *Nuclear magnetic resonance (NMR)*

<sup>1</sup>H NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. NMR samples were prepared as follows: 10 mg of product for <sup>1</sup>H experiment in around 0.4 mL of CDCl<sub>3</sub>. The chemical shifts were reported in part per million relative to tetramethylsilane. Spin multiplicity is expressed by s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

### *Size exclusion chromatography (SEC)*

Molar mass and molar mass distribution (dispersity, Đ) of polymers were determined by size exclusion chromatography using a GPC 50 Varian equipped with an RI refractive index detector. The system used two PLgel 5 μm Mixed D columns with THF as eluent with a flow rate of 1 mL.min<sup>-1</sup>. Poly(methyl methacrylate) (PMMA) standards were used for the calibration. The typical sample concentration was 5 mg.mL<sup>-1</sup>.

### *Thermogravimetric analysis (TGA)*

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of 10 °C.min<sup>-1</sup>. Approximately 10 mg of sample were placed in an aluminum pan and heated from room temperature to 500 °C under nitrogen atmosphere (60 mL.min<sup>-1</sup>).

### *Differential scanning calorimetry (DSC)*

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH Maia DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. 10–15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at 20 °C.min<sup>-1</sup> between -100 and

100°C. Thermograms were recorded during the second heating ramp after removing thermal history of the polymer was removed during first heating scan.

#### *Rheometer*

Rheological investigations are executed by using a MCR 302 rheometer by Anton-Paar in plate-plate geometry with a diameter of  $d = 25$  mm. The dynamic viscosity of oil-polymer blends was measured from 0 to 100 °C at a shear rate of  $100 \text{ s}^{-1}$  and the relative viscosity (RV) in function of temperature was calculated by using the equation below:

$$RV = \frac{\mu}{\mu_0}$$

where  $\mu$  and  $\mu_0$  correspond respectively to the dynamic viscosity of the polymer solution and the dynamic viscosity of the pure solvent.

#### *Densimeter*

Density measurements of all formulations were performed on the DMA 4100M densimeter of Anton Paar at 40 and 100 °C. Before starting the test, the oil-polymer blends were all stirred at 100 °C during 1 hour to ensure a good homogenization. Then, samples were cooled at the temperature of measurement and approximately 1 mL is loaded into the densimeter to start the test. The kinematic viscosity of oil-polymer blends at 40 and 100 °C were deducted by following the equation:

$$\nu = \frac{\mu}{\rho}$$

where  $\nu$ ,  $\mu$ , and  $\rho$  correspond respectively to the fluid kinematic viscosity ( $\text{mm}^2.\text{s}^{-1}$ ), the fluid dynamic viscosity ( $\text{Pa}.\text{s}^{-1}$ ), and the fluid density ( $\text{g}.\text{cm}^{-3}$ ). Finally, the viscosity indexes of the formulations were calculated according to the ASTM D2270-10 method by using the values of kinematic viscosity of polymer solutions at 40 and 100 °C.

## **Preparation of alkyl sulfur-functionalized from oleic acid through thiol-ene coupling**

### **Synthesis of 9-(octadecylthio)oleic acid (OA<sub>SC18</sub>)**

Oleic acid (0.106 mol, 30.0 g) was charged in bulk in a 200 mL two neck round bottom flask. Then AIBN (0.2 eq, 21 mmol, 3.5 g) and 1-octadecanethiol (3 eq, 0.319 mol, 91.5 g)

was added into the reaction mixture and stirred at 70 °C. After 24 h of reaction, a second addition of AIBN is added to the solution and the reaction is continued 24 h more. After the complete conversion of the internal unsaturation of oleic acid by thiol-ene coupling, the resulting oleic acid-based thiol derivative (OA<sub>SC18</sub>) was purified through flash chromatography using silica gel as stationary phase and CY-EtOAc (95:5, v/v) as eluent (yield = 78 %). Its structure was confirmed by <sup>1</sup>H NMR (Fig. 2, (A)).

**OA<sub>SC18</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 2.54-2.52 (-S-CH-, 1H, m), 2.46 (-CH<sub>2</sub>-S-, 2H, t, J=7.4 Hz), 2.34 (O=C-CH<sub>2</sub>, 2H, t, J=7.5 Hz), 1.63-1.59 (H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.51 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.43-1.24 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 54H, m), 0.87 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 6H, t, J=6.4 Hz).

