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ORIGINAL RESEARCH ARTICLE

Synthesis and characterization of butyl methacrylate/1-hexene copolymers catalyzed by $AlCl_3$ and organometallic acids and their performance assessment in lube oil

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ABSTRACT

In the present work, a series of butyl methacrylate/1-hexene copolymers were synthesized, and their efficiency as viscosity index improvers, pour point depressants, and shear stabilizers of lube oil was investigated. The effect of 1-hexene molar ratio, type, and concentration of Lewis acids on the incorporation of 1-hexene into the copolymer backbone was investigated. The successful synthesis of the copolymers was confirmed through FTIR and 1H NMR spectroscopy. Results obtained from quantitative 1H NMR and GPC revealed that an increase in the molar ratio of 1-hexene to butyl methacrylate, along with concentration of Lewis acids led to an increase in 1-hexene incorporation and a reduction in Mn and Đ. Similar trends were observed when the Lewis acid changed from $AlCl_3$ to organometallic acids. The maximum 1-hexene incorporation (26.4%) was achieved for sample BHY3, with a [1-hexene/BMA] ratio of 4 mol% and a [$Yb(OTf)_3$/BMA] ratio of 2.5 mol%. Evaluation of the synthesized copolymers as lube oil additives demonstrated that the viscosity index was more significantly influenced by samples with higher molecular weight. Sample BHA13 represents maximum VI of 137. The copolymer containing $Yb(OTf)_3$ as a catalyst exhibited superior efficiency as a pour point depressant. Furthermore, sample BHY3 showed the lowest shear stability index (6.4).

Keywords: copolymerization; butyl methacrylate; 1-hexene; viscosity index; shear stability

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1. Introduction

In the last few decades, the demand for lubricants has grown in a variety of applications, such as automobiles, to smooth the movement of one surface over another[1–3]. One of the most important characteristics of lubricants is their superior resistance to viscosity changes with temperature[4,5]. In order to describe the viscosity variation with temperature, the viscosity index (VI) can be employed, which depends on the kinematic viscosity of the oil as measured at 40 °C and 100 °C. High VI oil is less influenced by temperature variation than low VI oil. In recent years, polymeric additives have been extensively used and have performed as viscosity index improvers (VIIs) and pour point depressants (PPDs)[6,7]. Various parameters, such as molecular weight, polymerization temperature, initiator and catalyst concentration, have an influence on VI of lube oil filled with polymer additives[8]. Among them, co- and ter-polymers that involve desirable characteristics of two or more polymer groups have become prevalent. They exhibit collapsed globules at low temperatures and expand at higher temperatures, resulting in increased viscosity. It has been reported that an increase in the molecular weight of (co)polymers leads to a growth in (co)polymer volume in an oil solution, subsequently enhancing the viscosity index (VI). Additionally, it has been observed that the effectiveness of the copolymer as VII increases as the alkyl chain length of both acrylate and α-olefin monomers, along with the concentration of the copolymer, increases[9–11].

The copolymers of acrylates and α-olefin having different architecture and various molecular weights have attained the attention of all lubricant applied scientists. Nevertheless, the growing demand, the requirement for the synthesis of α-olefin/acrylates copolymers with controlled composition and molecular weight has increased[12,13]. For the synthesis of α-olefin/acrylates copolymers, both late transition metal-mediated polymerization and free radical polymerization techniques have been reported[14,15]. The free radical polymerization technique is widely recognized for its inherent challenge concerning the reactivity ratios of these two monomer types. Consequently, the resulting copolymers frequently contain a significant proportion of acrylates, yielding low quantities and relatively modest molecular weights. To address this issue, researchers have suggested introducing Lewis and Brønsted acids into the system as a potential solution[16,17].

