Studies on thermal and microwave assisted synthesis of poly myristyl acrylate and its evaluation as viscosity modifier in lubricating oil

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Homopolymer of myristyl acrylate was synthesized by two different ways; microwave (MW) assisted method and thermal method using benzoyl peroxide (BZP) and azobis iso butyro nitrile (AIBN) as initiator. Additive performances of each of them as viscosity modifier (VM) for lubricating oil (lube oil) were also evaluated by standard ASTM methods. Thermal stability of the polymers was determined by thermo gravimetric analysis and shear stability of each of the polymers were also studied in different concentration of base oil. A comparison of their performances has also been evaluated and reported.

Introduction

Base fluids mineral oil, used as lubricant, generally cannot satisfy the requirements of high performance lubricants used in modern additive technology. The additives\(^1\) used are synthetic chemicals that can improve or add performances of lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. One of the important property of the base oil which is modified by the lubricating additives is viscosity index\(^2\)\(^-\)\(^4\) and the additive imparting the property is called Viscosity index improvers (VII) or viscosity modifier\(^5\) (VM). They are long chain, high molecular weight polymers used to resist the change of viscosity of the oil by increasing the relative viscosity of oil more at high temperatures than at low temperatures\(^6\)\(^-\)\(^8\). The performance of VMs is generally expressed in terms of Viscosity Index (VI), which is an arbitrary number\(^9\) that indicates the resistance of a lubricant to viscosity change with temperature. The higher the VI, the less the changes of viscosity of oil for a given temperature change. The performance of the VII depends on the behaviour of the polymer molecules in the oil, where the polymer solubility, molecular weight and resistant to shear degradation are determinant parameters. Oil thickening property\(^10\) of the polymer, which is a direct measure of percent increase in the viscosity of the base stocks for addition of its unit amount of weight can also be taken as the measure of extent of interaction of the polymer with the base stock, greater the thickening property; greater is the extent of interaction. Fuel economy may also be predicted by the thickening power of a lube oil additive. Although high thickening power of high molecular weight polymer makes them economically more effective but the inferior shear stability\(^11\)\(^,\)\(^12\) results rapid loss of viscosity in service. Therefore, it is necessary to obtain an optimal relation between viscosity index improving quality and shear stability of the polymer. Shear stability is expressed in term of permanent viscosity loss (PVL) or permanent shear stability index (PSSI)\(^13\). Microwave irradiation is a well-known method for heating and drying materials and is utilized in many private households and industrial applications for this purpose. Both organic and inorganic reactions undergo an immense increase in reaction speed under microwave irradiation\(^14\) compared with conventional heating. Significant improvements in yield and selectivity have also been observed as a consequence of the fast and direct heating of the reactants themselves. Furthermore, high-pressure synthesis is easily accessible for reactions performed in closed vessels, facilitating the use of low boiling solvents and thereby paving the way to environmentally benign reaction conditions. With this view in mind and as a part of

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our ongoing studies on the synthesis and evaluation of polymeric additives, presently we have synthesized poly myristyl acrylate by using BZP and AIBN (both in thermal and microwave process) separately. VI, PVL and PSSI property of each of the additives were evaluated in two different base oils.

Materials and methods
Acrylic acid (GC Purity 99%) obtained from Thomas Baker, India. Myristyl alcohol (GC Purity 98%) obtained from S.D. Fine chemicals Ltd. India. Hydroquinone obtained from S.D. Fine Chemical Ltd., India. Benzoyl peroxide (GC Purity 98%) obtained from LOBA Chemicals Pvt. Ltd., India, was purified by crystallization from methanol-chloroform mixture. AIBN obtained from Spectrochem Pvt. Ltd., India and Toluene (GC Purity 99.5%) obtained from Merck, India, was used as a solvent.

Preparation of monomer (myristyl acrylate)
The monomer myristyl acrylate was prepared by reacting acrylic acid with myristyl alcohol (1:1 molar ratio). The reaction was carried out in a three necked round bottom flask in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent under continuous air bubbling. The reactants, which were mixed with toluene, was continuously refluxed and heated gradually from room temperature to 403K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water in dean stark apparatus to give the ester, myristyl acrylate.

Purification of the Prepared Acrylate Ester
The prepared ester was purified by the method as described in our earlier publication.

Thermal Polymerization
The polymerization was carried out in a four-necked round bottom flask equipped with a stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. The desired mass (20 g) of MA (Myristyl Acrylate) and initiator (BZP/AIBN) (0.5 g) were added in the round bottom flask in five different lots during reaction in toluene (10 ml) as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation from its hexane solution by methanol followed by drying under vacuum at 313 K.

