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Screening of the factors for novel pour point depressant copolymer synthesis to improve the copolymer yield

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Abstract. Pour point depressants (PPDs) commonly used in the oil and gas industry as a chemical wax inhibitor to control the temperature of the crude oil below their wax appearance temperature (WAT) points, and to improve the flowability of crude oil. In this study, different conditions of Stearyl Acrylate-Behenyl Acrylate (SABA) copolymer were synthesized by free-radical solution polymerization method at different range conditions of polymerization. Four factors considered during the synthesis of the copolymer are the mass ratio of monomers (1:1, 1:2, 1:3, 2:1, and 3:1 wt%), reaction temperature from 60 to 100 °C, the concentration of initiator from 0.5 to 2.5 wt% and reaction time from 5 to 9 hour. The results showed that the best conditions to obtain the highest yield of SABA copolymer were at the mass ratio of monomers of 1:1 (w/w), the reaction temperature of 90 °C, the reaction time of 7 h, and concentration of initiator at 1 wt%.

1. Introduction

In the previous years, copolymer synthesis with active functional groups as side alternatives of the significant chain was an active field of study in polymer science. In this case, the preparation of monomers consisting of a functional group is one of the most effective methods implemented for synthesizing copolymers [1].

In particular, one of the long-chain alkyl groups is stearyl acrylate (SA) is a category of acrylic monomer that has a good bond with nonpolar solvents, monomer finds out diffuse usage to synthesis pour point depressants. However, poly stearyl acrylate tends to be in a crystalline state. Thus, long alkyl side chains can crystallize despite an amorphous backbone that reduces oil absorbency. Regardless of various lower undesirable influences, the process of copolymerization with other monomers is used to obtain amorphous copolymers [2].

In the polymerization study, the monomer ratio, reaction temperature, reaction time, and concentration of initiator are crucial factors from the chemical industrial point of view, which contributes to improving the yield of the copolymer [3-4], particularly in tailor-made copolymers with desirable physical and chemical properties. Monomer ratios display some information about the relative reactivity of monomer pairs, clarification of copolymer synthesis, and monomer series distribution. [5, 6].

In last years, many studies were carried out on acrylic monomers because they form the tremendous multilateral category of monomers that used to form acrylate polymers based on acrylic acid structure, which contents of a carboxylic acid and a vinyl group [7-8]. Most researchers [4-5, 9-



12] have used acrylate and methacrylate monomers to produce PPD copolymers because of their very reactive double bonds at the vinyl group. Consequently, these copolymers can be utilized as a chemical inhibitor PPD to improve the flowability of crude oil and to reduce wax deposition into the pipeline. Substantially, acrylic and methacrylic ester groups are among the chemicals utilized for this goal since they show excellent capacity either as flow modifiers of crude oil or as wax deposition inhibitors [8].

In other words, pour point depressants (PPDs) can be widely applied as a chemical wax inhibitor to transport crude oil at a temperature below their wax appearance temperature points, widely improving safety and economics. In addition, PPD is a polymeric compound created fundamentally of hydrocarbon chains that interact with wax crystals to change wax morphology and preventing the aggregation stage [8, 13].

Recently studies revealed that PPD copolymers could decrease the viscosity of crude oils during transportation [14-17]. Styrene-maleic anhydride copolymer (PSMA) was synthesized by free-radical solution polymerization. It was found that the yield value and the dynamic viscosity have been decreased for the same sample and conditions [18]. Octadecyl acrylate-maleic anhydride copolymer was prepared by free-radical solution polymerization, According to the results, four types of chemical additives have shown excellent efficiency as PPDs and flow improvers in CQ crude oil with low asphaltene content [19]. Oleic acid-maleic anhydride copolymer (POMA) has been prepared by free-radical solution polymerization of various molar ratios. The obtained data showed that all chemical additives have a positive impact on the dynamic viscosity and Bingham values if they compared with the original results of the waxy crude oil [20].

Apart from that, one of the main problems facing the transportation of crude oil through the pipeline is high viscosity crude oil, which requires effective and expensive ways to transfer crude oil. Therefore, the higher viscosity of crude oil leads to an increase in pumping pressure from the ground, difficulties in transportation and refining operations.

Up till now, there are many monomers that have synthesized with stearyl acrylate to form a copolymeric particle such as styrene [9], glycidyl methacrylate [5], maleic anhydride [19, 21], and vinyl acetate [22]. Meanwhile, these monomers used as a chemical inhibitor to improve the flowability of crude oil. Therefore, for extending the application of polymerization, we have inserted a novel monomer that is behenyl acrylate (BA) to synthesized with (SA) for the formation of highly stable copolymeric particles. This study aims to synthesize and screening linear stearyl acrylate-behenyl acrylate copolymers at different conditions to obtain the optimum conditions and highest yield.

2. Experimental

2.1. Materials

Two monomers were used in this study; include stearyl Acrylate (SA, 97% purity) (purchased from Sigma Aldrich) and behenyl acrylate (BA, 95% purity) which was purchased from Aladdin chemicals. Other chemicals such as benzoyl peroxide 99% were used as the initiator, toluene 99% as solvent and methanol; all the chemicals were bought from Sigma Aldrich.

2.2. Experimental set up for synthesis of copolymer

Stearyl Acrylate-Behenyl Acrylate copolymer (SABA) was synthesized through the free-radical solution polymerization technique by utilizing different mass ratios between SA and BA (1:1, 1:2, 1:3, 2:1, and 3:1 wt%). The reaction was conducted in a 250 mL three-neck round-bottomed flask equipped with a thermometer, magnetic stirrer, reflux condenser, and nitrogen gas inlet. Figure 1 show the experimental apparatus. A mixture of monomers was dissolved in 50 mL of toluene under constant stirring at a range of temperature from 60 to 100 °C for 5 to 9 h of reaction time and a nitrogen atmosphere for 30 min. At this time, benzoyl peroxide (BPO) was dissolved in suitable toluene used as an initiator at a range between (0.5-2.5% w/w of a total of monomers). The solution of benzoyl peroxide was added drop by drop every 15 min during the first hour of the reaction. After the reaction had been completed, it was kept at room temperature; then, the precipitation of copolymer solution was initiated through the addition of methanol to reaction mixture alongside with rapid stirring.

Thereafter, the copolymer was filtered through a Buchner funnel and washed three times with methanol. The obtained product was dried in a vacuum oven at 40 °C for 12 h with the final state of SABA copolymer being a white powder.

