An Experimental Phase Diagram Study of Ternary Pentaerythritol-Pentaglycerine-Neopentylglycol Orientationally Disordered Plastic Crystals

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Abstract

This dissertation is on the experimental determination of Ternary Solid Solution Phase Diagrams of \( \text{C}_5\text{H}_{12}\text{O}_4\text{-C}_5\text{H}_{12}\text{O}_3\text{-C}_5\text{H}_{12}\text{O}_2 \) (PE-PG-NPG) Orientationally Disordered “Plastic Crystal” Compounds. “Plastic crystals’ are energy storage materials with layer or chain type low temperature crystal structures and transform to orientationally disordered phases at certain temperature; storing large amount of latent heat in addition to heat capacity. There are few pure compounds commercially available so to vary the phase transition temperatures, at which the thermal energy is stored, binary compounds have been made from these limited compounds. In order to further extend the range, ternary solid solution polyalcohol compounds have been made and characterized by in-situ differential scanning calorimetry, in-situ x-ray diffraction, and in-situ NMR methods. The PE-PG and PG-NPG binaries are well established, but there were discrepancies in PE-NPG binary phase diagram which was re-determined in this study. Phase stability studies of solid solutions have been made and ternary isothermal sections are derived using binary phase diagram data and the ternary experimental data. Results show single, two phase solid solution regions of \( \alpha \) and \( \beta \), as well as high temperature \( \gamma \) and \( \gamma_T \) form in their parent low and high temperature crystal structures and no intermediate or line compounds are formed. The \( \alpha \) phase has BCT structure and the \( \beta \) phase is monoclinic. All the \( \gamma \) phases have FCC type of structure that exhibit molecular O-H bond rotation/oscillation. Ternary isothermal sections are shown at 303K, 318K, 333K, 353K, 413K, 433K, 463K, 478K, 493K, 513K and 553K. The ternary tie triangles are established. Typically in the pure and binary polyalcohol’s the solid–liquid phase
transition enthalpies are significantly lower than the solid-solid ones, but in these ternaries the majority of these transitions show high enthalpy of transitions. For example, 45PE-45PG-10NPG mol% has 23.025 J/g of solid to liquid transition enthalpy. From the isothermal section at 353K we propose small $\alpha$, $\alpha+\gamma$, and $\gamma+\gamma_T$ region with a large $\alpha+\gamma_T$ phase region. The tie triangles $\alpha+\gamma + \gamma_T$ and $L + \gamma + \gamma_T$ are generally deduced based on phase rules. Liquid phases begin to appear at higher temperatures, for example at 413K, it was found that $\alpha$, $\alpha+\gamma$, $\gamma$-Liq., $\alpha+\gamma_T$, $\gamma + \gamma_T$, $\gamma_T + L$, and single liquid phase region coexist, along with 2 tie triangles, namely $\alpha + \gamma + \gamma_T$, $L + \gamma_T + \gamma$ regions. To our knowledge this is the first time PE-PG-NPG ternary phase equilibrium has been developed and that will widen the energy storage capabilities. Details of the thermal and crystallographic behavior of binary PE-NPG, and ternary PE-PG-NPG at different temperatures based on XRD, DSC and NMR results are presented.
Dedicated to my wonderful Parents,
Loving wife Preeti
and
My daughter Tamanna Kaur Singh
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Chapter 1

Introduction

As energy consumption increases, researchers all over the world are trying to develop new energy sources. Along with novel energy sources, there is a great need to improve energy storage devices. Solar energy conversion to water heating, building heating etc can use thermal energy storage materials for improving the process efficiency. In thermal energy storage, latent heat storage is very attractive because relatively large amount of energy can be stored at constant temperature and smaller volume. Latent heat storage is an area of study pioneered by Dr. Telkes while working at MIT in the 1940s. Till the energy crisis of late 1970s not much development was done and then in early 1980s it was extensively researched for use in solar heating systems. Although research into latent heat storage for solar heating systems continues, it is ever more significant for waste heat recovery and load leveling for power generation. Latent heat storage can be accomplished through solid-liquid, liquid-gas, solid-gas, and solid-solid phase transformations, but the only practical interest is the solid-solid phase change materials. The solid-gas and liquid-gas systems are of limited utility because of the large volumes required for such systems. Solid-solid systems have shown much promise, but are only recently being studied. Many Phase Change Materials (PCMs) systems have been investigated in the past.