The report by Hirooka et al.[18] on the copolymerization of propylene and acrylonitrile in the attendance of Lewis acid under mild conditions introduced the use of various types of Lewis acids in the copolymerization of polar and non-polar monomers. Xiao and coworkers[19] conducted the copolymerization of methyl (meth)acrylate and 1-octene in the presence of $AlCl_3$. They observed that the introduction of this acid promoted the decomposition of the azo initiator. Furthermore, they found that reducing the copolymerization temperature and increasing the molar ratio of $AlCl_3$ to methyl acrylate resulted in enhanced incorporation of the alkene into the polymer backbone. Jozaghkar et al.[13] studied the influence of monomer feed ratio and type of Lewis acid on the copolymerization of butyl methacrylate/1-octene. According to their findings, it was observed that when the molar percentage of 1-octene and Lewis acid increased, there was a corresponding increase in the inclusion of 1-octene and a decrease in M_n. In comparison to Al_2O_3, the utilization of $AlCl_3$ resulted in enhanced incorporation of 1-octene into the copolymer backbone. Sen et al.[20] investigated the copolymerization of α-olefin with methyl (meth)acrylate in the presence of $AlCl_3$ and scandium triflate ($Sc(OTf)_3$). The synthesized copolymer exhibited an alternating structure to a large extent with a maximum α-olefin incorporation of 48%. In a separate study, Carlson and coworkers[21] demonstrated that the introduction of $Sc(OTf)_3$ in the free radical copolymerization of 1-hexene with acrylamide led to increased 1-hexene incorporation in the copolymer backbone. It should be emphasized that, in order to attain optimal performance of polymeric additives in lubricating oil, it is essential to consider all aspects of their rheological behavior. Along with the aforementioned attributes, the solubility of the additive is also a key parameter.

To the best of our knowledge, there have been no reports on the investigation of the effects of different acids on the performance of polymeric additives in lubricating oil. Herein, synthesis and characterization of butyl methacrylate/1-hexene copolymers were conducted, assessing their efficacy as viscosity index improvers, shear stabilizers, and pour point depressants. For this purpose, different Lewis acids ($AlCl_3$, $Ir(OTf)_3$, and $Yb(OTf)_3$) were used as catalysts and the influence of type and concentration of Lewis acids and the molar ratio of 1-hexene to butyl methacrylate on the copolymerization properties was evaluated using ^1H NMR and GPC.

2. Experimental

2.1. Materials

Butyl methacrylate (BMA, ≥99%), 1-hexene (98%), toluene (≥99%), 2,2’-Azobis(isobutyronitrile) (AIBN, 98%), methanol (99.8%), Aluminum chloride ($AlCl_3$, anhydrous, 99.99%) and Ytterbium(III) trifluoromethanesulfonate (Yb $(CF_3SO_3)_3$, 99.99%) were purchased from Merck (Germany). Iridium trifuoromethanesulfonate ($Ir(CF_3SO_3)_3$, 99.9%) was supplied from American Element (United States). The monomers and initiator were stored at −5 ℃ and purified by distillation. AIBN was recrystallized from methanol. Other chemicals and reagents were used as received.

2.2. Synthesis of copolymers

The copolymerization of butyl methacrylate and 1-hexene was conducted in Pyrex glass ampoules, and degassing was attained under vacuum to remove impurities like oxygen. The reaction mixture was stirred at 70 °C for 6 h. After cooling, the prepared specimens were filtered and precipitated using an excess amount of methanol. Subsequently, the samples were dried under vacuum at approximately 40 °C for 24 h. Based on gravimetric calculations, the conversion of butyl methacrylate was determined to be at least 80%. The polymerization conditions, as well as the ^{1}H NMR and GPC results are presented in **Table 1**.

Table 1. Experimental conditions and results for a variety of poly(BMA-1-hexene) copolymers[a].

