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ORIGINAL PAPER

Novel insight into low-temperature performance of various poly(alkyl methacrylate) homopolymers in lube oil

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ABSTRACT

In this particular study, shear stability, pour point temperature and cold cranking simulation viscosity of different poly (alkyl methacrylate) homopolymers were investigated. The successful synthesis of the homopolymers was verified using FTIR and ^{1}H NMR spectroscopy. From the experimental results, it was perceived that shear stability and low-temperature performance of the modified oil are strongly dependent on alkyl length and synthesis reaction conditions. Higher shear stability was observed for the samples possessing shorter alkyl chain lengths. An increase in initiator concentration and reaction temperature led to a decrease in molecular weight and an increase in shear stability. Moreover, poly(alkyl methacrylate) homopolymers containing longer alkyl chain lengths represented better influence in the reduction of the size and cohesiveness of the crystal structure of paraffin wax. The results also revealed that the synthesized homopolymers with lower molecular weight play a greater performance in controlling friction at low temperatures. **Polyolefins J (2023) 10: 169-175**

Keywords: Poly(alkyl methacrylate) homopolymers; lube oil; shear stability; pour point temperature; VI improver.

INTRODUCTION

During the last decades, global warming and pollution have been critical health subjects [1-3]. In this regard, the automotive industry has interfered with a new challenge, i.e., decreasing fuel consumption. It is interesting to note that one of the serious reasons for fuel consumption is friction in engines [4-6].

Introducing high-performance polymeric additives to lube oil is one of the human beings' attempts to achieve less fuel consumption. Nowadays, the role of high-performance polymeric additives in the improvement of lubricant proficiency is undeniable. Keeping this view in mind, researchers have devoted their investigations to improving the characteristics of these additives. Some of these attempts include the synthesis

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of linear polymer to branch, comb and star as well as the blending of two polymers or the synthesis of their copolymers [7-9]. It has been reported that the copolymers of α-olefin/acrylates improve the solubility of the polymeric additive along with control of viscosity properties. These kinds of polymeric additives require achieving particular structural necessities since high molecular weight and narrow polydispersity are desired for better shear stability [10].

PAMAs involving particular composition and architecture are one of the most recurrent polymeric additives used as viscosity modifiers, principally in lube oils [11, 12]. It has been demonstrated that the length of alkyl groups and molecular weight of PAMAs has a significant effect on the viscosity index and pour point of modified lube oil [13]. Taking this into account, various polymerization techniques and different synthesis reaction conditions have been studied for producing desirable PAMAs [14, 15].

The researchers have also introduced low and broad molecular weight polar polymethacrylates and ionic liquid-involving ones to improve both viscosity index and wear prevention. From the previous studies, it has been concluded that functionalized PAMAs constitute boundary film provided that the polymer has a block topology [16, 17]. Cosimbescu et al. [18] reported that the structural characteristics of the polymer strongly affect the stability against shear forces.

Shear stability of the viscosity modifiers is one of the momentous principles that ascertain its eligibility in a lubricant formulation. The shear stability of the additive has an intense impact on lube oil capability to preserve its viscosity under shearing circumstances which remarkably depend on the architecture of the polymer [19, 20]. It is noteworthy that in the last few decades, major investigations were focused on viscosity index improvement and studies on shear stability enhancement have been rare. Thereupon, in continuation of our attempts for developing polymeric additives for lube oil, in this study, we investigate the shear stability and pour point temperature and cold cranking simulation viscosity of PAMAs with respect to different alkyl chain lengths. The effect of reaction temperature and initiator concentration is surveyed herein to attain outstanding shear stability using low molecular weight PAMAs.

EXPERIMENTAL

Materials

Six types of monomers including 1-butanol, 2-ethyl hexanol, 1-octanol, 1-decanol, 1-dodecanol and 1-octadecanol were used in this study. The characteristics of all materials used in this study have been presented in our previous study [21]. The monomers were purified by distillation and then stored over molecular sieves under argon. AIBN as an initiator was recrystallized from methanol.