Thermal energy can be stored as - (1) Sensible heat, and (2) Latent heat or a combination of these two. In Sensible Heat Storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS system is based on the heat capacity and the change
in temperature of the material during the process of absorbing and releasing heat. The amount of stored heat depends on the specific heat of medium, the temperature change and the amount of storage material. With all those properties, water seems to be the best SHS material. Above 100 °C, oils and molten salt baths are used because water evaporates at 100°C.

Latent Heat Storage (LHS) is the absorption or release of heat when a storage material undergoes a reversible phase change from solid-solid, solid to liquid or liquid to gas. The storage capacity of the LHS system with a PCM medium is given by

\[
Q = \int_{T_i}^{T_f} mC_p \, dT + ma_m \Delta h_m + \left[ mC_p \, dT \right]_{T_m}^{T_f}
\]

\[
Q = m[C_{p,s}(T_m - T_i) + a_m \Delta h_m + C_{p,l}(T_f - T_m)]
\]

\[a_m = \text{Fraction melted} ; \Delta h_m = \text{heat of fusion per unit mass} ; T_m = \text{melting temperature}\]

\[C_{p,s} = \text{Average specific heat between } T_i \text{ and } T_m ; C_{p,l} = \text{Average specific heat between } T_m \text{ and } T_f\]

The energy absorbed and released in breaking and restructuring of molecular bonds in a completely reversible chemical reaction is the basis of thermal energy storage materials. The heat stored in the material is a function of the amount of storage material, the endothermic heat of reaction, and the extent of conversion.

\[Q = a_r m \Delta h_r\]

\[a_r = \text{fraction reacted} , \Delta h_r = \text{heat of reaction per unit mass} , m = \text{mass of the material}\]

From the above mentioned thermal energy storage options, Latent heat storage is a very promising approach because it can provide high energy density storage at a constant
temperature of phase transition of the material. Phase change can take place in the following ways – solid-solid, solid-liquid, solid-gas, and liquid-gas.

In solid–solid transitions, heat is stored in the system with the corresponding transformation of the material from one crystalline structure to another. Solid-solid transitions generally have small volume changes than solid–liquid transitions. Solid–solid PCMs present the benefit of more flexible container requirements and greater design flexibility. Most promising materials are organic solid solution of pentaerythritol (solid-solid transition at 188°C, latent heat of fusion 323 kJ/kg), Pentaglycerin (solid-solid transition at 88°C, latent heat of fusion 216 kJ/kg) and KHF₂ (melting point - 196 °C, latent heat of fusion 135 kJ/kg). Trombe wall with the phase change materials could provide better performance than a plain concrete Trombe wall.

Large changes in volume during the charging and discharging of the system make the system complex and impractical. Although, solid–gas and liquid–gas phase transitions have higher latent heat of phase transition but it is accompanied with large volume changes on phase transition and leads to containment problems which rules out the potential utility of such phase transitions in thermal-storage systems. Even though solid–solid phase transformations have relatively less latent heat than liquid–gas, these transformations involve small volume change (~ < 10%).

In thermal energy transfer systems, due to low thermal conductivity PCMs cannot be used as heat transfer medium. A separate heat transfer medium must be used via a heat exchanger to transfer the energy from the heat source to the PCM and from PCM to the end use. The volume changes of the PCMs during phase change transitions require special containment designs so as to keep the PCM from leaking out of it. The container
design should not only be able to accommodate the phase change related volume changes
but also should not react with the PCM being used. Any latent heat energy storage system
should possess at least following three components1:

(i) A suitable PCM with the phase change transition in the desired temperature range,
(ii) A suitable heat exchange surface, and
(iii) A suitable container compatible with the PCM.

Therefore, the research and development of a latent heat based thermal energy storage
system, necessitates the understanding of - phase change materials, containers materials
and heat exchangers. A wide range of technical options available for storing thermal
energy is shown in Figure 1-19.