Sample Name	**[1-hexene/BMA]**	**[Acid/BMA]**	**1-hexene incorp. (mol%)**	**M_n ($\times 10^{-4}$)[b]**	**Đ [b]**
BHA1	1	0.5	5.7	4.3	1.88
BHA2	1	1	6.6	4.0	1.86
BHA3	1	1.5	7.1	3.9	1.85
BHA4	1	2.5	7.9	3.8	1.83
BHA5	2.5	0.5	5.8	4.3	1.86
BHA6	2.5	1	6.8	3.9	1.85
BHA7	2.5	1.5	9.4	3.7	1.80
BHA8	2.5	2.5	9.9	3.4	1.79
BHA9	4	0.25	6.5	3.9	1.87
BHA10	4	0.5	7.0	3.8	1.77
BHA11	4	1	10.2	3.3	1.71
BHA12	4	1.5	11.6	3.2	1.68
BHA13	4	2.5	12.6	3.2	1.61
BHI1	4	0.5	15.1	2.9	1.67
BHI2	4	1.5	18.2	2.7	1.56
BHI3	4	2.5	22.9	2.6	1.44
BHY1	4	0.5	15.2	2.9	1.60
BHY2	4	1.5	21.7	2.5	1.57
BHY3	4	2.5	26.4	2.3	1.42

2.3. Sample coding

Butyl methacrylate and 1-hexene monomers are abbreviated as B and H, respectively. A, I, and Y represent $AlCl_3$, $Ir(OTf)_3$ and $Yb(OTf)_3$, respectively. For instance, BHA refers to the copolymerization of BMA and 1-hexene carried out by using $AlCl_3$ as a catalyst.

2.4. Characterization

^{1}H NMR spectroscopy was conducted using a Bruker Avance 400 MHz NMR spectrometer (Germany) in deuterated chloroform ($CDCl_3$). The spectra were acquired with 32 K data points, an acquisition time of 1.56 s, a spectral width of 16 ppm, a pulse width of 30°, a relaxation delay of 10 s, and 4 scans. Infrared spectroscopy was performed using a Bruker-IFS48 spectrometer (Germany), scanning from 4000 to 400 cm^{-1}. The molecular weight and polydispersity (Đ) of the synthesized copolymers were determined using gel permeation chromatography (GPC) with an Agilent 1100 system (USA).

The rheological characteristics of the synthesized copolymers solutions in the SN-180 mineral base oil were evaluated according to standardized procedures: viscosity index by ASTM D-2270, pour point by ASTM

D-98-87, and shear stability by DIN-51382. In order to analyze the rheological behavior, 5 wt% of copolymers were added to the Lube oil and stirred at 110 °C for 2 h.

3. Results and discussion

3.1. Structure analysis of copolymer

The first evidence of the successful synthesis of poly(BMA-1-Hexene) copolymer was attained through FTIR analysis. The FTIR spectrum of sample BHA2 is illustrated in **Figure 1**. The synthesized copolymer exhibits sharp peaks in the range of 3000–2800 cm^{-1} attributed to the stretching vibration of C–H bands for sp^3 carbon atoms of both co-monomers. The absence of an absorption peak at 1650 cm^{-1} and in the range of 3300–3000 cm^{-1} may be attributed to the presence of CH_2 (sp^2), indicating the elimination of a carbon-carbon double bond. This confirms the synthesis of the copolymer structure. Besides, the lack of absorption peak in the range of 1670–1640 cm^{-1}, corresponding to the stretching vibration of C=C bands, confirmed the synthesis of the copolymer. A sharp peak appeared at approximately 1720 cm^{-1}, while peaks at wave numbers around 1230, 1140 and 1060 cm^{-1} respectively correspond to the stretching vibrations of the carboxyl group and C–O–C bonds. Additionally, essential peaks at 750 cm^{-1} and 840 cm^{-1} are assigned to the bending vibrations related to the C–H band of long hydrocarbon chains of the polymers[22,23].