Microwave Assisted Polymerization
Polymerization was carried out in a focused mono-mode microwave oven (CEM corporation, Matthews, NC) applying 300 WT for 15 minute at 90°C without any solvent by adding 0.01% (w/w) BZP or AIBN with respect to the monomer as initiator. The desired mass (20 g) of MA (Myristyl acrylate) and initiator (BZP/AIBN) (0.5 g) were taken in vial and sealed with a Teflon septum. Then argon was bubbled through the solution to get oxygen free atmosphere. The reaction mixture was magnetically stirred at 90 °C with microwave heating for 30 min applying 300 WT without any solvent, which were subsequently quenched by quickly cooling to room temperature and purified following the procedure as mentioned above.

Measurements
Spectroscopic Measurements
IR spectra were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm⁻¹. NMR spectra were recorded in Brucker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl₃ was used as solvent and TMS as reference material.

Determination of intrinsic viscosity and viscometric molecular weight of the polymers
Intrinsic viscosity and viscometric molecular weight were determined by using the experimental viscosity of the polymer solutions in Huggins (eq.1) and Mark Houwink – Sukurda equation (eq.2) respectively.

Huggins (H)

\[
\frac{\eta_s}{C} = [\eta]_h + k_h [\eta]_h^2 C 
\]

Where, C is mass concentration, \( \eta_s = \eta_r - 1 \), \( \eta_s \) is the specific viscosity, \( \eta_r = \frac{t}{t_0} \), \( \eta_r \) is the relative viscosity or viscosity ratio (where t is the time of flow of the solution and \( t_0 \) is the time of flow of the pure solvent). \([\eta]_h \) is intrinsic viscosity, respective to Huggins equation, \( k_h \) is the Huggins coefficient. According to Mark Houwink – Sukurda (eq.2), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:
Where, \( [\eta] \), the intrinsic viscosity, can be calculated by using Huggins equation, parameter ‘K’ and ‘a’ depends on the type of polymer, solvent and temperature. For the determination viscosity – average molecular weight of polyacrylate system, the constants \( K = 0.00387 \) dl/g and \( a = 0.725 \) were employed in Mark Houwink – Sukurda relation.

### Thermogravimetric Analysis (TGA)

The thermo grams in air were obtained on a mettler TA – 3000 system, at a heating rate of 10°C / min.

### Viscosity index determination

Kinematic viscosity (KV) of polymyrystyl acrylate doped base oil was determined separately in 40°C and 100°C by counting the time of flow of polymer solution in base oil and the density was determined by the equation, \( KV = (Kt – L/t) d \), where \( K \) and \( L \) are viscometric constant and their values, 0.03853 and 2.46896 respectively are determined by taking toluene as solvent. ‘t’ and ‘d’ are the time of fall and density of the solution respectively. With this the viscosity index of each polymer solution was determined as per ASTM D-7042 method and also by using the method of viscosity index calculation reported in literature.

### Shear stability determination

Shear stability of the lube oil additive is one of the important criteria that determine its suitability in a lubricant formulation. The shear stability of the doped additive has strong influence on multigrade engine oil’s ability to retain its viscosity under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be of two kinds, namely a temporary viscosity loss (TVL) or a permanent viscosity loss (PVL). PVL is similar to TVL, except that the viscosity loss is measured by KV before and after shear. The PVL values are more frequently expressed in terms of shear stability index (SSI). Shear stability of the various solution of pure polymyrystyl acrylate in lube oils (BO1 and BO2) was determined as per ASTM D - 3945 method by the relations, PVL = \( (V_i - V_s) / V_i \) and SSI = \( (V_i - V_s) / V_i - V_0 \) , where \( V_0 \) = Kinematic viscosity (KV) of the base oil before addition of polymer, \( V_i = KV \) of unshared solution, \( V_s = KV \) of sheared solution. KV of the base oil and sheared polymer solution in base oil was determined by ASTM D- 445 procedure. Properties of the base oils, BO1 and BO2 are given in Table 1, below.