Synthesis method

Synthesis of PAMAs was carried out via free radical polymerization according to our previous study. The polymerization was performed in a 4-neck round-bottom flask under an inert atmosphere. Toluene was utilized as a medium of reaction. The reaction mixture was stirred at different temperatures for 10 h. After cooling down, the prepared specimens were filtered and precipitated by a surplus quantity of methanol. Then, the samples were dried under a vacuum at 50°C for 24 h. The synthesis reaction conditions and molecular weights obtained from GPC spectroscopy are represented in Table 1.

Characterization

^{1}H NMR spectroscopy was carried out on a Bruker Avance 400 MHz NMR spectrometer (Germany) in deuterated chloroform ($CDCl_3$). By means of 32 K data points, acquisition time 1.56 s, spectral width 16 ppm, pulse width 30°, relaxation delay 10 s, and 4 scans, ^{1}H NMR spectra were obtained. Infrared spectroscopy was carried out on a Bruker-IFS48 spectrometer (Germany) from 4000 to 400 cm^{-1}. Molecular weight and polydispersity (Đ) of synthesized copolymers were attained by gel permeation chromatography (GPC) on an Agilent 1100 (USA).

Performance evaluation in lube oil

The performance of the synthesized PAMAs solutions in the SN 150 mineral oil was examined according to standard procedures of shear stability by DIN-51382, pour point by ASTM-98-87 and cold cranking simulation viscosity by ASTM D-5293.

Table 1. Experimental conditions and results for a variety of PAMAs.

Polymer	Sample Code	Initiator (wt%)	Reaction Temperature (°C)	M_w (g/mole)[(a)]
Poly(hexyl methacrylate)	PAH1	0.25	70	64000
	PAH2	1.00	70	34100
	PAH3	1.50	70	28900
	PAH4	0.25	60	72500
	PAH5	1.00	60	44200
	PAH6	1.50	60	32500
	PAH7	0.25	80	34900
	PAH8	1.00	80	21300
	PAH9	1.50	80	19850
Poly(octyl methacrylate)	PAOC	0.25	70	61600
Poly(decyl methacrylate)	PADE	0.25	70	60200
Poly(dodecyl methacrylate)	PADO	0.25	70	58000
Poly(octadecyl methacrylate)	PAOD	0.25	70	56800

[(a)] Obtained from GPC results [20]. Polydispersity of the synthesized samples is in the range of 1.78-2.21.

RESULTS AND DISCUSSION

Structure analysis of the synthesized PAMAs

The successful synthesis of alkyl methacrylate homopolymers was verified by FTIR and ^{1}H NMR. Figure 1 demonstrates the FTIR spectrum of poly(octadecyl methacrylate) as an example. As can be seen, the absorption peaks in the range of 3100-2850 cm^{-1} are related to the stretch vibrations of aliphatic C-H bands. The sharp peak appeared at 1726 cm^{-1} corresponds to the stretch vibration of C=O bands of ester groups. Bending vibrations of C-H bands of CH_2 and CH_3 groups appeared at 1460 and 1369 cm^{-1}, respectively. Characteristic absorption peaks at a wavenumber of 1236 cm^{-1} and 1146 cm^{-1} correspond to the stretch vibrations of C-O bands. The other essential peaks in the range of 950-700 cm^{-1} are assigned to the out-of-plane bending vibrations related to the CH_2 groups in the long-chain bands of alkyl-substituted acrylate [22, 23].

To further elucidate of chemical structure, ^{1}H NMR spectrum of poly(octadecyl methacrylate) is depicted in Figure 2. From the figure, it can be perceived that the chemical shifts appeared in the range of 0.89-1.90 ppm correspond to various saturated aliphatic protons of CH, CH_2 and CH_3 groups of poly(octadecyl methacrylate). A short peak appeared in the range of 3.81-4.12 ppm corresponds to the acidic proton of methacrylic acid. The absence of vinyl protons in the chemical range of 4.5-7 ppm confirms that there is no unreacted monomer in the system [24, 25].

Shear stability performance

The efficiency of PAMA additives can be analyzed

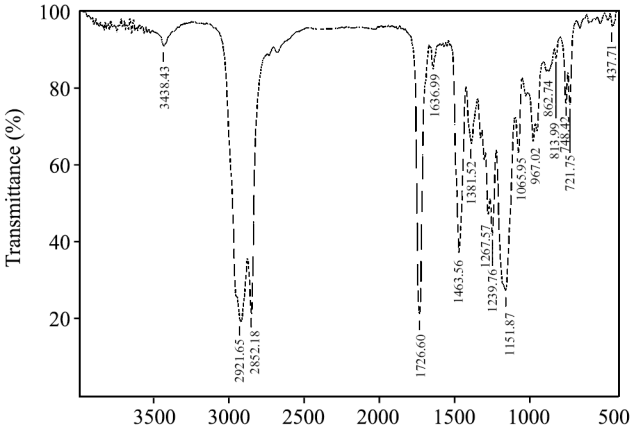

Figure 1. FTIR spectrum of poly(octadecyl methacrylate) synthesized via free radical polymerization at 70°C.

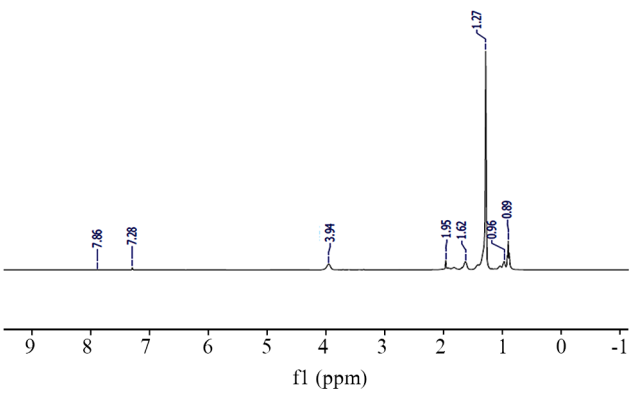

Figure 2. ^{1}H NMR spectrum of poly(octadecyl methacrylate) synthesized via free radical polymerization at 70°C.

not only by viscosity index but also by shear stability, cold cranking simulation viscosity and pour point temperature. In our previous work, it turned out that by the increase in chain length of the alkyl side chain of PAMA, viscosity index enhances. A similar result was reported in the system containing fatty acid-based methacrylate polymers [26]. In addition, decreasing reaction temperature and initiator concentration leads to similar consequences. In the following, we try to assess the influence of the aforementioned parameters on shear stability, cold cranking viscosity and pour point of modified SN-150. To evaluate the loss of viscosity induced by shear force, shear stability index (SSI) was used and calculated as follows:

$$SSI/\% = (v_i - v_f) \times 100 / v_i \quad (1)$$

Where v_i and v_f imply oil viscosity before and after applying shear rate. The lower the SSI value, the higher the shear stability of polymeric additive [27]. Figure 3 exhibits SSI values of 4 wt% solutions of PAMAs in the base oil. The results reveal that by increasing side chain length of PAMA, SSI shifts to higher values, indicating higher viscosity loss and lower shear stability of synthesized samples under shear force. The maximum shear stability index was attained for sample PAOD possessing the longest side chain length.

Poly(hexyl methacrylate) was chosen for characterizing the effect of reaction temperature and initiator concentration on the shear stability of synthesized samples. As it can be observed from Figure 4, initiator concentration has a significant impact on the SSI value of the synthesized PAMAs. Indeed, the increase in initiator concentration leads to a decrease in molecular weight and consequently better shear stability. Sample PAH3 with M_w of 28900 g/mol represented greater shear stability rather than two other samples with higher M_w A similar trend was observed when the reaction temperature increased. Sample PAH9 demonstrated lower SSI in this case due to its lower M_w compared to two other samples, which were synthesized at lower temperatures. Considering these results and the results obtained from our previous work, it can be pointed out that in order to achieve the best performance of polymeric additive in lube oil, the researcher should consider all aspects of rheological behavior. Along with the aforementioned attributes, the solubility of additive is also a key parameter.

Pour point temperature

To survey the role of synthesized PAMAs and synthesis reaction conditions on the pour point temperature of the base oil, the samples were tested according to ASTM-98-87. It should point out that the absolute major part of crude oils and of their products contain striking contents of oil waxes called paraffin. If the temperature is lowered, the paraffin crystals can grow, resulting in a crystal net. Crystalline net can trap the molecules of liquid hydrocarbon and prevent oil to flow. The pour point temperature is the temperature at which this phenomenon occurs [28, 29]. From the application point of view, the polyacrylates can lessen the size and cohesiveness of the crystal structure of paraffin waxes and diminish pour point, suggesting augmentation of flow at lower temperatures [30]. In-

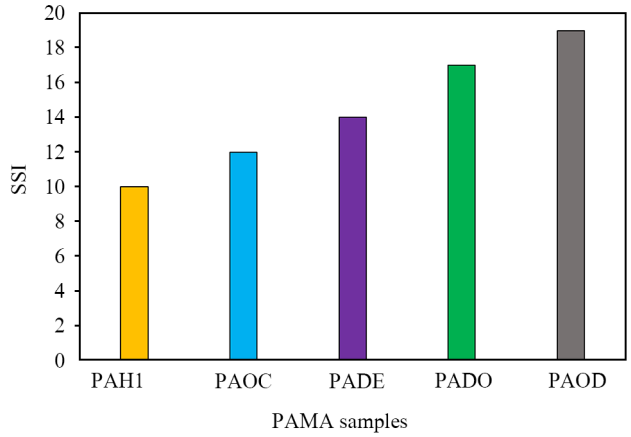

Figure 3. Effect of side chain length on shear stability index of different PAMAs.

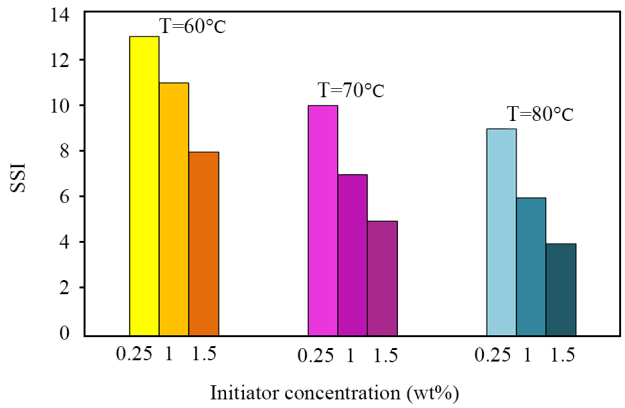

Figure 4. Effect of initiator concentration and reaction temperature on shear stability index of poly(hexyl methacrylate).

Table 2. Results of shear stability, pour point temperature and cold cranking simulation viscosity for different PAMAs.

Sample Code	SSI	PPT (°C)	CCS (mPa.s) (-15°C)
PAH1	10	-14	8210
PAH2	7	-9	8960
PAH3	5	-7	9150
PAH4	13	-17	8060
PAH5	11	-15	8110
PAH6	8	-11	8490
PAH7	9	-12	8520
PAH8	6	-8	8720
PAH9	4	-6	9230
PAOC	12	-16	8020
PADE	14	-19	7960
PADO	17	-25	7840
PAOD	19	-27	7780

deed, the long hydrocarbon paraffin chains have a tendency to interact with the polymer alkyl groups, acting as crystallization nuclei dangling from the polymeric matrix.

As it can be attained from Figure 5, the sample with longer alkyl length offers greater performance as pour point depressants. Increase in reaction temperature and initiator concentration leads to decrease in M_w, indicating an improvement in the efficiency of these additives as a pour point depressant (Figure 6). It has been previously confirmed that the pendant hydrocarbon group can interact with long hydrocarbon paraffin chains and act as crystallization nuclei. This results in less free paraffin to prevent fluidity, which indicates a lower pour point temperature [31].

Cold cranking simulation (CCS) viscosity

The CCS viscosity measurement ascertains the internal fluid friction in motor oils and represents the energy amount needed to overwhelm the resistance attendance in a lubricant at a low temperature. The higher the CCS values, the higher energy is required for pumping and circulation and the greater starting difficulties [32, 33]. The CCS results at -15°C plainly designate a robust affiliation on the alkyl length of PAMAs as well as reaction temperature and initiator concentration. The statistical correlation between CCS and the aforementioned parameters is presented in Table 2. From Table 2, it can be seen that the alkyl chain in the polymer backbone is responsible for providing better properties at low temperature. The PAMAs containing lower molecular weight showed better performance which reveals the influence of initiator concentration and reaction temperature on providing additives with eligible fluidity for controlling the friction at low temperatures. Sarpal and coworkers [34] reported that molecular weight and molecular weight distribution, average chain length, content of terminal and branched methyl affect the low-temperature rheological characteristics. Their experimental results also illustrated that the presence of the long side of the terminal carbon of the alkyl chain results in better low-temperature performance.

CONCLUSIONS

This study provided new insight to survey the effect of molecular structure and synthesis reaction conditions on the low-temperature performance of various

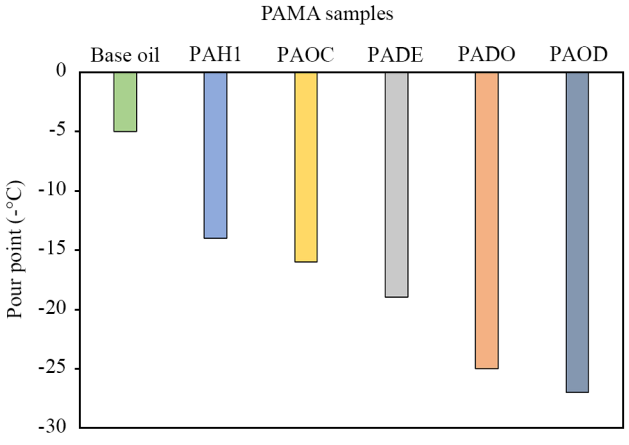

Figure 5. Effect of side chain length on pour point temperature of different PAMAs.

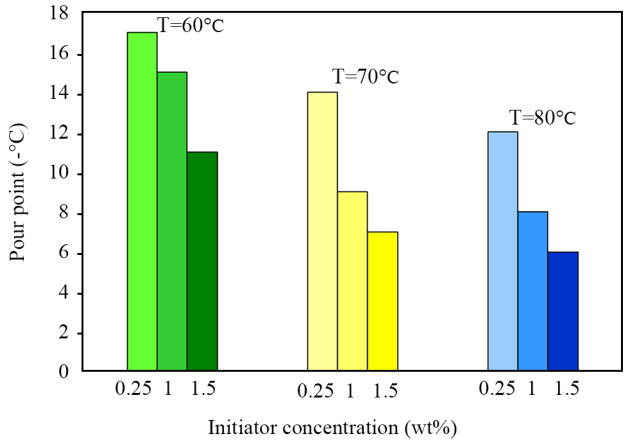

Figure 6. Effect of initiator concentration and reaction temperature on pour point temperature of poly(hexyl methacrylate).

poly(alkyl methacrylate) homopolymers containing different alkyl chain lengths. The main conclusion of this study could be this strategic matter that by tailoring the structure and the synthesis reaction conditions, the better performance of lube oil additives and consequently lower environmental issues would achieve. From the experimental results, it was revealed that by increasing side chain length of PAMA shear stability of synthesized samples enhanced, pour point temperature decreased and low-temperature performance of modified oil improved. Increase in initiator concentration and reaction temperature led to decrease in molecular weight and increase in shear stability as well as a decrease in pour point temperature and cold cranking simulation viscosity.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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