A Comparative Study on the Aqueous Polymerization of Methacrylonitrile and Acrylonitrile initiated by Potassium Persulphate at 50°C in an inert Atmosphere of Nitrogen Gas

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Abstract:
The structural difference between the methacrylonitrile, [(CH$_2$= C(CH$_3$)CN] and acrylonitrile, [CH$_2$=CH(CN)] is the replacement of the $\alpha$ hydrogen of acrylonitrile by a methyl group. Due to this structural difference the two monomers differ not only in their physical properties but also differ in their chemical properties during the polymerization processes.

In the present work, we have studied the behaviour of methacrylonitrile in aqueous and emulsion systems in details. Along with this, a few experiments of aqueous polymerization of acrylonitrile have been performed under identical conditions. Considering these results and those reported in the literature, a comparison of properties of these two monomers has been made in this chapter.

The rates of polymerizations under various conditions have been followed by the conventional gravimetric method. The molecular weights of the polymers have been estimated from the intrinsic viscosity data and also by the gel permeation chromatographic method as a function of monomer and initiator, potassium persulphate (KPS) concentrations. It has been found that

$$R_p \propto [\text{MAN}]^{1.60 \pm 0.05} [\text{KPS}]^{0.50 \pm 0.05}$$

and

$$R_p \propto [\text{AN}]^{1.46 \pm 0.04} [\text{KPS}]^{0.46 \pm 0.04}$$

Both in the MAN-KPS and AN-KPS systems, the injection of initiator late in a run increases the rate of aqueous polymerization but has no measurable effect on the viscosity average molecular weight ($\bar{M}_v$) of the polymers, whereas the addition of extra amount of monomer late in a run increases both the rates of polymerization and the ($\bar{M}_v$). The rate of the aqueous polymerization is higher in the AN-KPS system than that in MAN-KPS system. The particle size distribution has been measured.
### Difference of physical properties between acrylonitrile and methacrylonitrile.

<table>
<thead>
<tr>
<th>Sl. Physical Property</th>
<th>Acrylonitrile</th>
<th>Ref</th>
<th>Methacrylonitrile</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Solubility in water (w/w)</td>
<td>8.5 (at 25°C)</td>
<td>1</td>
<td>2.5 (at 25°C)</td>
<td></td>
</tr>
<tr>
<td>2 Refractive index</td>
<td>1.3088 (at 25°C)</td>
<td>2</td>
<td>1.401 (at 25°C)</td>
<td></td>
</tr>
<tr>
<td>3 Density</td>
<td>0.8060 (at 20°C)</td>
<td>3</td>
<td>0.7998 (at 20°C)</td>
<td>3</td>
</tr>
<tr>
<td>4 Partition coefficient of monomer between the polymer phase &amp; the aqueous phase at 50°C</td>
<td>0.50±0.10</td>
<td>4</td>
<td>1.8 ± 0.2 (at 50°C)</td>
<td></td>
</tr>
<tr>
<td>5 Value of $k_p$ (in lit./mol./sec) at 25°C</td>
<td>3000</td>
<td>3</td>
<td>26</td>
<td>3</td>
</tr>
<tr>
<td>6 Value of $k_L$ (in bulk polymerization (in lit./mol./sec) at 25°C)</td>
<td>$2000 \times 10^6$</td>
<td>3</td>
<td>$21 \times 10^6$</td>
<td>3</td>
</tr>
<tr>
<td>7 Chain transfer constant $(C_M = k_{tm}/k_p)$</td>
<td>$(0.26 - 0.3) \times 10^{-4}$ (at 60°C)</td>
<td>3</td>
<td>$5.81 \times 10^{-4}$ (at 60°C)</td>
<td>3</td>
</tr>
<tr>
<td>8 Density of polymer (in gm/ml) at 25°C</td>
<td>1.17</td>
<td>2</td>
<td>1.10</td>
<td>2</td>
</tr>
<tr>
<td>9 Volume change (after 100% conversion)</td>
<td>31.0</td>
<td>2</td>
<td>27.0</td>
<td>2</td>
</tr>
</tbody>
</table>
RESULTS

