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# Well-Defined Alkyl Functional Poly(Styrene-*co*-Maleic Anhydride) Architectures as Pour Point and Viscosity Modifiers for Lubricating Oil

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**ABSTRACT**

A series of well-defined poly(styrene-*co*-maleic anhydride) copolymers (PSMA) allowing controlled grafting density and distribution of long alkyl side chains (C12 and C22) was synthesized and investigated as viscosity modifiers for two mineral base oils (API Group II and III). The PSMA copolymer backbones (multisite, multiblock, diblock, alternating linear, alternating star) were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization using industrial chain transfer agent (CTA-Ester) and subsequently esterified using long alkyl alcohols (lauryl and behenyl alcohol). The influence of grafting density and distribution, backbone, and side chain length of the polymers on the pour point (PPT) of blended fluids was investigated. The viscosity index (VI) and thickening efficiency (TE) were also studied. All the polymers showed improvement of base oil properties (PPT, VI, and TE). The alternating PSMA materials (high density of side chains) functionalized with shorter alkyl chains (C12) were found to be more efficient as pour point depressants (PPDs), regardless of the oil type and the molar mass or architecture of the polymer tested (ΔPPT= -36 °C and -30 °C in oil group II and III, respectively). A poly(lauryl acrylate) (PLAc) sample was also synthesized and used for comparison, showing the benefit of having styrene in copolymer additive composition. The VI and TE properties were shown to be dependent on molar mass and architectures used, where the best results were obtained for high molar mass PSMA star.

## 1. INTRODUCTION

One of the major challenges of crude oil and its derivatives (lubricating oils and fuel) is the precipitation of n-paraffin as wax at low temperature.[1] The wax formation leads to drastic changes on rheological properties and complicates oil flow at low temperatures. Wax crystallization is responsible for many problems occurring in oil production, storage and transportation, and complicates the use of fuels (diesel, gasoline and kerosene) in cold climates (deposits and blockages).[2-7] This problem can be addressed chemically by adding polymeric additives acting as pour point depressants (PPDs) or flow improvers (FIs). Copolymers with linear or comb-like structures have been largely investigated and proven efficient as wax precipitation inhibitors.[8, 9] Poly(ethylene-*co*-vinyl acetate) (EVA),[10-13] poly(ethylene-*co*-butene),[14-16] poly(α-olefins),[17] poly(alkylacrylates),[18, 19] poly(alkylmethacrylates),[20, 21] and copolymers of maleic anhydride with styrene, α-olefins or vinylic esters,[3,4,22,23] are among the most efficient commercially available PPDs. Despite many investigations and extensive literature, the basic mechanism of the pour point (PPT) phenomenon and how polymeric additives affect the pour point are currently not fully understood.[2, 3, 24-27] It is generally believed that the inhibition of wax crystallization occurs *via* nucleation, co-crystallization or adsorption of PPDs, altering the crystal morphology and growth characteristics. By destroying cohesive forces between crystals, it reduces the formation of interconnected three-dimensional wax networks that lead to gelation.[19, 28] Although it is important to understand that, the different compositions and the multiple applications of lubricating oils can require different additives, therefore a universal PPD system is unlikely.[3] It has been reported that the efficiency of the PPDs depends upon many factors, such as n-paraffin and polymer additives features (content, composition, molar mass and pendant chain nature).[20, 29-32] Moreover, it has been found that the higher chemical similarity between the polymer structure and the wax constituents, the better the

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performance as PPDs. For optimal pour point depressing results, the polymer additives must contain long aliphatic side chains and benzene rings interacting with paraffins or aromatics (asphaltenes) present in oils. Furthermore, the presence of polar groups (ester or carboxylic acids) and steric hindrance (graft or branched structure) helps to interfere with the wax crystallization process by changing the crystal size and morphology. The composition and structure of polymeric additives is thus fundamental to optimize oil derivative efficiency, durability and performance. In addition to PPDs and FIs, lubricating oils also require additives such as viscosity modifiers, antiwear, antioxidants and dispersants. The development of new additives combining multifunctional property modifications is therefore of great interest to reduce the overall costs.[33]

Poly(styrene-*co*-maleic anhydride) (PSMA) copolymers with aliphatic side chains are interesting graft materials which have already attract interest as PPDs/viscosity modifiers in crude oil industry.[4,34-36] Their effectiveness is dependent on polymer content, composition, the distance between pendant side chains, molar mass, polymer dispersity and the amorphous or crystalline nature of the additives.[4,5,37] However, most of the PSMA materials (and other graft copolymers) studied to date suffer from poor compositional and structural control due to the free-radical polymerization process typically used in industry. Thus, controlling structural parameters of these copolymers is a major challenge in the development of efficient additives. With the recent advances in controlled radical processes, it is now possible to access well-defined materials with novel polymeric architectures, opening the way for new materials with potential as oil additives.

In this study, we use the reversible addition-fragmentation chain transfer (RAFT) polymerization process and post functionalization to prepare a series of well-defined graft PSMA architectures with controlled grafting density and distribution of long alkyl side chains.[38] The effect of structure, composition, molar mass, side chain length and type of architecture on the viscometrics of two