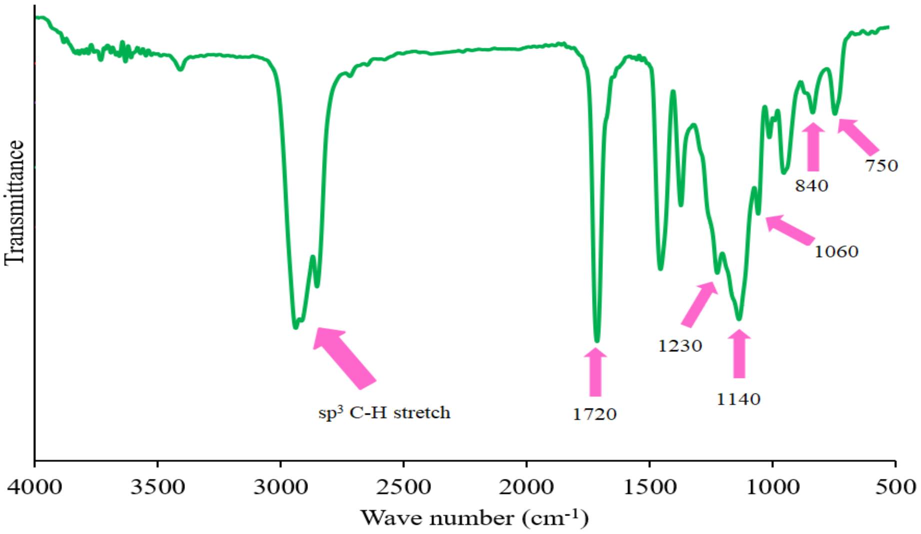

Figure 1. FTIR spectrum of BHA2, synthesized via free radical polymerization in the presence of $AlCl_3$ at 70 °C

To further elucidate the chemical structure and determine the comonomer incorporation percentage, ^{1}H NMR spectroscopy was carried out. **Figure 2** illustrates the ^{1}H NMR spectrum of sample BHA2. As depicted in **Figure 2**, the proton signals in the range of 0.89–2.2 ppm correspond to the saturated aliphatic protons of –CH, CH_2, and $–CH_3$ groups present in the synthesized copolymer. Moreover, the $–CH_2$ protons of ester group of BMA appeared at 3.96 ppm. The absence of a peak in the range of 4.5–6.5 confirms the absence of unreacted monomer in the system. The incorporation percentages of 1-hexene in the synthesized copolymers were calculated by the following equations:

$$Mole\ fraction\ of\ BMA = \frac{b/2}{(a-6b)/12 + b/2} \tag{1}$$

$$Mole\ fraction\ of\ 1-hexene = 1 - Mole\ fraction\ of\ BMA \tag{2}$$

where $b/2$ and $(a - 6b)/12$ represent the respective number of moles of BMA and 1-hexene in the copolymers[24,25].

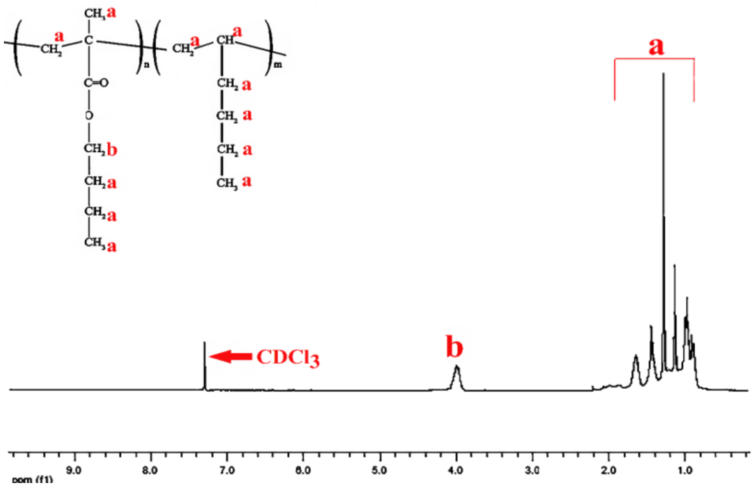

Figure 2. ^{1}H NMR spectrum of copolymer of BMA and 1-hexene (sample BHA2).