Table 1 shows the difference between methacrylonitrile and acrylonitrile during the aqueous polymerization in the absence of any surfactant and Table 2 shows that in the presence of the detergent, NaLS. Figure 1 and 2 show the conversion time curve at different monomer (AN) concentration and at different initiator (KPS) concentration respectively. Here we see that the rate of polymerization increases with the increase of monomer (AN) and initiator concentrations. The order of the monomer (AN) is found to be (1.36 0.04) and that of the initiator is found to be (0.44 ± 0.06). The molecular weights (\(M_w\)) of the polymers at a given conversion increases with the increase of monomer concentration and decreases with the increase of the initiator concentration (Table 3). Figure 3 shows the difference between the two monomers namely methacrylonitrile and acrylonitrile during the aqueous polymerization in the presence and the absence of NaLS. Here we see that under identical conditions the rate of polymerization of acrylonitrile is higher than that of methacrylonitrile. Table 4 shows the effects of the detergent (below CMC), present initially and when injected late in a run. The effects of injection of extra amounts of monomer and initiator late in a run are shown in Tables 5 and 6.

**TABLE 1**

Aqueous polymerization in absence of detergent

Recipe: \([\text{KPS}] = 2 \times 10^{-3} \text{ mol./lit}, [\text{NaLS}] = \text{Nil}\)

\([\text{MAN}] = 0.30 \text{ mol/lit.}, \text{ Temp.} = 50 \pm 0.2^\circ C, [\text{AN}] = 0.30 \text{ mol./lit.}\)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Methacrylonitrile</th>
<th>Acrylonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% conversion</td>
<td>% conversion</td>
</tr>
<tr>
<td></td>
<td>([\eta]) \times 10^2 \text{ (mL/gm)}</td>
<td>([\eta]) \times 10^2 \text{ (mL/gm)}</td>
</tr>
<tr>
<td>60</td>
<td>5.17</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>9.74</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>16.22</td>
<td>3.44</td>
</tr>
<tr>
<td>150</td>
<td>20.86</td>
<td>3.35</td>
</tr>
<tr>
<td>180</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### TABLE - 2

Aqueous polymerization in presence of detergent.

Recipe: [KPS] = 5 \times 10^{-3} \text{ mol./lit.}, [NaLS] = 2 \times 10^{-3} \text{ mol./lit.}, [MAN] = 0.30 \text{ mol./lit.}

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Methacrylonitrile % conversion ( [\gamma] \times 10^2 ) (ml/gm)</th>
<th>Acrylonitrile % Conversion ( [\gamma] \times 10^2 ) (ml/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.58</td>
<td>33.08</td>
</tr>
<tr>
<td>90</td>
<td>7.40</td>
<td>44.15</td>
</tr>
<tr>
<td>120</td>
<td>11.62</td>
<td>50.50</td>
</tr>
<tr>
<td>150</td>
<td>15.12</td>
<td>57.25</td>
</tr>
</tbody>
</table>

### TABLE - 3

Effect of variation of monomer concentration and initiator concentration on the molecular weight of the polymer during the aqueous polymerization of acrylonitrile.

<table>
<thead>
<tr>
<th>([\text{KPS}] \times 10^3) (mol./lit)</th>
<th>([\text{AN}]) (mol./lit)</th>
<th>((M_v) \times 10^{-5}) Different Conversion 10% 20% 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>1.60 1.54</td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>1.42 1.46</td>
</tr>
<tr>
<td>5.0</td>
<td>0.30</td>
<td>1.00 1.10</td>
</tr>
<tr>
<td>1.0</td>
<td>0.45</td>
<td>3.03 3.30 3.10</td>
</tr>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>1.60 1.54</td>
</tr>
<tr>
<td>1.0</td>
<td>0.25</td>
<td>1.06 1.10</td>
</tr>
<tr>
<td>1.0</td>
<td>0.20</td>
<td>0.59</td>
</tr>
</tbody>
</table>