### Results and Discussion

All the polymers showed similar peaks in their IR and NMR (\(^1\)H and \(^{13}\)C) spectrum. The IR absorption at 1730 cm\(^{-1}\) showed the presence of ester carboxyl group. Peak at 1190 cm\(^{-1}\) was due to the ester C-O stretching vibration and peaks in the range 1053.8 cm\(^{-1}\) to 721.8 cm\(^{-1}\) for C-H bending vibrations. The \(^1\)HNMR signal centred at \( \delta 3.642 \) ppm indicates the presence of –OCH\(_2\) group of acrylate chain. Absence of peak between \( \delta 5 \) to \( \delta 6 \) ppm indicates the absence of olefinic double bond. The proton decoupled \(^{13}\)C-NMR of the above sample was in complete agreement with the homopolymer which shows the presence of ester carboxyl group at \( \delta 174.47 \) ppm and absence of any sp\(^3\) carbon in the range 130-150 ppm. The TGA data showed (Table 2) that the thermal stability of P-1 and P-2 and that of P-3 and P-4 are more or less similar but thermal stability of P-3 is much better than P-1 and similarly that of P-4 is more than P-2. The stability data also indicated that irrespective of the nature of the initiator, polymer P-3 and P-4 (prepared by microwave assisted method) is more linear than P-1 and P-2 (prepared by thermal method) respectively, since branching in polymer chain induces instability. The study reveals that with increasing concentration of polymer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization Process</th>
<th>Decom. Temp., °C</th>
<th>PWL</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>Thermally with BZP</td>
<td>255/366</td>
<td>13/84</td>
</tr>
<tr>
<td>P-2</td>
<td>Thermally with AIBN</td>
<td>260/269</td>
<td>13/85</td>
</tr>
<tr>
<td>P-3</td>
<td>Microwave method with BZP</td>
<td>277/395</td>
<td>15/94</td>
</tr>
<tr>
<td>P-4</td>
<td>Microwave method with AIBN</td>
<td>280/399</td>
<td>15/95</td>
</tr>
</tbody>
</table>

Decom. Temp., °C - Decomposition temperature.
Table 3—VI values of the Additives Doped in Base Oil

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base oil</th>
<th>Additives doped based oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>P-1</td>
<td>BO1</td>
<td>70.3</td>
</tr>
<tr>
<td></td>
<td>BO2</td>
<td>89.5</td>
</tr>
<tr>
<td>P-2</td>
<td>BO1</td>
<td>71.3</td>
</tr>
<tr>
<td></td>
<td>BO2</td>
<td>90.5</td>
</tr>
<tr>
<td>P-3</td>
<td>BO1</td>
<td>71.2</td>
</tr>
<tr>
<td></td>
<td>BO2</td>
<td>90.6</td>
</tr>
<tr>
<td>P-4</td>
<td>BO1</td>
<td>71.7</td>
</tr>
<tr>
<td></td>
<td>BO2</td>
<td>91.6</td>
</tr>
</tbody>
</table>

Table 4—[\eta]_a and [M_h]_b of Polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>[\eta]_a</th>
<th>[M_h]_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>2.397</td>
<td>7095</td>
</tr>
<tr>
<td>P-2</td>
<td>2.498</td>
<td>7511</td>
</tr>
<tr>
<td>P-3</td>
<td>2.599</td>
<td>7933</td>
</tr>
<tr>
<td>P-4</td>
<td>2.776</td>
<td>8687</td>
</tr>
</tbody>
</table>

*Intrinsic Viscosity, bViscometric Molecular Weight of Polymer according to Mark Houwink–Sukurda relation*

In lube oil the VI value increases (Table 3). A possible explanation for that is, with increasing temperature the polymer molecules change from tight coil to expanded ones as a result of increasing the interaction between the polymer chain and the base oil. This increase in volume causes an increase in the viscosity of the mixture and offsets the normal reduction in viscosity of the oil with increasing temperature. The increase of concentration of the polymer also leads to an increase in total volume of polymer micelles in the oil solutions. Consequently, a high concentration of polymer in base oils will impart a high viscosity index rather than a low concentration of the same polymer. Studies also indicate that shear stability of P-1 is more than that of P-2 and P-3 is more than P-4 (Figure 1 and 2 and also Figure 3 and 4) which can be explained by the respective molecular weight data (Table 4). Higher the molecular weight the lower is the shear stability and greater is the PVL and PSSI value (Figure 1-4). Thus the shear stability of VM is influenced by the nature of the initiator rather than the way of polymerization process. The lower decomposition temperature of AIBN compared to BZP may be responsible for giving high mol wt polymer and hence the less shear stable products.
Conclusion

1. Viscosity index of AIBN initiated polymer is more than that of BZP initiated both in thermal and microwave condition.

2. Shear stability of the VM is influenced by the nature of the initiator rather than the way polymerization process. Initiator BZP provides better shear stability compare to AIBN.

3. Irrespective of the nature of the initiator, polymer prepared by microwave assisted method showed better thermal stability over the one prepared by thermal method.

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References