3.2. Influence of initial comonomer composition and Lewis acids concentration

It is worth noting that the copolymerization characteristics significantly depend on the incorporation of 1-alkene molar percentage[26,27]. **Table 1** demonstrated the effect of the molar ratio of 1-hexene and Lewis acids (i.e., $AlCl_3$, $Ir(OTf)_3$ and $Yb(OTf)_3$) on the incorporation of 1-hexene, molecular weight, and molecular weight distribution of the synthesized copolymers. From **Table 1**, it can be observed that the initial monomer composition significantly influences the incorporation of 1-hexene into the synthesized copolymer chain. Indeed, an increase in the molar ratio of 1-hexene to BMA leads to enhanced 1-hexene incorporation. Additionally, it is found that the M_n and Đ of poly(BMA-co-1-hexene) decrease monotonically with increasing 1-hexene incorporation (**Figure 3**). The maximum incorporation of 1-hexene (26.4%) was attained for sample BHY3 with a [1-hexene/BMA] ratio of 4 mol% and a [$Yb(OTf)_3$/BMA] ratio of 2.5 mol%. Similar outcomes have been documented in the case of methyl acrylate/1-octene and butyl methacrylate/1-octene copolymer systems[13,28].

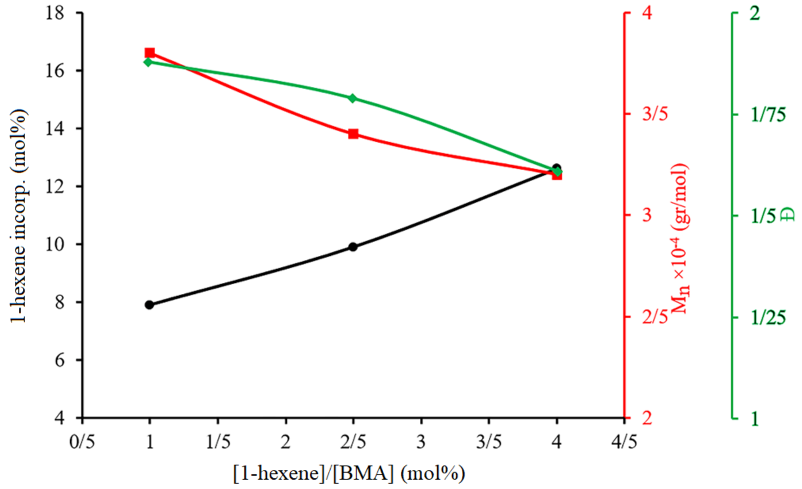

Figure 3. 1-hexene incorporation, M_n and Đ versus molar ratio of 1-hexene to BMA ([$AlCl_3$/BMA] = 2.5 mol%).

To possess a profound understanding of the copolymerization of BMA and 1-hexene, the influence of the molar ratio of $AlCl_3$, $Ir(OTf)_3$, and $Yb(OTf)_3$ to the acrylate monomer was assessed. As shown in **Figure 4**, an increase in the molar ratio of $AlCl_3$ results in an increase in the incorporation of 1-hexene, as well as a decrease in M_n and Đ. For instance, at a constant [1-hexene/BMA] of 4 mol%, increasing the molar ratio of $AlCl_3$ to BMA from 0.25 mol% to 2.5 mol% resulted in enhanced 1-hexene incorporation, increasing from 6.5 mol% to 17.1 mol%. A comparison between $AlCl_3$ and organometallic acids ($Ir(OTf)_3$ and $Yb(OTf)_3$) is demonstrated in **Figure 5**. From the presented results, it is evident that the organometallic acids have a more pronounced influence on the incorporation of 1-hexene compared to $AlCl_3$. Introducing the complexation of the acid with the carbonyl band of acrylate monomers enhances the electrophilicity of –C=C, which is significant for the copolymerization of acrylates with 1-alkene. However, the charge and size ratio at the center of the metal also play a substantial role in their ability to promote the aforementioned copolymerization. This role can be clearly observed in **Figure 5**[19,20].