N.B. The equation used to find out the molecular weight \((M_v)\) of the polymer is:

\[ [\gamma] = 33.5 \times 10^{-3} (M_v)^{0.72} \]
Fig. 1: Effect of monomer (AN) concentration variation on the percent conversion-time curve during the aqueous polymerization.
Fig. 2: Effect of initiator (KPS) concentration variation on the percent conversion-time curve during the aqueous polymerization of acrylonitrile monomer (AN)
**TABLE-4**

Effects of presence of detergent (below CMC) initially and injection of extra amounts of detergent late in a run during the aqueous polymerization of acrylonitrile.

<table>
<thead>
<tr>
<th>[KPS] x 10^3 (mol/lit)</th>
<th>[MAN] (mol/lit)</th>
<th>[NaLS] x 10^3 (mol/lit)</th>
<th>Time (minutes)</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>0</td>
<td>a = 5.55</td>
<td>11.00</td>
<td>16.15</td>
<td>19.65</td>
<td>22.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = -</td>
<td>1.60</td>
<td>-</td>
<td>1.54</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>1.0</td>
<td>a = 7.45</td>
<td>17.70</td>
<td>27.25</td>
<td>33.45</td>
<td>38.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 1.33</td>
<td>1.37</td>
<td>1.56</td>
<td>1.36</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>2.0</td>
<td>a = 6.93</td>
<td>16.33</td>
<td>23.30</td>
<td>30.00</td>
<td>41.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 1.31</td>
<td>1.43</td>
<td>1.51</td>
<td>1.52</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>0</td>
<td>a = 10.05</td>
<td>16.05</td>
<td>23.20</td>
<td>27.65</td>
<td>30.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 1.42</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>1.0</td>
<td>a = 18.30</td>
<td>31.30</td>
<td>40.60</td>
<td>45.65</td>
<td>48.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = -</td>
<td>32.30</td>
<td>42.00</td>
<td>44.00</td>
<td>46.70</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>*</td>
<td>a = 11.55</td>
<td>16.30</td>
<td>20.00</td>
<td>22.80</td>
<td>23.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>**</td>
<td>a = 11.15</td>
<td>15.40</td>
<td>19.60</td>
<td>22.60</td>
<td>22.60</td>
<td></td>
</tr>
</tbody>
</table>

N.B.: a = % conversion and b = molecular weight (M_v) x 10^-5 of the polymer. In the * marked set, extra amount of detergent (1.0 x 10^-3 mol/lit) has been injected late in a run with an initial detergent concentration as 1.0 x 10^-3 mol/lit. In the ** and *** marked sets, extra amount of 1.0 x 10^-3 NaLS and same volume of water have been injected respectively after 1 hour in a run with no NaLS initially.

**TABLE-5**

Effect of monomer injection

**Recipe:** [KPS] = 1.0 x 10^-3 mol/lit and [NaLS] = 0

<table>
<thead>
<tr>
<th>Run</th>
<th>Gill</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-A</td>
<td>a = -</td>
<td>5.50</td>
<td>9.24</td>
<td>12.66</td>
<td>15.36</td>
<td>16.38</td>
</tr>
<tr>
<td></td>
<td>b = -</td>
<td>-</td>
<td>-</td>
<td>1.06</td>
<td>1.20</td>
<td>1.16</td>
</tr>
<tr>
<td>Run-B</td>
<td>a = 12.70</td>
<td>24.96</td>
<td>35.06</td>
<td>41.56</td>
<td>60.83</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>b = 3.44</td>
<td>3.34</td>
<td>3.19</td>
<td>2.92</td>
<td>2.95</td>
<td>-</td>
</tr>
<tr>
<td>Run-C</td>
<td>a = -</td>
<td>9.37</td>
<td>20.83</td>
<td>32.10</td>
<td>37.76</td>
<td>40.76</td>
</tr>
<tr>
<td></td>
<td>b = -</td>
<td>2.57</td>
<td>3.25</td>
<td>3.26</td>
<td>3.12</td>
<td>3.07</td>
</tr>
</tbody>
</table>