### **Synthesis of 9-(dodecylthio)oleic acid (OA<sub>SC12</sub>)**

The alkyl sulfur-functionalized oleic acid derivative 9-(dodecylthio)oleic acid was obtained by following the same procedure than OA<sub>SC18</sub> using 1-octadecanethiol instead of 1-dodecanethiol (yield = 83 %) as reported previously (Lomège et al., 2018). Its chemical structure was confirmed by <sup>1</sup>H NMR (Fig. SI-1, (B)).

**OA<sub>SC12</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 2.54 (-S-CH-, 1H, m), 2.46 (-CH<sub>2</sub>-S-, 2H, t, J=7.4 Hz), 2.34 (O=C-CH<sub>2</sub>, 2H, t, J=7.5 Hz), 1.63-1.59 (H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.51 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.43-1.24 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub>, 42H, m), 0.87 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub>, 6H, t, J=6.4 Hz).

## **Preparation of methacrylate monomers from alkyl sulfur-functionalized oleic acid-based derivatives**

### **Synthesis of fatty ester 2-(methacryloyloxy)ethyl 9-(octadecylthio)oleate (MAEO<sub>SC18</sub>)**

OA<sub>SC18</sub> (0.031 mol, 17,6.0 g), DMAP (0.016 mol, 1.89 g) and HEMA (0.062 mol, 8.07 g) were introduced into a two neck round bottom flask with 200 mL of THF and stirred at room temperature. Then, the reaction mixture was put in an ice-water bath. In a separate beaker, DCC (0.034 mol, 7.03 g) was dissolved in a minimum of THF and was added dropwise to the solution mixture. The ice-water bath was removed after complete addition of DCC. After 24



h, the white precipitated urea was filtered off and THF was removed by rotary evaporator. Then, the resulting ester was dissolved in toluene and washed twice with distilled water and then dried under vacuum. The purified monomer MAEO<sub>SC12</sub> was obtained in 75 % yield. Its chemical structure was confirmed by <sup>1</sup>H NMR (Fig. 2, (B)).

**MAEO<sub>SC18</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 6.12 and 5.59 (C=CH<sub>2</sub>, 2H, s), 4.35-4.32 (OCH<sub>2</sub>-CH<sub>2</sub>O, 4H, ), 2.54-2.52 (-S-CH-, 1H, m), 2.46 (-CH<sub>2</sub>-S-, 2H, t, J=7.4 Hz), 2.32 (O=C-CH<sub>2</sub>, 2H, t, J=7.5 Hz), 1.95 (CH<sub>3</sub>-C, s), 1.63-1.59 (H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.54-1.49 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.45-1.26 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 54H, m), 0.88 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 6H, t, J=6.4 Hz).

### **Synthesis of fatty ester 2-(methacryloyloxy)ethyl 4-(dodecylthio)oleate (MAEO<sub>SC12</sub>)**

The alkyl sulfur-functionalized oleic acid-based methacrylate monomer was obtained by following the same procedure than MAEO<sub>SC18</sub> as reported previously (Lomège et al., 2018). (yield = 70 %). Its chemical structure was confirmed by <sup>1</sup>H NMR (Fig. SI-2, (A))

**MAEO<sub>SC12</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 6.13 and 5.59 (C=CH<sub>2</sub>, 2H, s), 4.35-4.32 (OCH<sub>2</sub>-CH<sub>2</sub>O, 4H, m), 2.54-2.52 (-S-CH-, 1H, m), 2.46 (-CH<sub>2</sub>-S-, 2H, t, J=7.4 Hz), 2.32 (O=C-CH<sub>2</sub>, 2H, t, J=7.5 Hz), 1.95 (CH<sub>3</sub>-C, s), 1.63-1.59 (H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.54-1.49 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.45-1.24 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub>, 42H, m), 0.88 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>, 6H, t, J=6.4 Hz).

### **Synthesis of alkyl sulfur-functionalized oleic acid-based polymethacrylates**

#### **Synthesis of poly(2-(methacryloyloxy)ethyl 9-(octadecylthio)oleate (PMAEO<sub>SC18</sub>)**

MAEO<sub>SC18</sub> (7 mmol, 3 g) and AIBN (0.08 mmol, 12 mg) were dissolved in 10 mL of THF at 60 °C. The reaction mixture was then added into a two necked flask equipped with a magnetic bar and purged with N<sub>2</sub> gas for 20 min. After reaching a maximum of monomer conversion, the reaction mixture was quenched by cooling in liquid nitrogen and purified by precipitation in MeOH at least two times to yield a viscous liquid. The resulting polymer

PMAEO<sub>SC12</sub> was dried under vacuum for 5 h at 80 °C (yield= 79 %). Its chemical structure was confirmed by <sup>1</sup>H NMR spectroscopy (Fig. 2, (C)).