mineral oils (API Group II and III) was investigated. The pour points of oil-polymer blends were measured at different concentrations (0.2 wt. %-0.8 wt. %). The viscosity index (VI) and thickening efficiency (TE) were also investigated to determine potential performance as lubricating oil additives.
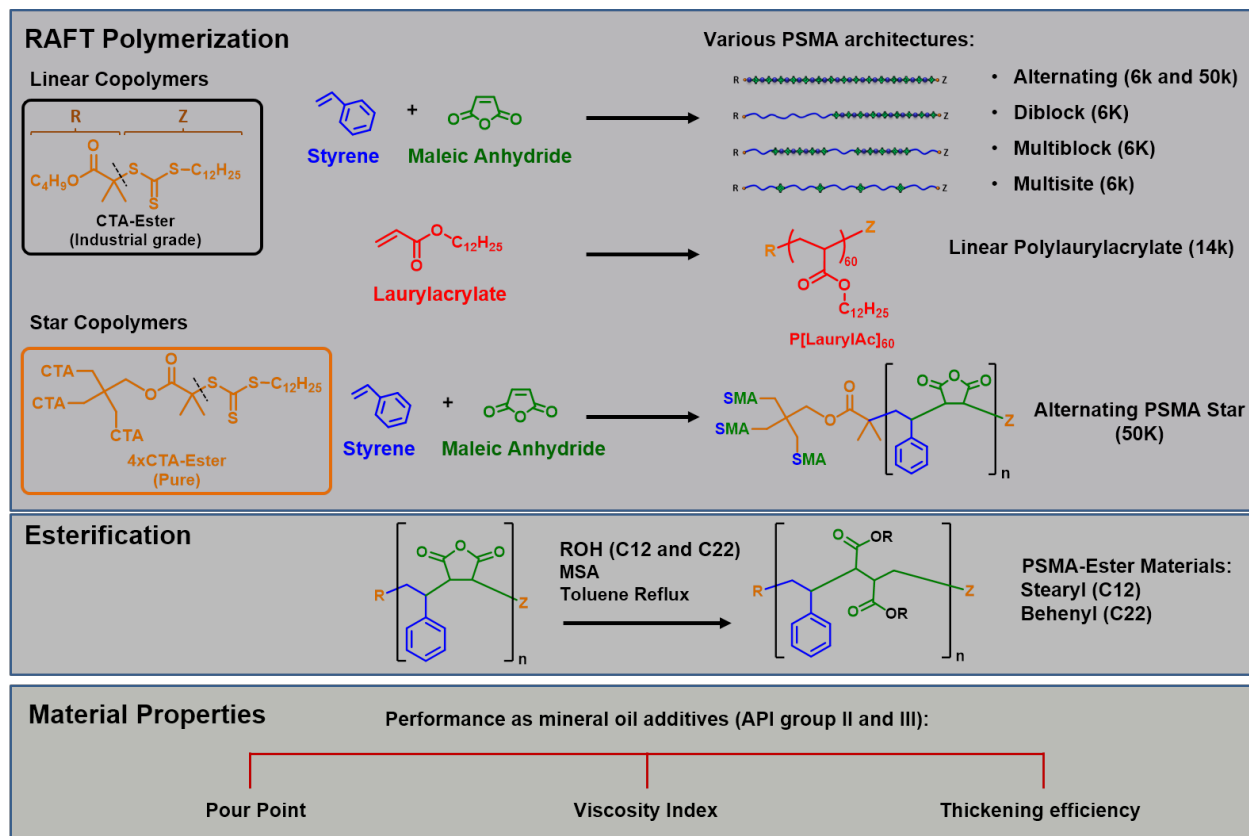


**Scheme 1.** Synthesis of a library of graft polymeric materials by RAFT polymerization and subsequent esterification.

## 2. EXPERIMENTAL

### 2.1. Materials

Styrene (Sty, ≥ 99 %) and lauryl acrylate (LaurylAc, 90 %) were obtained from Sigma-Aldrich and passed through neutral alumina prior to use to remove inhibitor. Maleic anhydride (MAnh, ≥ 99 %), 1,1'-Azobis(cyclohexane-1-carbonitrile) (V-40, $T_{1/2-10h}$ = 88 °C, 98 %), pentaerythritol (99 %) and methane sulfonic acid (MSA, 70 wt. % in $H_2O$) were obtained from Sigma-Aldrich and used as received. Dimethyl 2,2'-azobis(2-methylpropionate) (V601, $T_{1/2-10h}$ = 66 °C, 98 %) was obtained from Wako Chemicals. Industrial grade CTA-Ester (≈ 80 % pure), CTA-Acid (> 95 % pure), lauryl and behenyl alcohols, and mineral oils (API group II and III) were provided by Lubrizol and used without purification.[39, 40] The 4xCTA-Ester was prepared by esterification between CTA-Acid and pentaerythritol, following a method described in our previous paper.[38]

**Table 1. Mineral oils compositions**

| Properties | Oil Group II | Oil Group III |
|---|---|---|
| Origin | Chevron | SK Lubricants |
| Reference | 100N | 100N |
| Density at 15.6 °C (g cm$^{-3}$) | 0.848 | 0.833 |
| Kinematic Viscosity at 40 °C (cSt) | 19.80 | 19.23 |
| Kinematic Viscosity at 100 °C (cSt) | 4.12 | 4.25 |
| Viscosity Index | 108 | 129 |
| Pour point (°C) | -15 | -12 |

### 2.2. Preparation of Polymeric Additives

### PSMA Materials Synthesis and Characterization

All the PSMA copolymers were prepared by RAFT polymerization using industrial CTA-Ester following a method described in our previous work.[38]

A typical procedure to prepare an alternating PSMA material with a degree of polymerization of 250 (DP = 250) by RAFT consists of copolymerizing styrene (3.2 g, 30 mmol) and maleic anhydride (3.0 g, 30 mmol) in equimolar ratio in the presence of industrial grade CTA-Ester (0.06 g, 0.12 mmol ) and radical initiator (V601 – 0.01 g, 0.04 mmol). The polymerization was carried out under nitrogen atmosphere at 60 °C for 12 hours. The copolymer was purified by precipitation in diethyl ether from acetone. The copolymer was characterized using $^1$H NMR and size exclusion chromatography (SEC) (monomer conversion = 99 %, $M_{n,theo}$ = 50,700 g mol$^{-1}$, $M_{n,3d-SEC-CHCl3}$ = 48,200 g mol$^{-1}$, $Đ_{RI}$ = 1.19, and mass recovered = 5 g).

### PSMA Materials Esterification

The linear PSMA copolymer (DP =250, 3.0 g, 0.06 mmol) was reacted with long aliphatic alcohol (C$_{12}$OH, 16.6 g, 88 mmol, 6 equiv. / MAnh) in the presence of methane sulfonic acid (MSA) catalyst (1.1 g, 8.8 mmol, 0.1M equiv. / alcohol). The esterification was carried out using Dean-Stark apparatus under reflux of toluene ($\approx$ 70 wt. %). After reaction (*ca*. 20 hours), the mixture was precipitated several times in cold methanol and isopropyl alcohol from a minimum amount of diethyl ether. The precipitate was dried in an oven and recovered as an off-yellow solid (mass recovered = 10 g). The graft copolymer was characterized using infrared spectroscopy (IR), quantitative $^1$H NMR and $^{13}$C NMR spectroscopy and SEC (yield = 93 %, $M_{n,calc}$ = 128,900 g mol$^{-1}$, $M_{n,3d-SEC-CHCl3}$ =133,000 g mol$^{-1}$ and $Đ_{RI}$ = 1.28).

**Poly(lauryl acrylate) (DP = 60)**

The poly(lauryl acrylate) was synthesized following typical RAFT polymerization procedure using industrial grade CTA-Ester without purification. Laurylacrylate (8 g, 30 mmol), CTA-Ester (0.26 g, 0.5 mmol), V601 (0.01 g, 0.045 mmol) and toluene (19.6 mL) were introduced into a vial equipped with a magnetic stirrer bar and sealed with a rubber septum. The solution was degassed using nitrogen (*ca.* 15 min) before being placed in a thermostated oil bath set at 65 °C. After reaction completion (*ca.* 20 hours), the mixture was allowed to cool down to room temperature and then purified by precipitation in cold methanol (mass recovered = 6.8 g). The copolymer was characterized using $^1$H NMR spectroscopy and SEC (monomer conversion = 87 %, $M_{n,theo}$ = 13,000 g mol$^{-1}$, $M_{n,3d\text{-}SEC\text{-}CHCl3}$ = 17,700 g mol$^{-1}$ and $Đ_{RI}$ = 1.30).

## 2.3. Polymer Materials Characterization

The monomer conversion (conv.) and theoretical molar mass ($M_{n,theo}$) were determined using $^1$H NMR spectroscopy recorded on a HD 400 MHz Bruker Avance III system at 25 °C using deuterated solvents obtained from Sigma-Aldrich. The average number molar mass ($M_{n,RI}$) and dispersity ($Đ_{RI}$) were determined using SEC with conventional calibration (PS or PMMA) using Agilent Infinity II MDS instruments. The true molar mass ($M_{n,3d\text{-}SEC}$), intrinsic viscosity (IV), hydrodynamic radius ($R_h$), Mark-Houwink parameter ($\alpha$) and conformation data were determined by triple-detection SEC (3d-SEC) using differential refractive index (DRI), viscometer (VS), light scattering (LS) and dual wavelength UV detectors. Refractive index increments ($d$n/$d$c) of the materials were determined offline in respective eluents using a differential refractometer and the values are presented in Table 2.

**Table 2.Refractive index increments used for triple-detection SEC method**

| Materials | Solvent | Temp. °C | $dn/dc$ |
|---|---|---|---|
| Multisite PSMA | CHCl$_3$ | 30 | 0.170 |
| Multiblock PSMA | DMF | 50 | 0.160[a] |
| Multiblock PSMA | CHCl$_3$ | 30 | 0.200 |
| Diblock PSMA | CHCl$_3$ | 30 | 0.200 |
| Alternating PSMA | DMF | 50 | 0.160 |
| Multisite C22 | CHCl$_3$ | 30 | 0.125 |
| Multiblock C22 | CHCl$_3$ | 30 | 0.095 |
| Diblock C22 | CHCl$_3$ | 30 | 0.085 |
| Alternating C22 | CHCl$_3$ | 30 | 0.055 |
| PLaurylacrylate | CHCl$_3$ | 25 | 0.035[b] |

[a] not measured and assumed to be similar to alternating. [b] approximate value from literature for polyethylacrylate.[41]

DMF system (DMF + 5 mmol NH$_4$BF$_4$) was equipped with 2 x PLgel mixed D columns (300 x 7.5 mm), a PLgel 5 $\mu$m guard column, run at 1 ml min$^{-1}$ at 50 °C, and calibrated using PMMA standards (Agilent EasiVial 950-1,5M). Analyte samples were filtered through a nylon membrane with 0.22 $\mu$m pore size before injection. The chloroform system (CHCl$_3$ + 2 v/v % triethylamine) was equipped with 2 x PLgel mixed C columns (300 x 7.5 mm), a PLgel 5 $\mu$m guard column, run at 1 ml min$^{-1}$ at 30 °C, and calibrated using PS standards (Agilent EasiVial 900-360k). Analyte samples were filtered through a PVDF membrane with 0.22 $\mu$m pore size before injection.

Esterification yield was determined by quantitative $^{13}$C NMR spectroscopy measurements on a 600 MHz Bruker Avance III instrument using a relaxation time of 10 s, a high number of scans (>4k), and suppression of NOE (inverse gated decoupling). Aromatic carbons from styrene were considered as a reference (126 ppm) and the peak from methylene alkyl next to the ester linkage

(64.5 ppm) was used to determine the number of alkyl chains inserted. The yield of esterification was also confirmed by IR spectroscopy by following the disappearance of the MAnh ester symmetric stretch peak at 1,850 cm$^{-1}$ and the shift of the ester asymmetric stretch peak from 1,770 cm$^{-1}$ to 1,730 cm$^{-1}$. In addition, a more intense peak attributed to the alkane C-H stretch at 2,700-3,000 cm$^{-1}$ was observed after introduction of long alkyl chains.

### Pour point (PPT) Measurements

The polymer additives were mixed with mineral oils at different concentrations (0.2, 0.4, and 0.8 wt. %) and blended prior to measuring the PPT using standard method (ASTM D5950 Automated Tilt). The instrument was run using 3 °C intervals between the range of -54 °C to +51 °C.

### Rheology Investigations (Viscosity Index and Thickening Efficiency)

The kinematic viscosity (KV) of the different formulations was measured using a capillary viscometer (Houillon viscometer VH1 – Integrated Scientific LTD) following a standard method (ASTM D7279). The viscosity/temperature relationship, or Viscosity Index (VI), was calculated using the standard method ASTM D2270 by measuring the kinematic viscosity values measured at 40 °C and 100 °C (KV40 and KV100).

The thickening efficiency (TE) is a unitless number used to describe the contribution of a known amount of polymer in viscosity of an oil at 100 °C (boost in KV100). The TE gives an indication of the quantity of polymer required to reach a desired viscosity. The higher the TE, the lower the amount of polymer required (cost saving). Generally, polymers with higher molar mass exhibit greater thickening efficiency, however, it is usually counterbalanced by their low shear stability, thus leading to loss in durability of the fluid. The TE was calculated according to the following equation (1):

$$TE \ = \frac{\log(KV100_{measured}/KV100_{oil})}{\% \, wt. \, Polymer} \times 100 \qquad (1)$$

## 3. RESULTS AND DISCUSSION

### 3.1. Materials features

The graft PSMA materials were synthesized as described previously (Scheme 1).[38] All PSMA materials were subsequently functionalized by esterification of maleic anhydride moieties using long aliphatic alcohols (C12 and C22) in the presence of acid catalyst (MSA) under reflux of toluene (Dean-Stark). The materials were purified by performing several precipitations to remove the excess long alkyl chains which could affect the quality of performance measurements. The pure materials were characterized using infrared spectroscopy (IR), quantitative ^{1}H NMR and ^{13}C NMR spectroscopy and size exclusion chromatography (SEC). Table 3 displays the features of all materials including molar mass, dispersity, yield of esterification and material behavior in chloroform ($R_h$, IV, and $\alpha$). The PSMA backbones with different structures and compositions (Entry 1-4) had similar molar mass and narrow dispersity, allowing the systematic study of the influence of grafting density and distribution on material properties. The increase in grafting density was observed through the number of alkyl chains inserted and the increase of molar mass after esterification. Moreover, a small increase of molecular size ($R_h$) correlating with molar mass and grafting density was also observed. While increasing the side chain density was shown to give denser materials (lower IV), no differences of conformation were observed, as all materials were seen to adopt random coil conformation in chloroform ($\alpha > 0.5$).[42, 43] When functionalized with shorter side chains, similar conformation was observed ($\alpha > 0.5$), however, lower molecular size

and similar IV were observed (Entry 4 *vs*. 5). This was attributed to the inherent decrease of molar mass associated with the use of shorter alkyl chains.

**Table 3. Polymer Materials Features**

| Entry | Materials | | Backbones | | | Grafted PSMAs | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $M_{n,3d\text{-}SEC}$[a] g mol$^{-1}$ | $Đ_{RI}$[b] | Alkyl chains | % Yield[c] | $N_{graft}$[c] | $M_{n,3d\text{-}SEC}$[a] g mol$^{-1}$ | $Đ_{RI}$[b] | $R_h$[a] (nm) | IV[a] (dl/g) | α[a] |
| 1 | P[(Sty$_{10}$-*s*-MAnh$_{1.5}$)$_4$-*b*-PSty$_{10}$] | Multisite | 6,400[d] | 1.29[d] | C22 | 99 | 10 | 9,300[d] | 1.20[d] | 2.3[d] | 0.081[d] | 0.72[d] |
| 2 | P[Sty$_{10}$-*b*-(SMA)$_5$]$_2$-*b*-PSty$_{10}$ | Multiblock | 5,100[d] | 1.20[d] | C22 | 95 | 19 | 11,100[d] | 1.17[d] | 2.4[d] | 0.080[d] | 0.83[d] |
| 3 | P[Sty$_{27}$-*b*-(SMA)$_{14}$] | Diblock | 6,400[d] | 1.22[e] | C22 | 96 | 25 | 14,700[d] | 1.12[d] | 2.6[d] | 0.077[d] | 0.73[d] |
| 4 | P[SMA]$_{28}$ | Alt-Linear | 6,200[e] | 1.13[e] | C22 | 87 | 40 | 21,900[d] | 1.16[d] | 2.9[d] | 0.069[d] | 0.71[d] |
| 5 | P[SMA]$_{28}$ | Alt-Linear | 6,200[e] | 1.13[e] | C12 | 97 | 44 | 19,000[d] | 1.28[d] | 2.8[d] | 0.072[d] | 0.68[d] |
| 6 | P[SMA]$_{250}$ | Alt-Linear | 48,200[e] | 1.19[e] | C22 | 87 | 394 | 174,200[d] | 1.26[d] | 8.8[d] | 0.248[d] | 0.59[d] |
| 7 | P[SMA]$_{250}$ | Alt-Linear | 48,200[e] | 1.19[e] | C12 | 93 | 419 | 133,000[d] | 1.28[d] | 7.6[d] | 0.209[d] | 0.61[d] |
| 8 | 4xP[SMA]$_{60}$ | Alt-Linear | 44,900[e] | 1.15[e] | C12 | 91 | 364 | 138,900[d] | 1.20[d] | 6.7[d] | 0.139[d] | 0.50[d] |
| 9 | PLaurylAc$_{60}$ | Linear | - | - | C12 | - | 52 | 17,700 | 1.30 | 2.8 | 0.082 | 0.87 |

[a] Obtained from triple-detection SEC (3d-SEC) using $dn/dc$ values measured off-line. [b] Obtained using conventional SEC with RI detector. [c] Obtained from $^{13}$C-NMR using peak at 64.5 ppm corresponding to the average number of alkyl chains grafted ($N_{graft}$) and peak at 172 ppm corresponding to the number of MAnh units inserted. [d] SEC in Chloroform. [e] SEC in DMF.

To study the influence of molecular size and architecture, a linear PSMA with higher molar mass and a 4-arm star PSMA (4xPSMA) were synthesized (Entry 6-8). As expected, these materials exhibited larger molecular size and higher IV. Similarly to low molar mass materials, lower molecular size and lower IV values were observed when grafted with shorter side chain (Entry 6 *vs*. 7). The 4xPSMA exhibited a more compact structure compared to its linear counterpart as smaller molecular size, lower IV and lower α values were obtained (Entry 7 *vs*. 8). Finally, a linear poly(lauryl acrylate) (PLaurylAc) was synthesized to compare against the linear PSMA materials and elucidate the influence of the aromatic groups contained within the structure of these PPDs.

The molar mass and the narrow dispersity of the PLaurylAc material were shown to be similar to the PSMA material allowing good comparison (Entry 5 *vs*. 9).

The synthesis of all these materials and their accurate characterization opened the way for complete study of the influence of polymer composition, grafting density and distribution, molar mass, side chain length, and architecture on material properties.

### 3.2. Pour Point Measurements

The effectiveness of all polymeric materials as PPDs was studied on two mineral oils (API Group II and III) using polymer-oil blends at different concentrations (0.2, 0.4 and 0.8 wt. %). Table 4 shows the PPT values for pure mineral oils and for the different formulations. The poly(lauryl acrylate) and an internal reference from Lubrizol (LZPP3) were used as controls for comparison. Interestingly, the PPT of the two mineral oils was reduced for all formulations (min $\Delta$PPT = -6°C and max $\Delta$PPT = -36°C), confirming the potential of PSMA materials. Moreover, the PPT effectiveness appeared to be highly dependent on additive composition and structure. Overall, the additive concentration seemed to have relatively low impact on their effectiveness as similar results were obtained over a range of polymer concentrations.

**Table 4. Pour Point values for the different polymer-oil formulations**

| | | | Pour Point (°C) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | API Group II | | | API Group III | | |
| Entry | Materials | $N_{graft}$ [a] | 0.2 wt.% | 0.4 wt.% | 0.8 wt.% | 0.2 wt.% | 0.4 wt.% | 0.8 wt.% |
| 0 | Base oil | - | -15 | | | -12 | | |
| 1 | Multisite-C22 | 10 | -21 | -21 | -21 | -27 | -24 | -21 |
| 2 | Multiblock-C22 | 19 | -24 | -21 | -21 | -24 | -24 | -24 |
| 3 | Diblock-C22 | 25 | -24 | -21 | -21 | -24 | -24 | -24 |
| 4 | $Alt_{28}$-C22 | 40 | -21 | -27 | -27 | -27 | -27 | -27 |
| 5 | $Alt_{28}$-C12 | 44 | -48 | -48 | -51 | -42 | -42 | -42 |
| 6 | $Alt_{250}$-C22 | 394 | -24 | -21 | -21 | -27 | -24 | -12 |
| 7 | $Alt_{250}$-C12 | 419 | -48 | -45 | -48 | -36 | -39 | -39 |
| 8 | $4xAlt_{60}$-C12 | 364 | -45 | -48 | -48 | -39 | -42 | -42 |
| 9 | $PLaurylAc_{60}$ | 52 | -36 | -36 | -30 | -36 | -36 | -27 |
| LZPP3 | PSMA | - | -45 | -45 | -45 | -33 | -36 | -36 |

[a] Average number of alkyl chains grafted per backbone obtained from 13C-NMR.

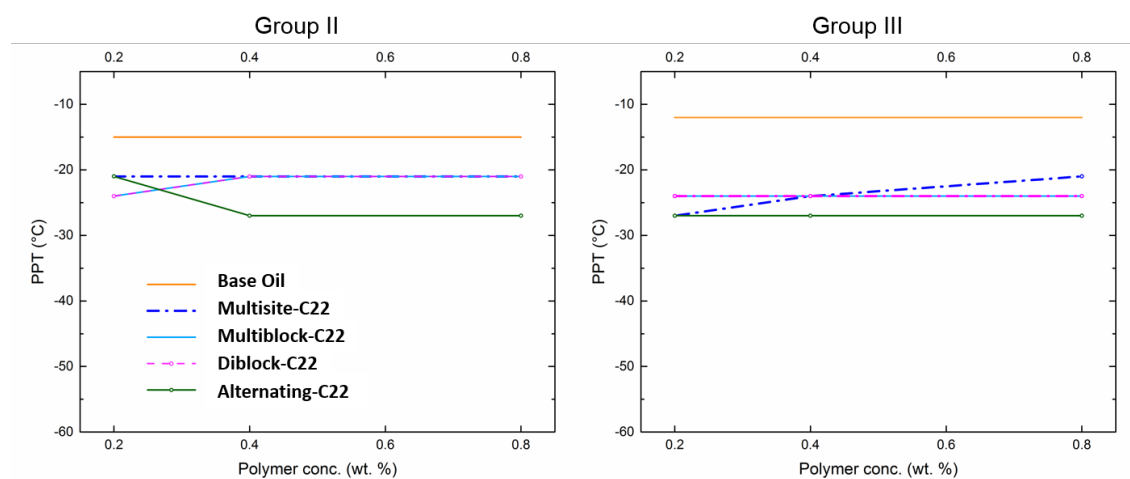**Influence of the grafting density and distribution**



**Figure 1.** Pour point results for grafted (C22) PSMA materials of similar backbone length (5-6k g mol[1]) with different structure and composition measured in two different mineral oils (API Group II and III).

The PSMA materials with different structures (multisite, multiblock, diblock and alternating) functionalized with behenyl (C22) alcohol (Table 3- Entry 1-4), were all shown to lower the PPT of both oils to values between -20 °C and -30 °C (Figure 1). In oil group II, the alternating material (higher density of side chains) appeared to be slightly more effective (ΔPPT -12 °C) compared to materials with lower side chain density (Table 4–Entry 1-4). In oil group III, similar activity was observed for all materials, with a slightly better performance for both alternating and multisite materials at low polymer concentration (ΔPPT -15 °C). The higher number of long alkyl side chains potentially facilitates the co-crystallization or adsorption of PPDs, with paraffin chains resulting in an improved effectiveness of alternating materials as PPDs. The results here showed that, the materials with highest grafting density (short spacing) was slightly more efficient, confirming an influence of this criterion. The space between pendent chains in graft copolymers was previously mentioned as a potential factor to improve PPD efficiency.[36] Moreover, the

increasing content of styrene in structures with lower side chain density might influence the PPD

solubility, resulting in lower efficiency, as polystyrene is barely soluble in oil. Because no obvious

positive contribution was observed by spacing the side chains, and because their synthesis is more

straightforward (one-step), further experiments were focused on alternating PSMA materials (see

next section).

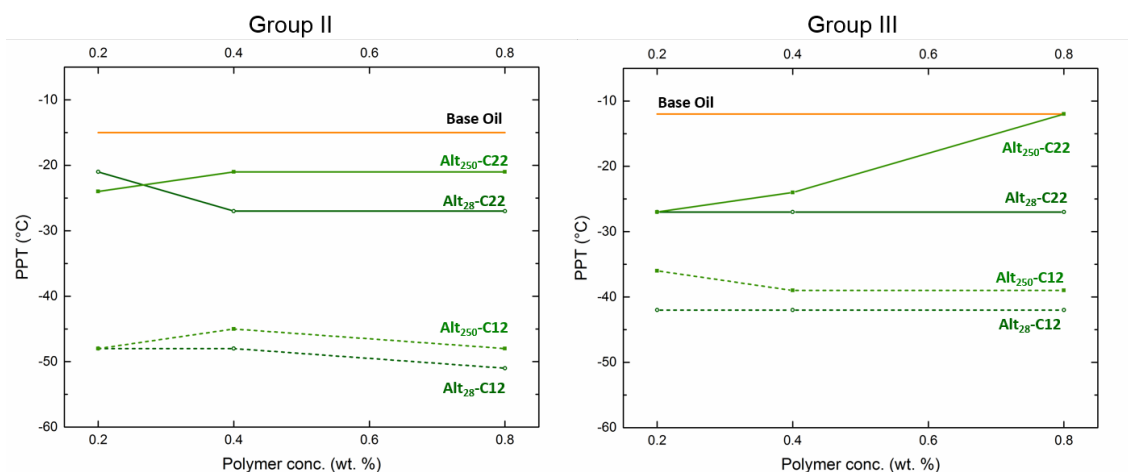**Influence of the backbone length and alkyl side chain length**



**Figure 2.** Pour point results for alternating PSMA (DP = 28 *vs*. DP = 250) of different

backbone length (5k *vs*. 50k g mol$^{-1}$, respectively) grafted with either lauryl (C12) or

behenyl (C22) side chain, measured in two different mineral oils (API group II and III).

Alternating PSMA materials with different side chain length (C12 *vs*. C22) and larger overall

molar mass compared to materials studied in previous section (> 100k g mol$^{-1}$ *vs*. 6k g mol$^{-1}$) were

tested (Figure 2). A greater depressing activity was obtained for shorter side chains (ΔPPT -36 °C

in group II and ΔPPT -30 °C in group III), however, increasing the overall molar mass had a small

impact on their effectiveness as PPDs. The trend observed in this study for lubricating oil is similar

to previous studies on fuels, where better depressing activity was observed with shorter alkyl side

chain polymers.[44,45] The lower ability of crystallization of shorter side chains is expected to reduce

wax crystal formation while increasing the additive solubility and promoting the interaction with paraffin chains in solution. Interestingly, an inverse trend is observed in crude oil (higher paraffin content), as longer side chains ( > C18) were shown to increase the PPT depressing activity.[4,31] These observations confirmed the dependence of PPDs activity with respect to many factors, such as n-paraffin details (content and composition) and polymer additive features (composition, molar mass and pendant chain nature).

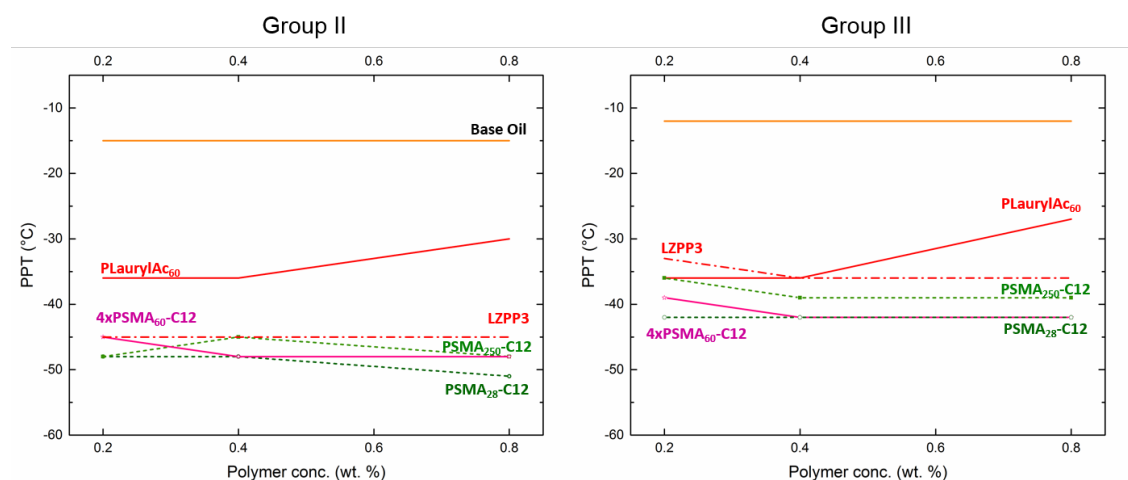**Influence of the architecture and aromatic groups**



**Figure 3.** Pour point results for alternating PSMA (DP = 28 vs. DP = 250) grafted with lauryl (C12) side chain, PLaurylAc (DP = 60), and Lubrizol internal reference (LZPP3) measured in two different mineral oils (API Group II and III).

To study the influence of more compact architectures on lubricant properties, a star PSMA material was tested (Figure 3). The 4xPSMA exhibited good depressing activity but showed no major improvement compared to its linear analogue ($\Delta$PPT -33 °C in group II and $\Delta$PPT -30 °C in group III). The high density of side chains and the steric hindrance near the core may reduce interaction of side chains with free paraffin chains in the core, resulting in no improvement over linear analogues. However, star materials are usually more compact materials (lower IV) and

exhibit better activity as viscosity modifiers (higher VI, better shear stability). In order to study the benefit of containing aromatic groups within the structure, a poly(lauryl acrylate) with comparable molar mass to the PSMA material grafted with lauryl side chains was also tested. The PLaurylAc homopolymer was shown to lower the pour point of both oils (ΔPPT -21 °C in group II and ΔPPT -24 °C in group III), however, a lower depressing activity was obtained compared to materials containing styrene. The benefit of having aromatic groups in the molecular structure of pour point depressants has been previously reported and explained by the ability of these groups to interact (π-π stacking) with aromatic compounds present in various oils (asphaltenes).[3,46] In fact, nucleation with these large aromatic groups can cause local defects in the structure, preventing the formation of strong interpenetrating networks. Overall, all the synthesized PSMA materials functionalized with lauryl side chains showed a relatively high effectiveness as PPDs when compared with a Lubrizol internal reference additive (Table 4).

### 3.3. Rheology study

All the synthesized polymeric materials showed promising activity as pour point depressants, however, controlling other properties such as viscosity index and thickening efficiency is also required to optimize the final lubricant formulation. The viscosity index and thickening efficiency were determined for polymer–oil blends at different concentrations (0.4 and 0.8% equal active concentration) in API group oil II and III for PSMA ester materials, the poly(laury lacrylate) and for the Lubrizol reference material (LZPP3) (Table 5).

**Table 5. Rheology data for tested materials**

| Entry | Materials | Conc. %wt. | Oil Group II | | | | Oil Group III | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | KV40 (cSt) | KV100 (cSt) | VI | TE | KV40 (cSt) | KV100 (cSt) | VI | TE |
| 0 | Base Oil | 100 | 19.80 | 4.11 | 108 | - | 19.23 | 4.25 | 129 | - |
| 1 | $Alt_{28}$-C12 (19k g mol$^{-1}$) | 0.4 | 19.99 | 4.17 | 111 | 1.6 | 19.41 | 4.27 | 128 | 0.5 |
| 2 | | 0.8 | 20.41 | 4.22 | 111 | 1.4 | 19.68 | 4.32 | 130 | 0.9 |
| 3 | $Alt_{250}$-C12 (133k g mol$^{-1}$) | 0.4 | 20.51 | 4.26 | 113 | 3.9 | 19.82 | 4.37 | 133 | 3.0 |
| 4 | | 0.8 | 21.14 | 4.40 | 119 | 3.7 | 20.37 | 4.5 | 138 | 3.1 |
| 5 | $4xAlt_{60}$-C12 (138k g mol$^{-1}$) | 0.4 | 20.35 | 4.23 | 112 | 3.1 | 19.76 | 4.35 | 132 | 2.6 |
| 6 | | 0.8 | 20.97 | 4.36 | 117 | 3.2 | 20.39 | 4.50 | 137 | 3.1 |
| 7 | $PLaurylAc_{60}$ (18k g mol$^{-1}$)k | 0.4 | 20.08 | 4.15 | 108 | 0.9 | 19.38 | 4.33 | 135 | 1.9 |
| 8 | | 0.8 | 20.17 | 4.19 | 111 | 1.0 | 19.62 | 4.30 | 129 | 0.6 |
| LZPP3 | PSMA | 0.4 | 20.79 | 4.33 | 117 | 5.6 | 20.13 | 4.44 | 135 | 4.7 |
| LZPP3 | | 0.8 | 21.97 | 4.60 | 127 | 6.1 | 21.16 | 4.69 | 145 | 5.3 |

In both oils, an increase of VI and TE, correlating with the molar mass of PSMA additives, was observed (Entry 1-2 *vs*. 3-4). This is usually explained by the expansion of solvated additives (increase of molecular size) occurring when temperature increases, counterbalancing the drop in oil viscosity at high temperature by thickening effects.[33] Moreover, the increase of additive concentration also increases the total volume of solvated polymer leading to better thickening effects. In this study, increasing the concentration of additives was shown to increase the VI, especially for high molar mass materials (Entry 1 *vs*. 2, 3 *vs*. 4 and 5 *vs*. 6). The extremely low kinematic viscosity results for short PSMA (low TE) compared to LZPP3 (Entry 1-2 vs. LZPP3), coupled with the good pour point results from Table 4, provide an added benefit for formulations that require low viscosity grades (*e.g*. SAE 0W-8/16). The comparison between the linear and the

4xPSMA of similar molar mass showed slightly lower VI and TE values for the star material (Table 5 – Entry 3-4 *vs*. 5-6). This was expected, as the expansion of a star material is limited compared to its linear analogue, as shown previously from the intrinsic viscosity and Mark-Houwink parameter values in chloroform (Table 3). While the molar mass of polymeric additives was found to have only a minor impact on pour point depressing activity, it is now clear that controlling the molar mass of materials is essential to improve the rheological properties of the final lubricant. Moreover, in contrast with the pour point results, the presence of styrene in polymer composition did not show significant impact, as similar VI and TE were obtained for PSMA and poly(lauryl acrylate) of similar size (Table 5 –Entry 1-2 *vs*. 7-8). When compared to an internal reference from Lubrizol (Table 5 – LZPP3), these materials showed promising results encouraging more investigation of well-defined polymeric system as lubricant oil additives.

## 4. CONCLUSION

In this study, well-defined graft copolymers (PSMA and PLaurylAc) were investigated as pour point depressant and viscosity modifiers in two mineral oils (API group II and III). The influence of additive composition, grafting density and distribution, molar mass, and side chain length on pour point, viscosity index and thickening efficiency was demonstrated. While all the materials were shown to lower the PPT, better depressant activity was obtained for materials with higher density of side chains (alternating PSMA) with an improvement of 36 °C in group II and 30 °C in group III (PPT= -51 °C and PPT= -42 °C, respectively). The molar mass of the polymers was shown to have minimal effect on the PPT effectiveness. In contrast, the length of aliphatic side chains was shown to have high impact on the PPT of both oils. While the molar mass of the polymeric additives did not appear to influence the pour point, high molar mass materials were shown to have more impact on the viscosity index and thickening efficiency of the two mineral

oils. Moreover, the presence of styrene monomer in the polymer composition was shown to be highly effective in improving the pour point, however, no effect on VI and TE was observed. Based on the results of this study, the use of alternating PSMA materials containing lauryl side chains (C12) is recommended to improve the pour point of lubricating oil from API group II and III. Moreover, varying the molar mass of the materials is suggested to control the viscosity of the final formulation. The use of compact architectures (star) seems also beneficial, however, the production of such materials is more challenging.

## ASSOCIATED CONTENT

**Supporting Information.**

Experiment and characterization details including synthesis procedures, NMR spectra, SEC traces, and IR spectra. The following files are available free of charge.

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The authors declare no competing financial interest

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# REFERENCES

(1) Kelland, M. A., *Production chemicals for the oil and gas industry*. CRC Press, **2014**.

(2) Binks, B. P.; Fletcher, P. D. I.; Roberts, N. A.; Dunkerley, J.; Greenfield, H.; Mastrangelo, A.; Trickett, K. How polymer additives reduce the pour point of hydrocarbon solvents containing wax crystals. *PCCP* **2015**, 17 (6), 4107-4117.

(3) Wu, Y.; Ni, G.; Yang, F.; Li, C.; Dong, G. Modified Maleic Anhydride Co-polymers as Pour-Point Depressants and Their Effects on Waxy Crude Oil Rheology. *Energy Fuels* **2012**, 26 (2), 995-1001.

(4) Al-Sabagh, A. M.; Noor El-Din, M. R.; Morsi, R. E.; Elsabee, M. Z. Styrene-Maleic Anhydride Copolymer Esters as Flow Improvers of Waxy Crude Oil. *J. Disp. Sci. Technol.* **2009**, 30 (3), 420-426.

(5) Al-Sabagh, A. M.; Noor El-Din, M. R.; Morsi, R. E.; Elsabee, M. Z. Styrene-maleic anhydride copolymer esters as flow improvers of waxy crude oil. *J. Pet. Sci. Eng.* **2009**, 65 (3), 139-146.

(6) Roenningsen, H. P.; Bjoerndal, B.; Baltzer Hansen, A.; Batsberg Pedersen, W. Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. *Energy Fuels* **1991**, 5 (6), 895-908.

(7) Holder, G. A.; Winkler, J. Crystal-Growth Poisoning of n-Paraffin Wax By Polymeric Additives and its Relevance to Polymer Crystallization Mechanisms. *Nature* **1965**, 207 (4998), 719.

(8) Yang, F.; Zhao, Y.; Sjöblom, J.; Li, C.; Paso, K. G. Polymeric Wax Inhibitors and Pour Point Depressants for Waxy Crude Oils: A Critical Review. *J. Disp. Sci. Technol.* **2015**, 36 (2), 213-225.

(9) Al-Sabagh, A. M.; El-Hamouly, S. H.; Khidr, T. T.; El-Ghazawy, R. A.; Higazy, S. A. Preparation the Esters of Oleic Acid-Maleic Anhydride Copolymer and Their Evaluation as Flow Improvers for Waxy Crude Oil. *J. Disp. Sci. Technol.* **2013**, 34 (11), 1585-1596.

(10) Taraneh, J. B.; Rahmatollah, G.; Hassan, A.; Alireza, D. Effect of wax inhibitors on pour point and rheological properties of Iranian waxy crude oil. *Fuel Process. Technol.* **2008**, 89 (10), 973-977.

(11) Marie, E.; Chevalier, Y.; Eydoux, F.; Germanaud, L.; Flores, P. Control of n-alkanes crystallization by ethylene–vinyl acetate copolymers. *J. Colloid Interface Sci.* **2005**, 290 (2), 406-418.

(12) Ashbaugh, H. S.; Guo, X.; Schwahn, D.; Prud'homme, R. K.; Richter, D.; Fetters, L. J. Interaction of Paraffin Wax Gels with Ethylene/Vinyl Acetate Co-polymers. *Energy Fuels* **2005**, 19 (1), 138-144.

(13) Machado, A. L. C.; Lucas, E. F.; González, G. Poly(ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behavior of organic solutions. *J. Pet. Sci. Eng.* **2001**, 32 (2), 159-165.

(14) Radulescu, A.; Schwahn, D.; Stellbrink, J.; Kentzinger, E.; Heiderich, M.; Richter, D.; Fetters, L. J. Wax Crystallization from Solution in Hierarchical Morphology Templated by Random Poly(ethylene-co-butene) Self-assemblies. *Macromolecules* **2006**, 39 (18), 6142-6151.

(15) Guo, X.; Pethica, B. A.; Huang, J. S.; Prud'homme, R. K.; Adamson, D. H.; Fetters, L. J. Crystallization of mixed paraffin from model waxy oils and the influence of micro-crystalline poly (ethylene-butene) random copolymers. *Energy Fuels* **2004**, 18 (4), 930-937.

(16) Ashbaugh, H. S.; Radulescu, A.; Prud'homme, R. K.; Schwahn, D.; Richter, D.; Fetters, L. J. Interaction of Paraffin Wax Gels with Random Crystalline/Amorphous Hydrocarbon Copolymers. *Macromolecules* **2002**, 35 (18), 7044-7053.

(17) El-Gamal, I. M.; Gobiel, S. Synthesis and evaluation of poly-α-olefins for improving the flow properties of gas oil. *J. Appl. Polym. Sci.* **1996**, 61 (8), 1265-1272.

(18) Al-Sabagh, A. M.; Khidr, T. T.; Moustafa, H. Y.; Mishrif, M. R.; Al-Damasy, M. H. Synergistic effect between surfactants and polyacrylates-maleicanhydride copolymers to improve the flow properties of waxy crude oil. *J. Disp. Sci. Technol.* **2017**, 38 (7), 1055-1062.

(19) Ding, X.; Qi, G.; Yang, S. Thermodynamic analysis for the interaction of polyacrylate with wax in heptane. *Polymer* **1999**, 40 (14), 4139-4142.

(20) Song, Y.; Han, S.; Ren, T. Impact of Alkyl Methacrylate-Maleic Anhydride Copolymers as Pour Point Depressant on Crystallization Behavior of Simulated Diesel Fuel. *Pet. Sci. Technol.* **2010**, 28 (8), 860-867.

(21) Soldi, R. A.; Oliveira, A. R. S.; Barbosa, R. V.; César-Oliveira, M. A. F. Polymethacrylates: Pour point depressants in diesel oil. *Eur. Polym. J.* **2007**, 43 (8), 3671-3678.

(22) Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21 (1), 19-30.

(23) Soni, H. P.; Kiranbala; Agrawal, K. S.; Nagar, A.; Bharambe, D. P. Designing maleic anhydride-α-olifin copolymeric combs as wax crystal growth nucleators. *Fuel Process. Technol.* **2010**, 91 (9), 997-1004.

(24) Chen, W.; Zhao, Z.; Yin, C. The interaction of waxes with pour point depressants. *Fuel* **2010**, 89 (5), 1127-1132.

(25) Azevedo, L. F. A.; Teixeira, A. M. A Critical Review of the Modeling of Wax Deposition Mechanisms. *Pet. Sci. Technol.* **2003**, 21 (3-4), 393-408.

(26) Pedersen, K. S.; Rønningsen, H. P. Influence of Wax Inhibitors on Wax Appearance Temperature, Pour Point, and Viscosity of Waxy Crude Oils. *Energy Fuels* **2003**, 17 (2), 321-328.

(27) Chi, Y.; Yang, J.; Sarica, C.; Daraboina, N. A Critical Review of Controlling Paraffin Deposition in Production Lines using Chemicals. *Energy Fuels* **2019**.

(28) Castro, L. V.; Vazquez, F. Copolymers as Flow Improvers for Mexican Crude Oils. *Energy Fuels* **2008**, 22 (6), 4006-4011.

(29) Yao, B.; Li, C.; Zhang, X.; Yang, F.; Sun, G.; Zhao, Y. Performance improvement of the ethylene-vinyl acetate copolymer (EVA) pour point depressant by small dosage of the amino-functionalized polymethylsilsesquioxane (PAMSQ) microsphere. *Fuel* **2018**, 220, 167-176.

(30) Lemos, B. C.; Gilles, V.; Gonçalves, G. R.; de Castro, E. V. R.; Delarmelina, M.; Carneiro, J. W. M.; Greco, S. J. Synthesis, structure-activity relationship and evaluation of new non-polymeric chemical additives based on naphthoquinone derivatives as wax precipitation inhibitors and pour point depressants to petroleum. *Fuel* **2018**, 220, 200-209.

(31) Wei, B. Recent advances on mitigating wax problem using polymeric wax crystal modifier. *J. Petrol. Explor. Prod. Technol.* **2014**, 5 (4), 391-401.

(32) Tinsley, J. F.; Jahnke, J. P.; Adamson, D. H.; Guo, X.; Amin, D.; Kriegel, R.; Saini, R.; Dettman, H. D.; Prud'home, R. K. Waxy Gels with Asphaltenes 2: Use of Wax Control Polymers. *Energy Fuels* **2009**, 23 (4), 2065-2074.

(33) Ghosh, P.; Hoque, M.; Karmakar, G.; Das, M. K. Dodecyl methacrylate and vinyl acetate copolymers as viscosity modifier and pour point depressant for lubricating oil. *Int. J. Ind. Chem.* **2017**, 8 (2), 197-205.

(34) Al-Sabagh, A. M.; Khidr, T. T.; Moustafa, H. M.; Mishrif, M. R.; Al-Damasy, M. H. Investigating the synergistic effect between oil soluble surfactants and styrene–maleic anhydride copolymers to enhance the flow properties of waxy crude oil. *Pet. Sci. Technol.* **2017**, 35 (13), 1381-1388.

(35) Cao, K.; Wei, X.-x.; Li, B.-j.; Zhang, J.-s.; Yao, Z. Study of the Influence of Imidization Degree of Poly(styrene-co-octadecyl maleimide) as Waxy Crude Oil Flow Improvers. *Energy Fuels* **2013**, 27 (2), 640-645.

(36) Xu, J.; Qian, H.; Xing, S.; Li, L.; Guo, X. Synthesis of Poly(maleic acid alkylamide-co-α-olefin-co-styrene) Co-polymers and Their Effect on the Yield Stress and Morphology of Waxy Gels with Asphaltenes. *Energy Fuels* **2011**, 25 (2), 573-579.

(37) Al-Sabagh, A. M.; Khalil, T. M.; Sabaa, M. W.; Khidr, T. T.; Saad, G. R. Poly(n-Alkyl Itaconate-Co-Vinyl Acetate) as Pour Point Depressants for Lube Oil in Relation to Rheological Flow Properties. *J. Disp. Sci. Technol.* **2012**, 33 (11), 1649-1660.

(38) Moriceau, G.; Tanaka, J.; Lester, D.; Pappas, G. S.; Cook, A. B.; O'Hora, P.; Winn, J.; Smith, T.; Perrier, S. Influence of Grafting Density and Distribution on Material Properties Using Well-Defined Alkyl Functional Poly(Styrene-co-Maleic Anhydride) Architectures Synthesized by RAFT. *Macromolecules* **2019**, 52 (4), 1469-1478.

(39) Lai, J. T.; Filla, D.; Shea, R. Functional Polymers from Novel Carboxyl-Terminated Trithiocarbonates as Highly Efficient RAFT Agents. *Macromolecules* **2002**, 35 (18), 6754-6756.

(40) Brzytwa, A. J.; Johnson, J. Scaled Production of RAFT CTA–a STAR Performer. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2011**, 52 (2), 533-534.

(41) Hiorns, R., *Polymer Handbook* **2000**, Vol. 49.

(42) Agilent, *A guide to multi-detector gel permeation chromatography.* **2012**, 5990-7196EN, 1-24.

(43) Striegel, A. M. Multiple Detection in Size-Exclusion Chromatography of Macromolecules. *Anal. Chem.* **2005**, 77 (5), 104-113.

(44) Xu, G.; Xue, Y.; Zhao, Z.; Lian, X.; Lin, H.; Han, S. Influence of poly (methacrylate-co-maleic anhydride) pour point depressant with various pendants on low-temperature flowability of diesel fuel. *Fuel* **2018**, 216, 898-907.

(45) Song, Y.; Ren, T.; Fu, X.; Xu, X. Study on the relationship between the structure and activities of alkyl methacrylate–maleic anhydride polymers as cold flow improvers in diesel fuels. *Fuel Process. Technol.* **2005**, 86 (6), 641-650.

(46) Soni, H. P.; Kiranbala; Bharambe, D. P. Performance-Based Designing of Wax Crystal Growth Inhibitors. *Energy Fuels* **2008**, 22 (6), 3930-3938.