N.B.: Run A and Run B are the control runs with the initial monomer (AN) concentration as 0.20 mol/lit. and 0.45 mol/lit. respectively. Run C is the run where extra amount of monomer (0.25 mol/lit) has been injected in Run A, after one hour.

a = % conversion and b = (M_v) x 10^-5 of the polymer.
DISCUSSION

The methacrylonitrile (MAN) and the acrylonitrile (AN) both are soluble in water; AN has higher solubility compared to that of MAN. The Poly-MAN and the Poly-AN, both are insoluble in water and also insoluble in their respective monomer. The rate dependence of the aqueous polymerization of these two monomers on the initiator concentration and on the monomer concentration indicates that the aqueous polymerization of these two monomers obey the free radical initiated homogeneous solution polymerization kinetics. Chain initiation occurs in the aqueous phase by the primary free radical \((\cdot \cdot \cdot \cdot)\) and also by the interaction of the monomer with the persulphate ion.

Under the identical conditions, it is seen that the rate of the aqueous polymerization is higher in the AN-KPS system than that in the MAN-KPS system. This is probably due to the higher value of the propagation constant \((k_p)\) of AN, compared to that of MAN. It has also been seen that the values of \(k_5\), \(k_{10}\), \(k_{tw}\) and \(k_{ip}\) for the acrylonitrile monomer are \(1.70 \times 10^{-5}\) lit/mol/sec, \(5.08 \times 10^{3}\) lit/mol/sec, \(5.95 \times 10^{10}\) lit/mol/sec and \(3.83 \times 10^{7}\) lit/mol/sec respectively at \(50^\circ\)C whereas the counter-part rate constants of the methacrylonitrile monomer are \(1.05 \times 10^{-5}\) lit/mol/sec, \(1.40 \times 10^{3}\) lit/mol/sec, \(1.29 \times 10^{5}\) lit/mol/sec and \(1.90 \times 10^{2}\) lit/mol/sec respectively.

### TABLE - 6

Effect of initiator (KPS) injection.

Recipe : \([AN] = 0.30\) mol/lit and \([NaS] = 1.0 \times 10^{-3}\) mol/lit.

<table>
<thead>
<tr>
<th>Run</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-A</td>
<td>(a = 7.45)</td>
<td>17.70</td>
<td>27.25</td>
<td>33.45</td>
<td>38.15</td>
</tr>
<tr>
<td></td>
<td>(b = 1.33)</td>
<td>1.37</td>
<td>1.36</td>
<td>1.36</td>
<td>1.44</td>
</tr>
<tr>
<td>Run-B</td>
<td>(a = 18.30)</td>
<td>30.30</td>
<td>40.60</td>
<td>45.45</td>
<td>48.70</td>
</tr>
<tr>
<td></td>
<td>(b = 1.00)</td>
<td>1.06</td>
<td>1.10</td>
<td>-</td>
<td>1.14</td>
</tr>
<tr>
<td>Run-C</td>
<td>(a = 21.05)</td>
<td>31.10</td>
<td>39.00</td>
<td>44.00</td>
<td>44.00</td>
</tr>
<tr>
<td></td>
<td>(b = 1.30)</td>
<td>1.27</td>
<td>1.25</td>
<td>1.25</td>
<td>1.24</td>
</tr>
</tbody>
</table>

N.B. : Run - A and Run - B are the control runs with the initial initiator concentration as \(1.0 \times 10^{-3}\) mol/lit and \(2.0 \times 10^{-3}\) mol/lit, respectively. Run-C is the run where extra amount of initiator \((1.0 \times 10^{-3}\) mol/lit) has been injected in run-A, after one hour.