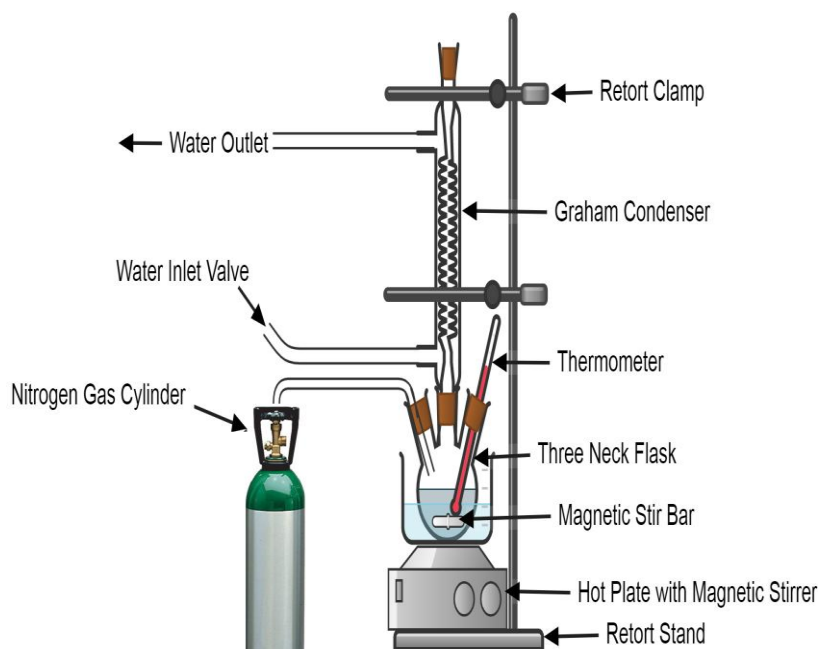


Figure 1. The experimental apparatus.

3. Results and discussion

3.1. Effect of SA: BA ratio on the yield

In this study, monomer ratios are critical factors in the polymerization, especially in tailor-made copolymers. Monomer ratios display information about the reactivity of monomer pairs, clarification of copolymer composition, and monomer sequence distribution [20]. Figure 2 illustrates the relationship between the mass ratio of stearyl acrylate (SA) and behenyl acrylate (BA) on the yield. As seen in Figure 2 there are slightly variations in the yields of the copolymers when the polymerization was conducted at different mass ratios. When the mass ratio of monomers was equal 1:1 (50 wt% to 50 wt%), the yield was high around 95.83%. However, if the mass ratio of stearyl acrylate monomer increases more than the behenyl acrylate monomer or vice versa such as (2:1, 1:2, 3:1, and 1:3), the yield gradually decreases from 95.83% to 80%. This is a clear indication that an equal amount of stearyl acrylate (SA) and behenyl acrylate (BA) can give an optimal copolymer yield. Thus, the highest yield of mass ratio was found at 95.83% of the yield at 1:1 ratio [23].

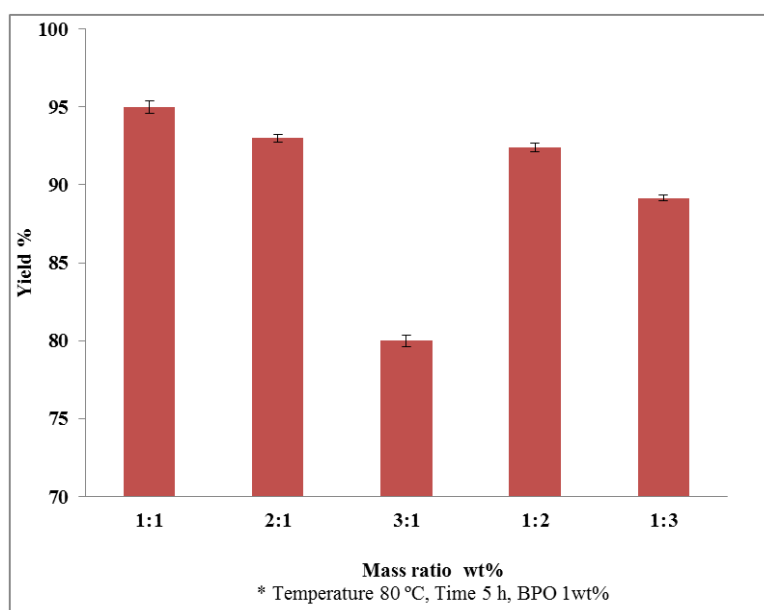


Figure 2. Relationship between the mass ratio of monomers and yield.

3.2. Effect of reaction temperature on the yield

A series of tests were conducted to observe the effect of temperature on the yields of the copolymer. The temperatures used during the polymerization were increased by 10 °C increments between 60 and 100 °C, as shown in Figure 3. From Figure 3, the yield of the copolymer increased with increasing the reaction temperature during the polymerization. However, at a temperature of 90 °C, the yield of the copolymer was slightly decreased from 92.5% at 90 °C to 90% at 100 °C. Therefore, the optimum polymerization reaction to completed and obtained the highest yield of copolymer was found 92.5% of the yield at 90 °C.

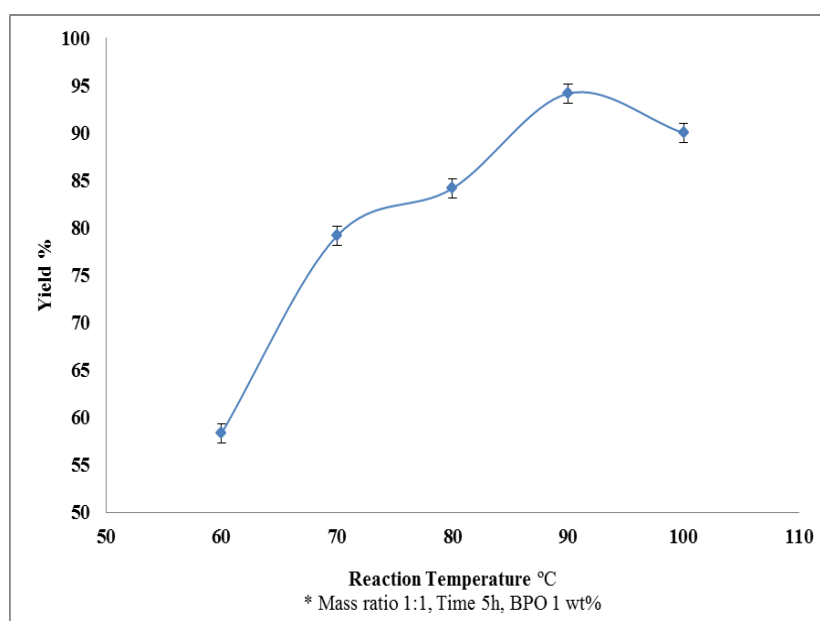


Figure 3. Relationship between reaction temperature and yield.

3.3. Effect of concentration of initiator on the yield

In order to understand the effective concentration of the initiator, a chain of the reaction was conducted at 90 °C whereby the initiator concentration fell between 0.5 and 2.5% wt of BPO, as shown in Figure 4. From Figure 4 the copolymer yields initially increased with increasing concentration of initiator from 80% to 95%. The highest yield was 95% at 1% of BPO. Nonetheless, beyond 1% of BPO, the copolymer yield started declining progressively until the yield remained rather similar at different concentration of BPO 1.5%, 2%, and 2.5%, respectively. At this point, the yield of copolymer remained unchanged at 94.16%. Therefore, this is an indicator for completion of the polymerization process at 1% of BPO, which is the highest yield. In terms of reaction yield, the highest yield of copolymer was 95% at 1% of BPO.

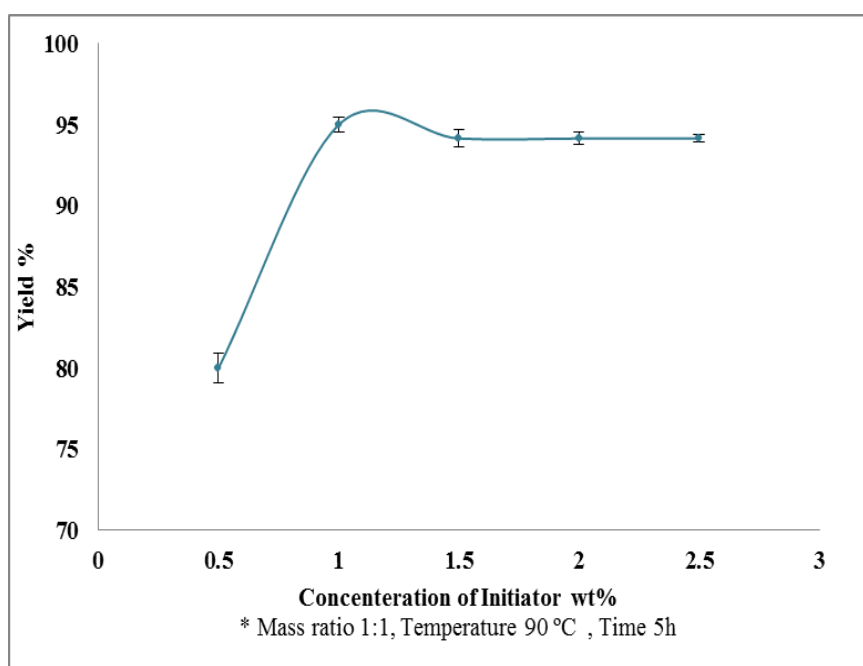


Figure 4. Relationship between the concentration of initiator and yield.

3.4. Effect of reaction time on the yield

As refer to Figure 5 the changing of the reaction time from 5 h to 9 h had a negligible influence on yield loss. Consequently, the result of copolymer yield exhibited a declining from 98.16% to 95.83% with increased reaction time from 7 to 9 hours as similarly reported by another researcher [24]. The copolymer yield showed a significant performance at the beginning of the process and attained the highest yield at 7 h. Meanwhile, there was a decline in the copolymer yields with increasing time. Therefore, this clearly showed that the polymerization process was completed at 7 h. In terms of the reaction yield, the highest yield polymerization of reaction time at 7h was 98.16%.

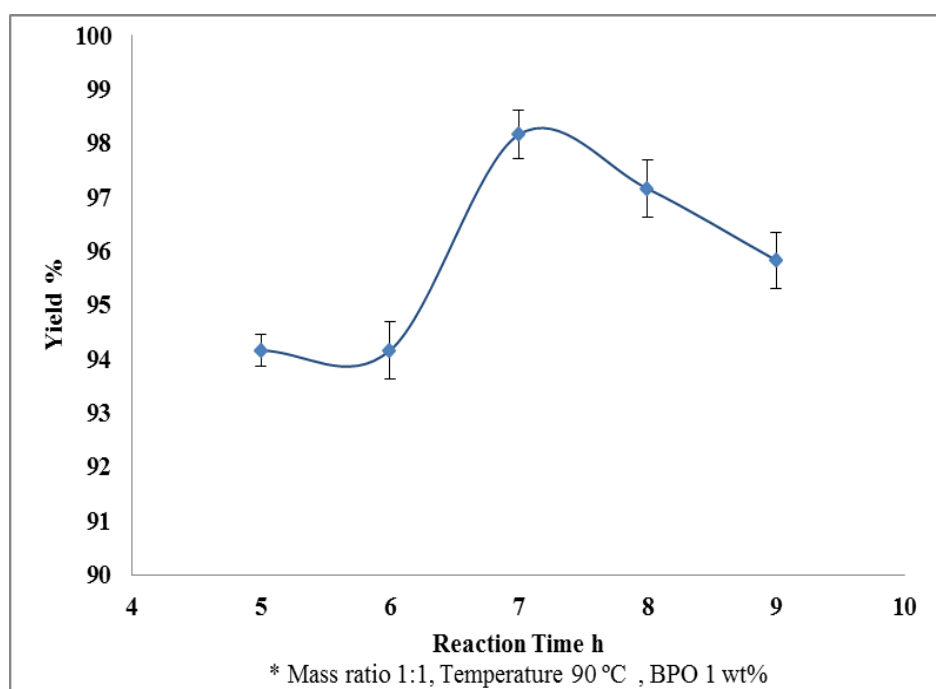


Figure 5. Relationship between reaction time and yield.

4. Conclusion

This study had investigated the screening of factors for synthesizes a novel pour point depressant copolymer. The best operating condition the obtain the highest yield of SABA copolymer is at a mass ratio of monomers is 1:1 (w/w), the reaction temperature of 90 °C, the reaction time of 7 h, and concentration of initiator of 1 wt%. Measuring viscosity will discuss further in the next study.

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