Evaluation of Effect of Solvents in Solution Polymerization of Polyvinyl Acetate

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Introduction

The most usage of PVAc, beside floors covering, glues and paper covers, is PVA. The effects of alcohol it depends on the kind of it on PVA agglomeration. Therefore consideration of alcohol effecting in solution polymerization of PVAc has been down. In this paper consideration has been down that solution polymerization of PVAc in two different kind of solvent, in 60°C with AIBN. Therefore by using viscometer the change of Weight average molecular weight with time is calculated and considered.

Experimental

Materials. The monomer Vinyl acetate (Merk) was distilled under vacuum at the most 24 h before use. The first 20-50 ml of distillate were discarded and was stored at 5°C when not in use. Methanol and Isopropyl and AIBN (Merk), were also used as packaged.

Polymerization. Experiment were performed in a four-necked round bottom flask at 60°C, with constant agitation with magnet (300 rpm). The temperature was controlled by means of a heater. The flask, reactor, was washed with THF and dried with acetone before each experiment. The monomer and solvent (less 5-10 mL of solvent used for initiator injection) were introduced into the reactor, heated, and degassed with nitrogen for 10-15 min. The initiator dissolved in the remaining solvent is then injected, at which point the reaction is assumed to have started.

Table 1. Parameters for Solution Polymerization of Vinyl Acetate

<table>
<thead>
<tr>
<th>Materials</th>
<th>Weight (gr)</th>
<th>Volume (CC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>47.52</td>
<td>60</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>48</td>
<td>60</td>
</tr>
<tr>
<td>VAC</td>
<td>46.5</td>
<td>50</td>
</tr>
<tr>
<td>AIBN</td>
<td>0.07</td>
<td>-</td>
</tr>
</tbody>
</table>

Analytical techniques. The purity of VAC was evaluated by GC. PVAC was also analyzed by by ¹H-NMR and ¹³C-NMR.

Results and discussion

Modeling. In the classical representation of free radical polymerization kinetics, the rate of reaction in a bath reactor is given by the following expression [5]:

\[
\frac{r_p}{[M_0]} = \frac{-[M_0](1-x)}{a} = k_p [I]_0 (1-x) \left( \frac{2k_d[I]_0 e^{-k_d t}}{k_p} \right)^{1/2}
\]

where [M₀] is the initial monomer concentration, x the conversion, [I] the initiator concentration, kₚ the propagation constant and kᵣ the initiator decomposition constant, kᵢ is the initiator efficiency.

Rate data. Conversion was estimated using the well-known gravimetric technique. Rate data (conversion vs. time) is presented in (Figure 1), for solution polymerization in Methanol and Isopropyl with AIBN.

Figure 1. Effect of solvents in solution polymerization of VAC

In analyzing the results of a single polymerization experiment, eq.(1), should be used: one plots -ln(1-x) against t, and from the slope determines either \(k_p^2/k_d^2\) if \(k_d\) is known. The data regressed using eq.(1) and results showed in (Table 2).
Table 2. Evaluation of Effect of Solvents in Rate and Kinetic Parameter of Reaction

<table>
<thead>
<tr>
<th>Concentration (AIBN)</th>
<th>Solvent</th>
<th>$\frac{2k}{k_1}$</th>
<th>$\rho$</th>
<th>$R_g$(1/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0034</td>
<td>Methanol</td>
<td>4.44</td>
<td>0.0901</td>
<td></td>
</tr>
<tr>
<td>0.0034</td>
<td>Isopropyl</td>
<td>16.17</td>
<td>0.1333</td>
<td></td>
</tr>
</tbody>
</table>

Molecular Weight. Molecular Weight measurements were performed on an Ostwald viscometer. (Table 3) showed the Mark Houwink parameters for Poly Vinyl Acetate[1].

Table 3. Mark Houwink parameters for Poly Vinyl Acetate.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp</th>
<th>$k \times 10^{-4}$</th>
<th>$\alpha$</th>
<th>Mw Range (Mw-4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aceton</td>
<td>30</td>
<td>1.01</td>
<td>0.73</td>
<td>6-150</td>
</tr>
</tbody>
</table>

Measured value of the weight average molecular weight of PVAc against time in Methanol and Isopropyl, showed in (Figure 2) and (Figure 3).

Figure 2- Measured Values of the Mw of PVAC in Methanol

Figure 3 - Measured Values of the Mw of PVAC in isopropyl

Conclusion
Solution polymerization of Vac in Methanol and isopropyl has shown different conclusion. As you saw above, rate of polymerization in isopropyl is more than as methanol, also the viscometer’s calculation is shown that Weight average molecular weight in methanol is more than any other solvent, therefore chain transfer to solvent of isopropyl was more than as methanol.

References