**PMAEO<sub>SC18</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 4.24-4.12 (OCH<sub>2</sub>-CH<sub>2</sub>O, 4H, m), 2.54-2.52 (-S-CH-, 1H, m), 2.47-2.43 (-CH<sub>2</sub>-S-, 2H, m), 2.33-2.30 (O=C-CH<sub>2</sub>, 2H, m), 1.94-1.92 (CH<sub>3</sub>-C, m), 1.63-1.59 (-CH<sub>2</sub>-C and H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.56-1.54 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.30-1.26 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 54H, m), 1.02 and 0.88 (CH<sub>3</sub>-C, 3H, m), 0.88 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub>, 6H, t).

## **Synthesis of poly(2-(methacryloyloxy)ethyl 4-( dodecylthio)oleate)**

### **(PMAEO<sub>SC12</sub>)**

The polymer was obtained by following the same procedure than the homopolymerization of MAEO<sub>SC18</sub> (yield= 76 %). Its chemical structure was confirmed by <sup>1</sup>H NMR (Fig. SI-2, (B)).

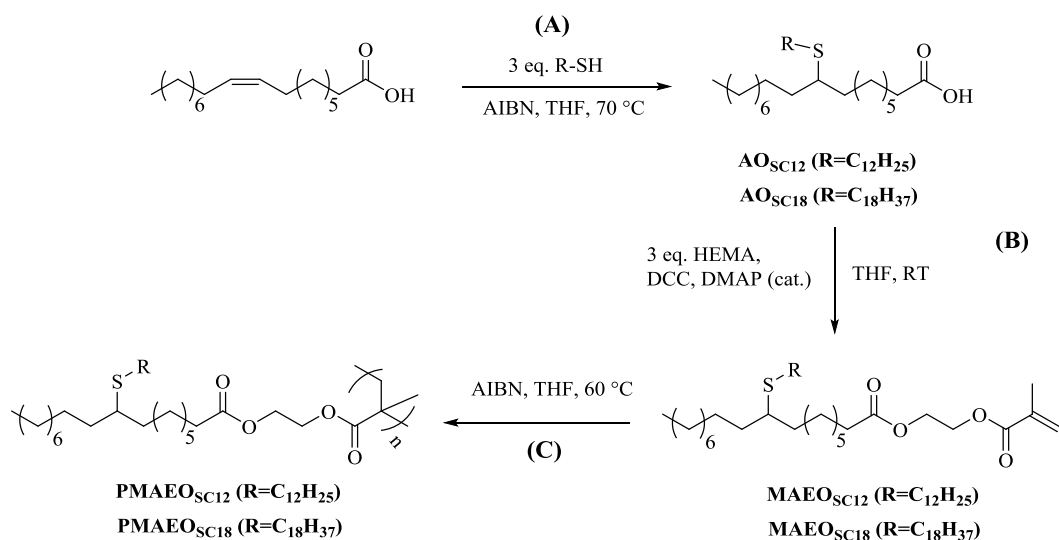
**PMAEO<sub>SC12</sub>:** δ (ppm, 400 MHz, CDCl<sub>3</sub>): 4.24 and 4.14 (OCH<sub>2</sub>-CH<sub>2</sub>O, 4H, m), 2.54-2.51 (-S-CH-, 1H, m), 2.47-2.43 (-CH<sub>2</sub>-S-, 2H, m), 2.33-2.30 (O=C-CH<sub>2</sub>, 2H, m), 1.63-1.59 (-CH<sub>2</sub>-C and H<sub>2</sub>C-H<sub>2</sub>C-C=O, 4H, m), 1.56-1.52 (-CH<sub>2</sub>-CH-CH<sub>2</sub>, 4H, m), 1.40-1.26 (-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub> and S-CH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub>, 42H, m), 1.02 and 0.88 (CH<sub>3</sub>-C, 3H, m), 0.88 (-CH<sub>2</sub>-CH<sub>3</sub> and S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub>, 6H, t).

## **Results and discussions**

### **Synthesis of sulfur-functionalized methacrylate monomers**

#### **Alkyl sulfur-functionalized oleic acid derivatives**

Thiol-ene coupling of oleic acid (OA) was carried out in THF at 70 °C by using an excess of 1-dodecanethiol (3 eq) and AIBN (0.1 eq) as thermal initiator (Scheme 1(A)). After 24 h, 70 % of internal double bond were converted and therefore a second AIBN addition (0.1 eq) was conducted to reach a quantitative conversion after 24 h more of reaction (Fig. SI-3).



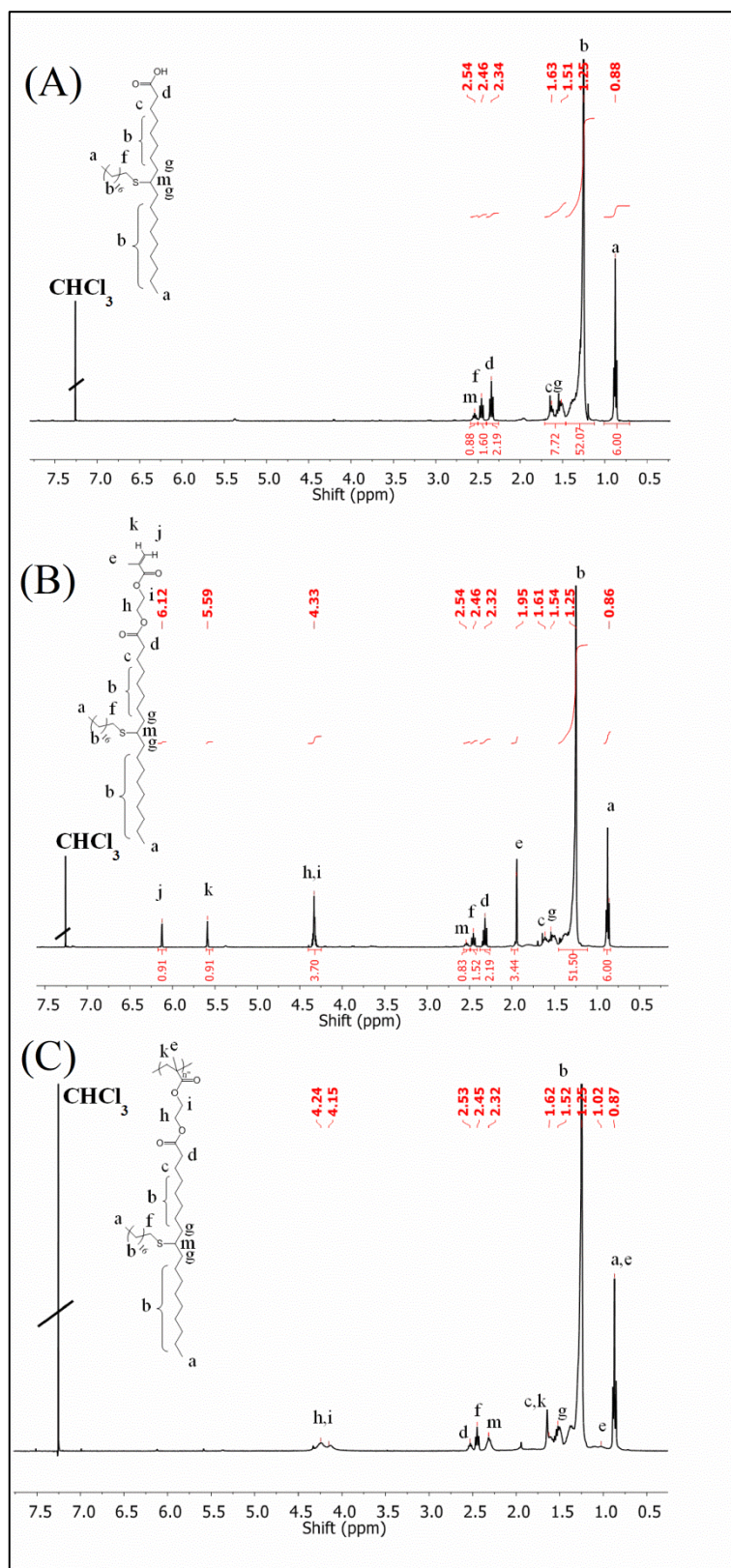
**Scheme 1:** Thiol-ene coupling on oleic acid internal unsaturations with alkyl thiol SHR (R=C<sub>12</sub>H<sub>25</sub> or C<sub>18</sub>H<sub>37</sub>), (A) Steglich esterification of the resulting derivatives (B), Free radical homopolymerization of alkyl sulfur-functionalized methacrylate monomers (C)

Fig. 2 (B) exhibits the <sup>1</sup>H NMR spectra of the AO<sub>SC18</sub>. All peaks have been assigned and confirmed the complete disappearance of both signals (CH=CH) at 5.34 ppm and (CH<sub>2</sub>-CH=) at 2.01 ppm proved a quantitative conversion of the double bond. Then, the occurrence of the characteristic signals corresponding to the CH<sub>2</sub>-S and the S-CH protons at 2.46 and 2.54 ppm respectively confirmed the alkyl thiol addition onto the oleic acid internal unsaturations. The side-reaction leading to formation of disulfide was not observed. The thiol-ene coupling was also successfully performed with 1-octadecanethiol by following the same procedure. The resulting structure of the final product, AO<sub>SC12</sub>, is shown in Fig. SI-1, (B).

## Alkyl sulfur-functionalized methacrylate oleic acid-based monomers

Both alkyl sulfur-functionalized oleic acid-based derivatives were converted into suitable and novel radically polymerizable monomers by grafting HEMA through Steglich esterification onto their backbones. The reaction was conducted in THF at room temperature and catalyzed *via* DMAP in the presence of DCC as coupling agent (Scheme 1, (B)). After 24 h, the reaction was completed and the oleic acid derivatives were both quantitatively converted into monomers and purified through liquid-liquid extraction. Fig. 2, (B) shows the <sup>1</sup>H NMR spectrum of MAEO<sub>SC18</sub> monomer where all peaks have been assigned. The

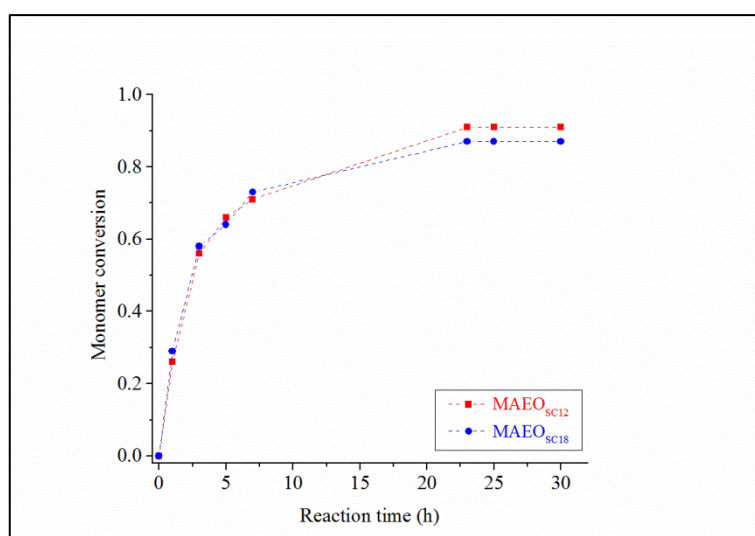
appearance of the vinyl protons belonging to the methacrylate function at 6.13 and 5.59 ppm as well as the methyl protons of the methacrylate function at 1.95 ppm confirmed the effectiveness of the functionalization. The spectrum of monomer MAEO<sub>SC12</sub> is shown in Fig. SI-2, (A).



**Fig. 2:**  $^1\text{H}$  NMR spectra of  $\text{AO}_{\text{SC18}}$  (A)  $\text{MAEO}_{\text{SC18}}$  (B),  $\text{PMAEO}_{\text{SC18}}$  (C)  $\text{CDCl}_3$

## Alkyl sulfur-functionalized oleic acid-based polymethacrylates

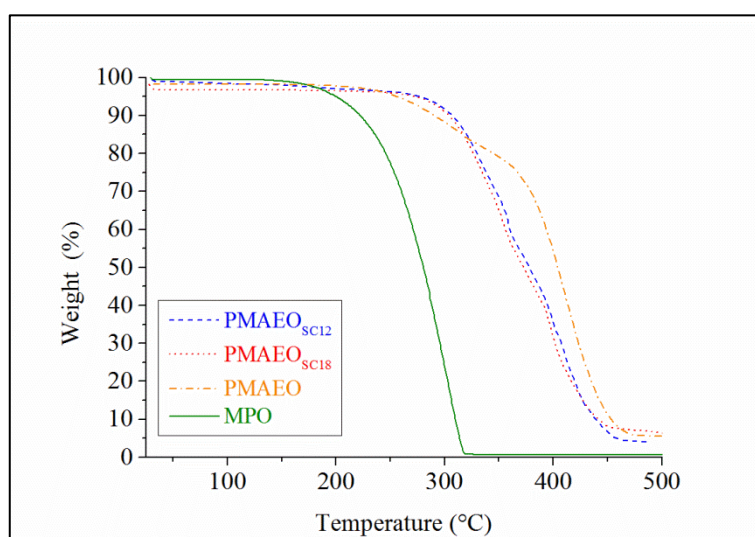
The alkyl sulfur-functionalized methacrylate monomers,  $\text{MAEO}_{\text{SC12}}$  and  $\text{MAEO}_{\text{SC18}}$ , were homopolymerized through radical polymerization in THF at  $60\text{ }^\circ\text{C}$  by using AIBN as radical source (Scheme 1, (C)). The rate of polymerization was monitored by  $^1\text{H}$  NMR spectroscopy by following the decrease in intensity of the methacrylate proton signals. Despite the difference of chain length in their structures, both monomers exhibited similar reactivity and conversion (around 90 %) into polymers after 24 h of reaction as shown in Fig. 3. Fig. 2, (C) shows the  $^1\text{H}$  NMR spectrum of  $\text{PMAEO}_{\text{SC18}}$  while that of  $\text{PMAEO}_{\text{SC12}}$  is shown in Fig. SI-2, (B). The complete disappearance of peaks assigned to the vinyl protons of the methacrylate group indicated the efficient removal of unreacted monomer after precipitation in cold methanol. The  $\text{O-CH}_2$  protons of side chain appeared at 4.24 and 4.14 ppm while methyl protons of the polymer backbone are assigned to the peak between 1.02 and 0.88 ppm. The resulting alkyl sulfur-functionalized polymers were obtained with a weight average molecular weight ( $\overline{M}_w$ ) of 146 and 155  $\text{kg}\cdot\text{mol}^{-1}$  and a broad dispersities ( $\mathcal{D}$ ) of 3.2 and 3.5 for respectively  $\text{PMAEO}_{\text{SC12}}$  and  $\text{PMAEO}_{\text{SC18}}$  (determined through SEC measurements). They both displayed suitable high molar masses for VII application as demonstrated in previous studies (Lomège et al., 2018; Lomège et al., 2019).



**Fig. 3:**  $\text{MAEO}_{\text{SC12}}$  and  $\text{MAEO}_{\text{SC18}}$  conversions versus time during the radical polymerization

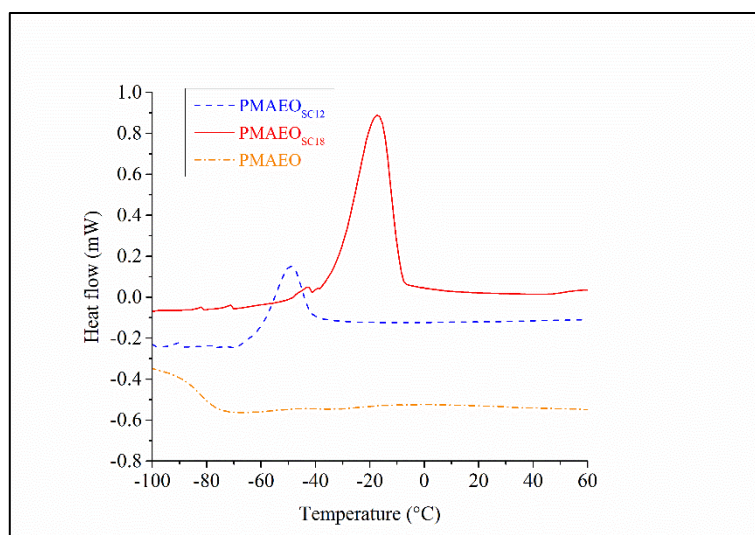
## Thermal properties of the alkyl sulfur-functionalized oleic acid-based polymethacrylates

In order to confirm that the synthesized polymers have enough thermal stability to be used as additives in the selected lubricating oil for the study, thermogravimetric analysis (TGA) was performed (Fig. 4). The results indicated that the temperature at 5 % weight loss ( $T_{d5\%}$ ) was around 280 °C for both alkyl sulfur-functionalized polymethacrylates while the temperature at 5 % weight loss was 200 °C for the mineral paraffinic oil (MPO). Therefore, as polymers have a higher thermal stability than the lube oil, they can be suitably used as additives in this oil. Moreover, the alkyl sulfur-functionalized polymers have a higher thermal stability than PMAEO described in our previous study (Lomège et al., 2018).



**Fig. 4:** TGA analysis of the alkyl sulfur-functionalized polymethacrylates and the lube oil

The thermal behavior of the alkyl sulfur-functionalized polymers has been also characterized by DSC analyses. Both homopolymers demonstrated crystalline behaviors at -50 °C and -20 °C for respectively PMAEO<sub>SC12</sub> and PMAEO<sub>SC18</sub> (Fig. 5) while PMAEO did not. According to the results, the longer the alkyl chain, the higher the crystallization temperature ( $T_c$ ) of the polymers, in accordance with the literature (Çayli et al., 2008). The  $T_c$  values of both polymers are lower than the pour point of the lube oil which is around -15 °C. Therefore, they should not negatively affect the rheological flow behavior of oil at temperatures above the oil pour point. In summary, the alkyl sulfur-functionalized polymers demonstrated suitable thermal properties to be used in MPO over a wide range of operating temperatures.



**Fig. 5:** DSC analyses of the alkyl sulfur-functionalized polymers

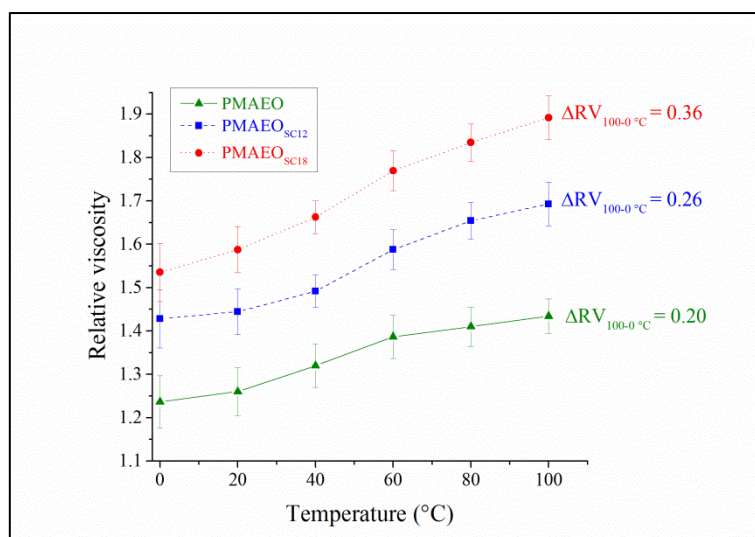
## Evaluation of the alkyl sulfur-functionalized polymethacrylates as VII

### Rheological viscosity dynamic measurements

The rheological behavior of oil-polymer blends (5 wt. %) was studied between 0 and 100 °C in order to evaluate the tendency of polymer thickening power with temperature and therefore determine if they have similar properties than common PMAs. For this purpose, dynamic viscosity measurements of oil-polymer blends with temperature were firstly performed and then the relative viscosity (RV) between MPO and MPO-polymer blends was calculated and plotted versus temperature. The calculated RV represents the polymer contribution on oil viscosity. Therefore, the RV should increase with the temperature if the incorporated polymer in oil behaves as an efficient VII (Covitch et al., 2015).

According to the rheological measurements shown in Fig. 6, similar behavior in temperature was observed for both alkyl sulfur-functionalized polymers. Indeed, the influence of these polymers on the viscosity of MPO was more important at high temperature than at low temperature, which is characteristic of common polymer VII additives. For instance, the RV of MPO-PMAEO<sub>SC18</sub> blend was improved from 1.54 at 20 °C to 1.90 at 100 °C. These results can be assigned to a coil polymer expansion with temperature due to the gradual increase of polymer solubility in MPO. Moreover, the data indicated that the longer the alkyl chain of the grafted alkyl thiol on the polymer backbone, the higher the improvement of the

polymer thickening power with temperature. Indeed, while the RV improvement between 0 and 100 °C was 0.26 for PMAEO<sub>SC12</sub>, it was 0.36 for PMAEO<sub>SC18</sub>. This result may be also explained by the slightly lower molar mass of PMAEO<sub>SC12</sub> ( $\overline{M}_w = 146 \text{ kg.mol}^{-1}$ ,  $\overline{D}=3.2$ ) compared to PMAEO<sub>SC18</sub> ( $\overline{M}_w = 155 \text{ kg.mol}^{-1}$ ,  $\overline{D}=3.5$ ) which may induce a lower coil size dimension and therefore a lower contribution on oil viscosity as previously reported (Lomège et al., 2018).



**Fig. 6:** RV of oil/alkyl sulfur-functionalized polymer blends vs temperature in MPO

Finally, the behavior of these polymers with temperature was also compared to the previously reported poly(2-(methacryloyloxy)ethyl oleate) (PMAEO,  $\overline{M}_w = 160 \text{ kg.mol}^{-1}$ ,  $\overline{D}=3.6$ ) in order to demonstrate the importance of the additional grafted alkyl chain (Lomège et al., 2018). According to the Fig. 6, the alkyl sulfur-functionalized polymers have shown a better thickening power improvement with temperature compared to PMAEO ( $\Delta RV_{100-0 \text{ °C}} = 0.20$ ) despite their slightly lower molar masses. In fact, the additional aliphatic chains on their backbone have promoted the interactions with the aliphatic chains of MPO, inducing a higher contribution on oil viscosity, especially at high temperature where the solubility of polymer is enhanced. In the meantime, despite their higher RV improvement with temperature, the thickening power of alkyl sulfur-functionalized polymers is also higher at low temperature compared to PMAEO and may induce more energy to put the oil in motion at those low operating temperatures. However, in case high viscosity might be problematic at low temperature for some lubricant applications (such as engine oils), the thickening power of the synthesized polymers can be easily modulated by varying the polymer concentration in oil



allowing to select the proper viscosity according to the desired application as previously reported (Lomège et al., 2018).

## Viscosity Index (VI) calculations

The alkyl sulfur-functionalized homopolymers were tested for their effectiveness as VII by calculating the VI of the pure oil and those of oil-polymer blends owing to the ASTM D2270-10 method. This method includes the determination of the kinematic viscosities of the different lubricant formulations at 40 and 100 °C. The resulting data are shown in Table 2 and indicated the effectiveness of adding alkyl sulfur-functionalized polymers for improving the MPO VI. Indeed, while the MPO has an initial VI of 102, it was only increased to 154 by adding PMAEO in the lube oil compared to 186 and 195 by adding alkyl sulfur-functionalized homopolymers respectively PMAEO<sub>SC12</sub> and PMAEO<sub>SC18</sub> in the lube oil. The improvement of VI was more pronounced in the case of the homopolymer containing the longer alkyl sulfur as it induced more interactions with the paraffin content of the MPO and therefore a higher thickening power improvement with temperature. These results showed that the polymer confers a higher viscosity to oil and that this contribution is higher at high temperature, which is the demonstration of a VII. Hence, as the addition of PMAEO<sub>SC18</sub> in MPO induced the highest increase of relative viscosity with the temperature ( $\Delta RV_{100-0\text{ °C}} = 0.36$ ), it demonstrated the best VII efficiency

**Table 2:** Kinematic viscosities and viscosity index measurements of pure MPO and oil-polymer blends

Oil-polymer blends	KV 40 °C (mm <sup>2</sup> .s <sup>-1</sup> )	KV 100 °C (mm <sup>2</sup> .s <sup>-1</sup> )	Viscosity Index	$\Delta RV_{100-0\text{ °C}}$
Pure MPO	26.92	4.87	102	-
MPO + PMAEO	35.80	6.91	154	0.20
MPO + PMAEO <sub>SC12</sub>	40.11	8.23	186	0.26
MPO + PMAEO <sub>SC18</sub>	44.69	9.25	195	0.36

## Conclusion

Viscosity Index Improvers (VIIs) from oleic acid for mineral paraffinic lube oils have been reported in this work. The synthesizing process began by the successful thiol-ene coupling of oleic acid with either 1-dodecanethiol or 1-octadecanethiol followed by the quantitative methacrylation of the resulting derivatives through Steglich esterification. The alkyl sulfur-functionalized oleic acid-based methacrylate monomers have shown a good reactivity through radical polymerization leading to high molecular weight polymers which is desirable for the targeted application. The good thermal stability of these homopolymers coupled with their similar “comb-like” structures than current PMAs as well as their high hydrophobicity made them suitable candidates for being evaluated as VII in MPO. Therefore, the behavior of the resulting polymers in MPO as a function of temperature was characterized by rheological measurements and demonstrated that their thickening power in the lube oil was significantly improved as the temperature rises. According to the results, the longer the aliphatic chains contained in the polymer additive backbone, the greater the relative viscosity improvement in temperature. Moreover, viscosity index measurements have confirmed the ability of the alkyl sulfur-functionalized polymers to considerably improve the initial lube oil’s VI. Consequently, from the above discussion, it is clear that both alkyl sulfur-functionalized oleic acid-based polymethacrylates have performed as excellent VII with high thickening power in a mineral paraffinic oil (MPO) and may be considered as promising alternative to current PMAs.

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## Conflict of Interest

The authors declare that they have no conflict of interest.

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