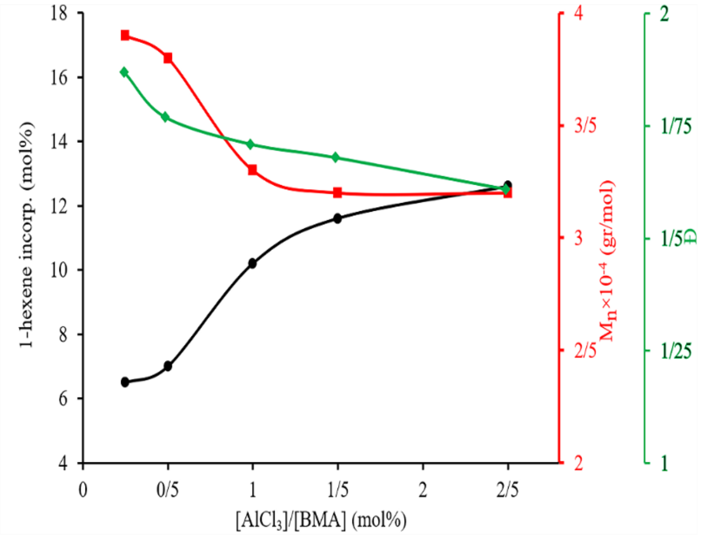

Figure 4. Incorporation of 1-hexene, M_n and Đ as a function of molar ratio $AlCl_3$ to BMA ([1-hexene/BMA] = 4 mol%).

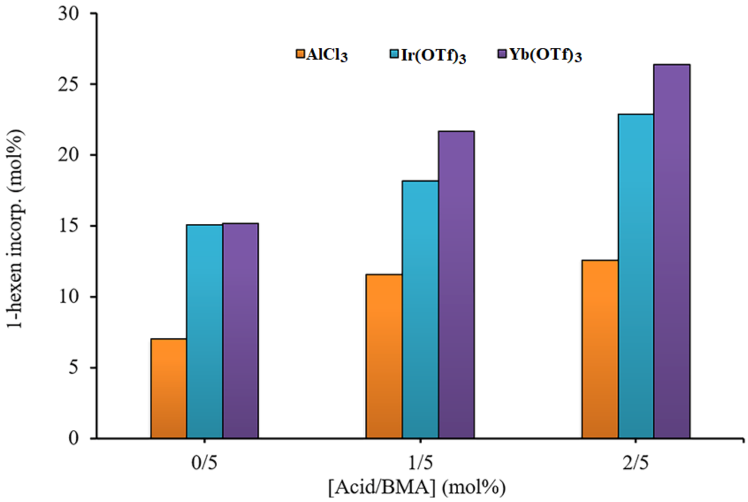

Figure 5. Influence of Lewis acid types on the incorporation of 1-hexene at various [Lewis acid/BMA] (0.5, 1.5 and 2.5 mol%) and constant [1-hexene/BMA] (4 mol%).

3.3. Evaluation of the synthesized copolymers as Lube Oil Additives

3.3.1. Determination of viscosity index

Viscosity, as a significant physical characteristic, plays an indispensable role in assessing the cold flow properties and shear, as well as the temperature dependency of lubricating oil. The influence of polymeric VIIs primarily depends on the characteristics of the polymer molecules in the base oil. It is well-known that polymeric additives enhance the viscosity of the oil relatively more at higher temperatures than at lower temperatures because the polymer coil expands as the temperature increases[28–30].

Figure 6 displays the VI of base oil containing various synthesized copolymers, with the corresponding values tabulated in **Table 2**. The viscosity results of the samples demonstrate that the synthesized copolymers can impact the VI of the base oil. However, it was observed that the VI of SN-180 was significantly more affected by samples with higher molecular weight. Indeed, one of the most important parameters directly influencing the VI of the oil is the molecular weight of polymeric additives. Consequently, increasing the molecular weight enhances the hydrodynamic size, significantly affecting the VI across a wide range of temperatures[31,32]. Jalilian and his coworkers[33] reported a maximum VI of 138 for a poly(hexyl methacrylate) solution. However, the homopolymer represents rather difficult solubility in lube oil. The synthesized copolymers in this study exhibit a VI lower than the homopolymer synthesized by Jalilian and his coworkers. Nonetheless, the presence of 1-alkene in the copolymer backbone suggests higher solubility in lube oil. Moreover, higher incorporation of 1-alkene is advantageous for increasing the solubility of polymeric additives in base oil. Due to the lower incorporation of 1-hexene in the copolymerization system containing $AlCl_3$, achieving solubility of the copolymer in the oil posed a significant challenge, and satisfactory solubility was observed only for BHA13. These results are valuable for selecting suitable lubricating oils to produce multi-grade engine oils with eligible viscosity indices by incorporating various grades of the synthesized copolymers.

Table 2. Dependence of viscosity index (VI), and pour point depressant (PPD) on the type and the molar ratio of Lewis acids.

Sample	VI	PPD (℃)
Blank	96	–4
BHA13	137	–7
BHI1	126	–13
BHI2	124	–14
BHI3	120	–17
BHY1	124	–15
BHY2	119	–19
BHY3	114	–24

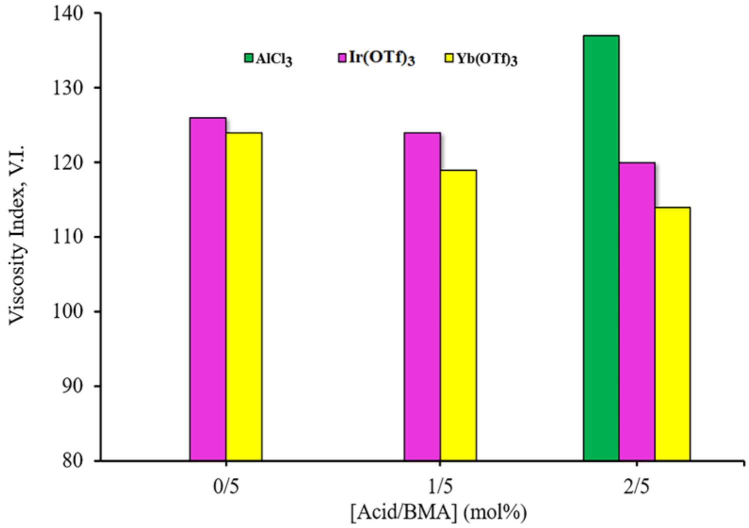

Figure 6. Effect of type and concentration of Lewis acid on VI of lube oil ([1-hexene/BMA] = 4 mol%).

3.3.2. Determination of pour-point

To examine the effectiveness of the copolymers as PPD in base oil, the synthesized samples underwent testing following ASTM D-98-87 standards. It is noteworthy that a substantial portion of crude oils and their derivatives comprises paraffin, which constitutes waxy substances. As temperatures decrease, these paraffin molecules can crystallize, forming a network of crystals. This crystal network can trap liquid hydrocarbon molecules and hinder the oil flow. The pour point temperature denotes the precise temperature at which this phenomenon transpires. Based on the application attributes provided in **Table 2**, it is evident that the synthesized copolymers reduced the size and cohesiveness of the crystal structures of paraffin waxes, suggesting a reduction in pour point and an enhancement of flow at lower temperatures[34]. It is apparent from

Figure 7 that using organometallic acids in the copolymerization system can improve the efficiency of these additives as pour point depressants. This improvement may be attributed to the lower molecular weight of the copolymers in this system. The minimum pour point (–24 °C) was observed for sample BHY3, which utilized $Yb(OTf)_3$ as a catalyst.

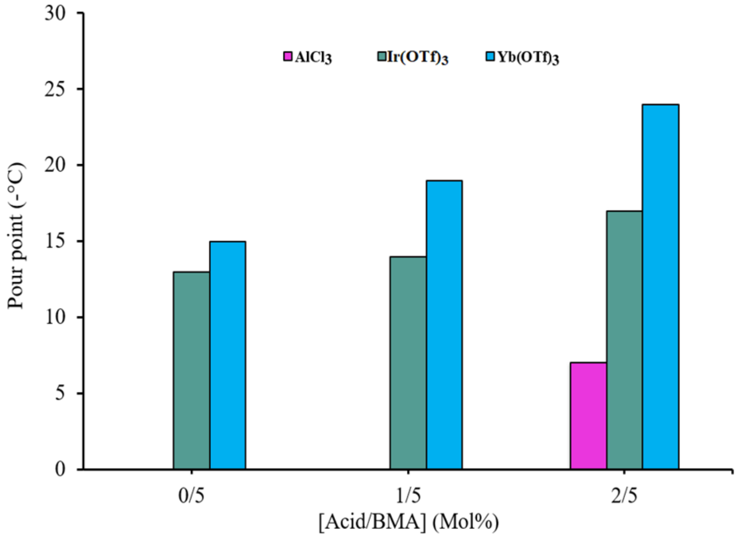

Figure 7. Effect of type and concentration of Lewis acid on the pour point of lube oil ([1-hexene/BMA] = 4 mol%).

3.3.3. Determination of shear stability

It is important to note that, along with the viscosity index, shear stability in lubricating conditions is also one of the essential parameters affecting oil performance. The shear stability index is used to determine the loss of viscosity induced by shear force and can be calculated as follows[11]:

$$SSI/\% = (v_i - v_f).100/v_i \quad (3)$$

where v_i and v_f are respectively oil viscosity before and after applied shear rate. Lower values of SSI indicate lower viscosity loss, suggesting higher stability of the polymeric additive against shear force. SSI values of 5 wt% solutions of copolymers in base oil are presented in **Figure 8**. The results demonstrate that the shear stability of polymeric additives increased with lower molecular weight, and sample BHY3 exhibited superior shear stability compared to other samples. A similar effect of molecular weight on the shear stability of polymeric additives was observed in our previous study[8].

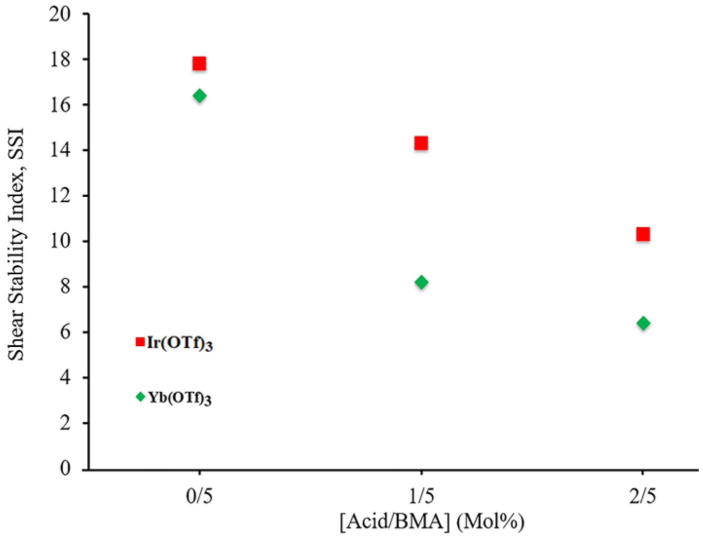

Figure 8. Effect of type and concentration of Lewis acid on SSI of lube oil ([1-hexene/BMA] = 4 mol%).

4. Conclusion

In this study, the free radical copolymerization of BMA and 1-hexene was successfully performed in the presence of $AlCl_3$, $Ir(OTf)_3$, and $Yb(OTf)_3$. Analysis of GPC and ^1H NMR revealed that the increased molar ratio of 1-hexene and Lewis acid concentration enhanced the incorporation of 1-hexene into the copolymer backbone and reduced M_n. Changing Lewis acid from $AlCl_3$ to organometallic acids led to an increase in the incorporation of 1-hexene in the copolymer chain. Compared to $Ir(OTf)_3$, the efficiency of $Yb(OTf)_3$ in increasing 1-hexene incorporation was remarkable. The synthesized copolymers were efficient as VIIs, and the VI of the lubricant oil was more affected by the samples containing higher molecular weight. Samples BHA13 and BHY3 showed maximum (137) and minimum (114) VI, respectively. Shear stability index was lowest for copolymer systems containing $Yb(OTf)_3$, suggesting the best shear stability of these polymeric additives in this study. The efficiency of synthesized copolymers as PPD was augmented by an enhancing molar ratio of Lewis acids and 1-hexene, due to a decline in the molecular weight of the copolymers. At the same concentration, copolymer systems containing $Yb(OTf)_3$ showed the best performance in reducing the pour point of base oil.

Author contributions

Conceptualization, SMJ; validation, FZ; writing, MRJ; review and editing, SMJ and MRJ; supervision, SMJ. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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