\(a = \%\) conversion, and \(b = (\bar{M}_p) \times 10^{-5}\) of the polymer.
Moreover, the higher solubility in water of AN compared to MAN is also responsible for the increased rate of the aqueous polymerization of AN compared to MAN.

Both in the case of MAN and AN the injection of extra amount of initiator late in a run increases the rate of aqueous polymerization but have no measurable effect on the viscosity average molecular weight ($\bar{M}_v$) of the polymer whereas the addition of extra amount of monomer late in a run increases both the rate of polymerization and the viscosity average molecular weight of the polymer.

The addition of extra amount of monomer late in a run, would increase the monomer concentration in the particles and so the rate of polymerization would increase. However, some new latex particles may also be formed on injection of extra amount of monomer or initiator.

Table 4 shows that the presence of NaLS (below CMC) causes the increase of rate of polymerization of AN but we have seen that in the case of MAN, that causes the decrease of the rate of the aqueous polymerization. Here we also see that the injection of extra amount of NaLS (below CMC) late in a run, increases the rate of polymerization of AN when there is certain amount of NaLS initially in the control run and that remains almost unchanged when there is no NaLS initially in the control run. In the MAN system, we have seen that the injection of NaLS late in a run with or without NaLS have no measurable effect on the rate of polymerization.

The increased rate of the aqueous polymerization of AN in the presence of detergent is due to the increased water solubility of the growing chain and increased stability of the colloidal latex. However, the adsorption of the detergent molecule on the latex surface of polyacrylonitrile (PAN) does not hinder the arrival of the monomer (AN) to the latex surface. But in the case of MAN-KPS-NaLS system, the adsorption of detergent on the latex particle is so strong that the arrival of monomer (MAN) to the latex surface is hindered.

**Experimental**

Polymerizations of MAN and AN were studied gravimetrically in a 1-litre round bottom pyrex flask fitted with a Hg seal stirrer and side-tubes for passing nitrogen and extracting solutions under nitrogen pressure for analysis. The details of the experimental procedure, purification and processing of monomer, molecular weight determination, etc., have been reported elsewhere. The polymerizations of both the monomers were studied within their solubility regions [i.e. < 2.8% (w/w) in case on MAN and < 8.5 (w/w) in case of AN] at 50°C in an atmosphere of nitrogen, and in order to avoid complications during polymerizations, no buffer solution was used. The pH of the medium was always above 3.5 when the $H^+$ catalysed decomposition of persulphate ions is not significant. The polymer formed was a stable colloid. The colloidal stability (C.S.) of the latex solution was measured by titrating a known volume of the latex solution with a standard (0.04 or 0.02 $M$) MgSO$_4$ solution. Molecular weight of the polymers was estimated by viscosity method.

The intrinsic viscosity ($\eta$) was measured in dimethyl formamide (DMF) at 30°C and the specific viscosity of the polymer solutions was determined in the concentration range of 0.1 to 0.30 g/100 cm$^3$. The viscosity average molecular weights ($\bar{M}_v$) of the polymers are given by
\[ \eta = K \times (M_w)^a \]

where \( K = 306 \times 10^{-3} \text{ dm}^3 \text{ g}^{-1} \), \( a = 0.503 \) for poly-MAN and
\( K = 33.5 \times 10^{-3} \text{ dm}^3 \text{ g}^{-1} \), \( a = 0.72 \) for poly-AN.

The weight-average molecular weight \( (M_w) \), number average molecular weight \( (M_n) \), molecular weight distribution and dispersity for the polymer samples were measured by GPC 200 (Waters, USA) and using N, N-dimethyl formamide as the mobile phase. The particle size distribution of the latex solution was determined by SALD-1000 laser diffraction particles size analyzer (M/s. Chemito, India).

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References: