The present chapter deals with the curing study of acrylated poly(ester-amide)s (APEAs VIa-j, APEAs VIIa-j and APEAs VIIIa-j described in Chapter 2) using benzoyl peroxide (BPO) as a catalyst. The curing study was monitored on a Differential Scanning Calorimeter (DSC). Following by the Thermogravimetric Analysis (TGA) of APEAs VIa-j, APEAs VIIa-j and APEAs VIIIa-j is also presented.

3.1 Curing study of APEAs by Different Scanning Calorimeter (DSC)

This method is employed to study the curing reaction of APEAs VI - VIIIa-j using benzoyl peroxide as a catalyst, which is an important stage in the application of these resins. The cross linked network of cured resin furnishes desirable properties for the fabrication of fiber reinforced composites and for the formulation of structural adhesives. There are many reports about the curing of unsaturated polyesters [1-4].

The curing reaction is associated with the formation of insoluble substances with the evolution of heat during the reaction. For a given resin sample the amount of curing agent decides the curing time and the amount of heat liberated in a given time.

DSC is an excellent thermal method used for the estimation of the kinetic parameters such as activation energy (Ea), order of reaction (n), heat of polymerization (ΔHp) and the extent of curing reaction of the polymers.

Various methods have been developed to estimate the kinetic parameters of the polymers by analyzing the DSC curves. Some of the methods developed are as follows;

(A) Borchardt and Daniel Method [5] (This method was also validated by Reed et. al. [6]).

(B) Barrett et. al. method [7]

(C) Rogers and Smitile method [8]

(D) Ellerstein method [9]

Among all the above, Borchardt and Daniel method is widely used for the estimation of curing parameters such as activation energy (Ea), order of reaction (n) and heat of polymerization (ΔHp).
3.1.1 Scanning experiment

The Universal V3.0GTA Instrument was employed to obtain the data of the exothermic curing reactions. The differential scanning calorimeter was calibrated using a standard material i.e. Indium metal with known heat of fusion ($\Delta H = 28.45 \text{ Jg}^{-1}$) according to the instrumental manual.

The calibration constant ‘E’ was computed by employing the following relation,

$$\frac{\Delta H_{m, \text{ cal.}}}{\text{mg}} = \frac{Ea (\Delta T_s) T_s}{M_b}$$ .......................... (3.1)

Where,

- $E$ = Calibration co-efficient cal.deg$^{-1}$.min$^{-1}$.
- $A$ = Peak area in square inch.
- $\Delta T_s$ = Y-axis sensitivity deg.inches$^{-1}$.
- $M$ = Sample mass in mg.
- $b$ = Heat rate deg.min$^{-1}$.
- $T_s$ = X-axis sensitivity deg.inches$^{-1}$.

The values of ‘E’ were estimated for different standard materials using the given cell. The total area under the exotherm, at which the exotherm commences and terminates, is obtained from the DSC thermogram.

3.1.2 Analysis of the DSC Scan

The equation derived by H. J. Borchardt and F. Daniels [5] correlating the shape of differential thermal analysis (DTA) curve to the degree of reaction (rate constant-K) can also be applied to the curve obtained from the DSC. The well known relation used for studying the reaction kinetics of various thermosetting resins is deduced by Barrett on the lines and assumptions made by Borchardt and Daniels.
The Barrett relation [7] can be described as;

\[
K = \frac{d\alpha}{dt} = \frac{d\theta}{dt} \frac{A}{A - a} \quad \cdots (3.2)
\]

Where,

\[
\alpha = \text{Fractional conversion}
\]

\[
A = \text{Total area}
\]

\[
a = \text{Area at a particular temperature (t)}
\]

The exothermic peak obtained in the scan was analyzed to obtain a heat flow data relative to the base line drawn manually by joining the points of start and completion of the exothermic transition.

From the data obtained for the heat flow as a function of temperature and time, the overall rate constant \( K \) at different temperatures were estimated using the Barrett relation [7]. After obtaining the rate constant \( K \) at different temperatures, the plot of \( \ln K \) vs \( 1/T \) was made directly by the linear computation programme installed in the instrument, which directly gives the values of activation energy (Ea) and the order of reaction (n). Assuming that, the curing reaction obeys Arrhenius type kinetics.

\[
\ln K = \frac{E_a}{R} \cdot \frac{1}{T} + \ln A \quad \cdots (3.3)
\]

Where,

\[
K = \text{Rate Constant}
\]

\[
E_a = \text{Activation energy}
\]

\[
R = \text{Gas constant}
\]

\[
T = \text{Absolute temperature}
\]

\[
A = \text{Frequency factor}
\]
3.2 Experimental

The curing study of APEAs VI - VIIIa-j was monitored on a Universal V3.0GTA instrument, using benzoyl peroxide as a catalyst. The sample cell of aluminum was used for the DSC scan. Empty cell was used as a reference calibration of the DSC instrument was performed by determining the heat of fusion of the standard indium metal supplied by Du Pont.

0.05 % benzoyl peroxide based on the total weight of the resin sample was added and mixed well in a porcelain disc. The sample weight used for the investigation was in the range of 4-5 mg. and was carefully placed in a sample cell covered with a lid and then it was placed in a DSC cell along with the empty reference cell. The DSC thermograms of all the resin samples were scanned at a constant heating rate of 10°C/min. from 30°C to 300°C.

The values of the activation energy (Ea), order of reaction (n) and the DSC data of all the APEAs VI - VIIIa-j samples obtained from the DSC thermograms are furnished in Tables 3.1 to 3.3 respectively. The DSC thermograms of all the APEAs VI - VIIIa-j are shown in Figures 3.1 to 3.30.
<table>
<thead>
<tr>
<th>APEAs VI a-j</th>
<th>Initial Temp. (°C)</th>
<th>Peak Temp. (°C)</th>
<th>Final Temp. (°C)</th>
<th>Activation Energy (Ea) KJ/mol</th>
<th>Order of Reaction (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIa</td>
<td>133</td>
<td>163</td>
<td>197</td>
<td>234.7</td>
<td>1.87</td>
</tr>
<tr>
<td>VIb</td>
<td>135</td>
<td>162</td>
<td>200</td>
<td>236.2</td>
<td>1.86</td>
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<tr>
<td>VIc</td>
<td>117</td>
<td>150</td>
<td>165</td>
<td>240.1</td>
<td>1.82</td>
</tr>
<tr>
<td>VIId</td>
<td>126</td>
<td>155</td>
<td>171</td>
<td>246.3</td>
<td>1.79</td>
</tr>
<tr>
<td>VIe</td>
<td>140</td>
<td>155</td>
<td>168</td>
<td>210.6</td>
<td>1.92</td>
</tr>
<tr>
<td>VIIf</td>
<td>139</td>
<td>160</td>
<td>182</td>
<td>184.4</td>
<td>1.94</td>
</tr>
<tr>
<td>VIg</td>
<td>123</td>
<td>153</td>
<td>168</td>
<td>224.4</td>
<td>1.90</td>
</tr>
<tr>
<td>VIh</td>
<td>120</td>
<td>149</td>
<td>176</td>
<td>249.6</td>
<td>1.76</td>
</tr>
<tr>
<td>VIi</td>
<td>118</td>
<td>150</td>
<td>172</td>
<td>248.7</td>
<td>1.77</td>
</tr>
<tr>
<td>VIj</td>
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<td>148</td>
<td>160</td>
<td>176.6</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Figure 3.1 DSC of VI a

Figure 3.2 DSC of VI b
Figure 3.3 DSC of VIc

Figure 3.4 DSC of VId
Figure 3.5 DSC of VIe

Figure 3.6 DSC of VI f
Figure 3.7 DSC of VIg

Figure 3.8 DSC of VIh
Figure 3.9 DSC of VI i

Figure 3.10 DSC of VI j
Table 3.2
DSC Curing Data of APEAs VIIa-j

<table>
<thead>
<tr>
<th>APEAs VIIa-j</th>
<th>Initial Temp. (°C)</th>
<th>Peak Temp. (°C)</th>
<th>Final Temp. (°C)</th>
<th>Activation Energy (Ea) KJ/mol</th>
<th>Order of Reaction (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIIa</td>
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<tr>
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<td>150</td>
<td>181.4</td>
<td>1.93</td>
</tr>
<tr>
<td>VIIc</td>
<td>128</td>
<td>166</td>
<td>181</td>
<td>192.3</td>
<td>1.91</td>
</tr>
<tr>
<td>VIIId</td>
<td>124</td>
<td>140</td>
<td>156</td>
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<td>1.89</td>
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<tr>
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<td>114</td>
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<td>151</td>
<td>210.7</td>
<td>1.92</td>
</tr>
<tr>
<td>VIIf</td>
<td>112</td>
<td>150</td>
<td>163</td>
<td>190.3</td>
<td>1.90</td>
</tr>
<tr>
<td>VIIg</td>
<td>110</td>
<td>132</td>
<td>149</td>
<td>214.6</td>
<td>1.91</td>
</tr>
<tr>
<td>VIIh</td>
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<td>150</td>
<td>234.6</td>
<td>1.86</td>
</tr>
<tr>
<td>VIIi</td>
<td>120</td>
<td>150</td>
<td>164</td>
<td>236.3</td>
<td>1.86</td>
</tr>
<tr>
<td>VIIj</td>
<td>121</td>
<td>154</td>
<td>172</td>
<td>186.6</td>
<td>1.91</td>
</tr>
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</table>
Figure 3.11 DSC of VIIa

Figure 3.12 DSC of VIIb
Figure 3.13 DSC of VIIc

Figure 3.14 DSC of VIId
Figure 3.15 DSC of VIIe

Figure 3.16 DSC of VIIf
Figure 3.17 DSC of VIIg

Figure 3.18 DSC of VIIh
Figure 3.19 DSC of VIIi

Figure 3.20 DSC of VIIj
Table 3.3
DSC Curing Data of APEAs VIII.a-j

<table>
<thead>
<tr>
<th>APEAs VIII.a-j</th>
<th>Initial Temp. (°C)</th>
<th>Peak Temp. (°C)</th>
<th>Final Temp. (°C)</th>
<th>Activation Energy (Ea) KJ/mol</th>
<th>Order of Reaction (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIIIa</td>
<td>110</td>
<td>146</td>
<td>160</td>
<td>176.4</td>
<td>1.94</td>
</tr>
<tr>
<td>VIIIb</td>
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<td>180</td>
<td>180.3</td>
<td>1.95</td>
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<tr>
<td>VIIIc</td>
<td>102</td>
<td>140</td>
<td>150</td>
<td>202.6</td>
<td>1.88</td>
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<tr>
<td>VIIIId</td>
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<td>140</td>
<td>160</td>
<td>213.4</td>
<td>1.91</td>
</tr>
<tr>
<td>VIIId</td>
<td>122</td>
<td>154</td>
<td>174</td>
<td>188.7</td>
<td>1.91</td>
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<td>VIIIE</td>
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<td>1.85</td>
</tr>
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<td>220.3</td>
<td>1.90</td>
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<tr>
<td>VIIIG</td>
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<td>144</td>
<td>163</td>
<td>240.6</td>
<td>1.83</td>
</tr>
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<td>143</td>
<td>159</td>
<td>235.8</td>
<td>1.86</td>
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<tr>
<td>VIIJ</td>
<td>112</td>
<td>148</td>
<td>161</td>
<td>190.3</td>
<td>1.89</td>
</tr>
</tbody>
</table>
Figure 3.21 DSC of VIIIa

Figure 3.22 DSC of VIIIb
Figure 3.23 DSC of VIIIc

Figure 3.24 DSC of VIIIId
Figure 3.25 DSC of VIIIe

Figure 3.26 DSC of VIIIf
Figure 3.27 DSC of VIIIg

Figure 3.28 DSC of VIIIh
Figure 3.29 DSC of VIIIi

Figure 3.30 DSC of VIIIj
3.3 Results and Discussion

The curing study of all the APEAs VI - VIIIa-j samples were carried out by using benzoyl peroxide (BPO) as a catalyst. 0.05 % Benzoyl peroxide based on the total weight of the resin sample was added. The results obtained from the DSC scan are furnished in Tables 3.1 to 3.3 respectively. Examination of the DSC thermograms of all the APEAs VI - VIIIa-j reveals that,

1. From the DSC thermograms, the cure onset temperature (Ti), peak exotherm temperature (Tp) and the temperature of completion (Tf) for each of the APEAs VI - VIIIa-j samples were obtained.
2. All the APEAs VIa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 117 to 200 °C.
3. All the APEAs VIIa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 110 to 181 °C.
4. All the APEAs VIIIa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 102 to 180 °C.
5. From the DSC thermograms the values of kinetic parameters such as activation energy (Ea) and the order of reaction (n) were also obtained. This suggests that it is a second order reaction.
6. The results also show that the curing temperature of reaction is up to 150 °C thus they can be processed (i.e. making article) easily.
3.4 Thermogravimetric Study

The thermal properties of the polymers can be studied by employing different techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivatographic analysis (DGA) [10-11].

Thermogravimetric analysis of a polymer is a very useful technique in assessing the thermal stability of a polymer. For the comparative study of the thermal behavior of a related polymer samples, any one or more of the above methods of analysis under identical experimental conditions can be employed. For example, TGA is carried out in air and in oxygen free nitrogen. It is carried out at different heating rates. It may be noted that the results of the thermal analysis of a given polymer sample by a given method depends on various aspects [11]. The amount and the particle size of the material being examined influence the nature of the thermogram. The speed of the recorder noting the change in the weight and the shape of the sample container also influence the thermogravimetric results. The rates of heating the sample and the ambient atmosphere during the analysis are very important factors to be controlled during thermal analysis. The information furnished by TGA, DTA and DGA are to some extent complimentary. From the results of TGA and DTA, it is possible to note the temperature up to which the material does not lose weight. It is also possible to know the temperature at which the material starts decomposing and pattern of the decomposition.

Besides the quantitative information derived from the mere inspection of the thermograms, other information’s such as, the order of the degradation reaction and the activation energy of the degradation reaction can be obtained by analysis of the thermal data furnished by either TGA or DTA.

The present section deals with the thermogravimetric analysis (TGA) of the APEAs VI - VIIIa-j.
3.4.1 Thermogravimetric analysis

The thermal behavior of the APEAs VI - VIIIa-j samples has been studied by TGA. The loss in weight due to pyrolysis of the polymeric material with increase in temperature forms a TG curve \[11\]. Normally a polymer sample starts loosing its weight at a very slow rate upto a particular temperature around 300^\circ C. The loss of weight increases at a faster rate after this temperature. The shape of the TG curve depends upon the nature of the degradation reaction. The analysis of these data by Broido method is often carried out with a view to estimate kinetic parameters like activation energy of the degradation reaction \[12\].

The advantages of TGA are enumerated here \[11-12\].

(i) A relatively small set of data is to be treated.

(ii) Continuous recording of weight loss as a function of temperature ensures equal weightage to examination over the whole range of study.

(iii) As single sample is analyzed over the whole range of temperature, the variation in the value of the kinetic parameters, if any, will be indicated.

For the estimation of the kinetic parameters, several methods are employed. All of them involve two assumptions. One, it is assumed that the difference in the thermal and diffusion processes is negligible. Secondly, it is also assumed that the Arrhenius relation is valid over the whole range of temperatures. Since small materials are employed in TG analysis the barriers between the thermal and diffusion processes are quite negligible. Hence, it is reasonable to assume the validity of the Arrhenius relation \[12\].

Various methods are proposed to analyze the TGA data depending upon the nature of the experimentation \[12-18\]. Out of these, the method proposed by Broido, which is applied to a single set of TGA data is selected for the analysis of the TGA data \[12\].
3.5 Experimental (TGA)

The thermogravimetric analysis (TGA) of APEAs VI - VIIIa-j samples has been carried out by using a “Universal V3.0G TA Instrument Thermo gravimetric analyzer” in a slow stream of air. The boat prepared from the platinum foil holds the polymer sample that is to be analyzed. It was properly washed and dried. It was suspended on the quartz rod in the TGA balance. The sample (about 5 mg) was placed in the boat. The sample in the boat is covered by quartz tube in which the flow of air was maintained. The weight of the sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by heating the system at a constant rate of 10 °C / min. Simultaneous change in the weight was recorded automatically with time (temperature). This will reveal the percentage weight loss of the material as a function of time and also of the temperature. The experiment was stopped at about 800 °C.

The thermograms were analyzed to obtain the information about the percentage weight at different temperatures. The results of these analyses are furnished in Tables 3.4 and 3.6 respectively. The typical TGA thermograms of the APEAs VI - VIIIa-j are shown in Figures 3.31 to 3.60.
Table 3.4
TGA Data of APEAs VI a-j

<table>
<thead>
<tr>
<th>APEAs VI a-j</th>
<th>% Weight loss at various Temperature (°C) from TGA</th>
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<tr>
<td></td>
<td>150</td>
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<tr>
<td>VIa</td>
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<td>VIb</td>
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<td>VIc</td>
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<td>VIf</td>
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<td>VIf</td>
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<td>Vlg</td>
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<td>Vlh</td>
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<tr>
<td>Vli</td>
<td>1.97</td>
</tr>
<tr>
<td>Vlj</td>
<td>1.96</td>
</tr>
</tbody>
</table>
Figure 3.31 TGA of VI a

Figure 3.32 TGA of VI b
Figure 3.33 TGA of VI c

Figure 3.34 TGA of VI d
Figure 3.35 TGA of VI\text{e}

Figure 3.36 TGA of VI\text{f}
Figure 3.37 TGA of VI g

Figure 3.38 TGA of VI h
Figure 3.39 TGA of VI i

Figure 3.40 TGA of VI j
Table 3.5  
TGA Data of APEAs VIla-j

<table>
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<th>APEAs VIIa-j</th>
<th>% Weight loss at various Temperature (°C) from TGA</th>
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<td>VIla</td>
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<td>VIib</td>
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<td>VIic</td>
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<td>VIId</td>
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<tr>
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</tr>
<tr>
<td>VIIj</td>
<td>1.25</td>
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</table>
Figure 3.41 TGA of VIIa

Figure 3.42 TGA of VIIb
Figure 3.43 TGA of VIIc

Figure 3.44 TGA of VII d
Figure 3.45 TGA of VIIe

Figure 3.46 TGA of VIIf
Figure 3.47 TGA of VII g

Figure 3.48 TGA of VII h
Figure 3.49 TGA of VII i

Figure 3.50 TGA of VII j
Table 3.6
TGA Data of APEAs VIIIa-j

<table>
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<th>% Weight loss at various Temperature (°C) from TGA</th>
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<td>VIIIg</td>
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<td>VIIIh</td>
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<td>VIIIj</td>
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Figure 3.51 TGA of VIIIa

Figure 3.52 TGA of VIIIb
Figure 3.53 TGA of VIIIc

Figure 3.54 TGA of VIIIId
Figure 3.55 TGA of VIII\text{e}

Figure 3.56 TGA of VIII\text{f}
Figure 3.57 TGA of VIIIg

Figure 3.58 TGA of VIIIh
Figure 3.59 TGA of VIIIi

Figure 3.60 TGA of VIIIj
3.6 Results and Discussion (TGA)

Examination of the TGA thermograms data of all the APEAs VI - VIIIa-j samples reveals that;

1. Most of the polymer samples degrade in a single step.

2. All the APEAs VIa-j samples start their degradation at around 150 °C and weight loss of about 1.34 to 1.97% was observed. The rate of degradation of all the APEAs VIa-j samples increase rapidly between 300 to 450 °C and weight loss of about 50 to 60% was observed. The products lost upto 74 to 80% at 600 °C.

3. All the APEAs VIIa-j samples start their degradation at around 150 °C and weight loss of about 1.01 to 1.76% was observed. The rate of degradation of all the APEAs VIIa-j samples increase rapidly between 300 to 450 °C and weight loss of about 40 to 48% was observed. The products lost upto 70 to 80% at 600 °C.

4. All the APEAs VIIIa-j samples start their degradation at around 150 °C and weight loss of about 1.06 to 1.98% was observed. The rate of degradation of all the APEAs VIIIa-j samples increase rapidly between 300 to 450 °C and weight loss of about 40 to 48% was observed. The products lost upto 70 to 80% at 600 °C.
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