1.1 Latent Heat Storage Materials (LHS)

Phase change materials (PCM) are also known as ‘‘Latent’’ heat storage materials. In
these materials, thermal energy charging and discharging takes place when a material
changes from solid to solid, solid to liquid, or liquid to solid. This is referred to as a
change in ‘Phase’. PCMs absorb thermal energy just like conventional storage materials;
depending on their heat capacity, temperature increases as the material absorbs heat. But,
at phase transition temperature, PCMs absorb and release heat at an almost constant
temperature corresponding to the phase transition temperature. According to Abhat et
al.7, these materials can store 5–14 times more heat per unit volume than sensible storage
materials such as water, masonry, or rock. A large number of PCMs are known to melt
with a heat of fusion in any required range7. However, for their employment as latent
heat storage materials these materials must exhibit certain desirable thermodynamic,
kinetic and chemical properties. Moreover, economic considerations and easy availability
of these materials has to be kept in mind. There are certain thermophysical, kinetics and
chemical properties which are required for the PCMs to be used in thermal energy storage
systems. These properties are as follows:

1.1.1 Thermophysical properties

(i) Suitable phase transition temperature range.

(ii) High latent heat of transition.

(iii) High specific heat to provide for additional significant sensible heat storage.

(iv) High thermal conductivity of both solid and liquid phases to assist the charging and
discharging of energy of the storage systems.

(v) Small volume changes on phase transformation and high density is desirable.

(vi) Favorable phase equilibria.

1.1.2 Kinetic properties

(i) No super cooling of the liquid phase.

(ii) Good crystallization rate.

1.1.3 Chemical properties

(i) Chemical stability.

(ii) Completely reversible phase transitions.

(iii) No degradation after a large number of freeze / melt cycle.

(iv) Compatible with containment materials.

(v) Non-toxic, non-flammable and non-explosive materials for safety.

Moreover, low cost and large-scale availability of the phase change materials is also very
important.
1.1.4 Economics

(i) Abundant.

(ii) Available.

(iii) Cost effective.

Low cost and large-scale availability of the phase change materials is also very important. Depending on the area of utilization, a large number of phase change materials (organic, inorganic and eutectic) have been investigated for use at various temperature ranges. A classification of PCMs is shown in Figure 1-2. Organic and inorganic types of PCMs are given in Table 1-1 and Table 1-2 respectively. As no single material can have all the required properties for an ideal thermal storage application, the available materials fall short of the necessary working temperature range. For example metallic fins can be used to increase the thermal conductivity of PCMs, super cooling may be suppressed by introducing a nucleating agent in the storage material. For their very different thermal and chemical behavior, the properties of each sub group, which affects the design of latent heat thermal energy storage systems using PCMs of that sub group, are discussed in detail below.

1.2 Organic phase change materials

Organic materials include congruent melting materials which freeze and melt reversibly without phase segregation. Organic materials such as paraffins self nucleate which means they crystallize with little or no supercooling.
Figure 1-19. Flow chart showing different stages involved in the development of a latent heat storage system.

Figure 1-2. Classification of Phase Change Materials

- Paraffin Compounds
- Non-Paraffin Compounds
- Salt Hydrate
- Metallics
- Organic-Organic
- Inorganic-Inorganic
- Inorganic-organic
1.2.1 Paraffins

Paraffins are a family of saturated hydrocarbons with very similar properties and have a general chemical formula of \( \text{C}_n\text{H}_{2n+2} \). Paraffin wax consists of a mixture of mostly straight chain alkanes \( \text{CH}_3-(\text{CH}_2)\text{-CH}_3 \). During melting, the straight chains are broken and thus the material absorbs heat energy and during cooling, the crystallization of the (\text{CH}_3)- chains releases the stored energy as latent heat.

Paraffins between \( \text{C}_5 \) and \( \text{C}_{15} \) are liquids, and the rest are waxy solids. Abhat et al.\(^8\) reported that paraffins consist of mainly straight chain hydrocarbons that have melting temperatures from 23 to 67 °C \(^8\). Commercial grade paraffin wax is a combination of different hydrocarbons obtained from petroleum distillation. In general, the longer the average length of hydrocarbon chain, the higher the melting temperature and heat of fusion\(^10\). Paraffins are easily available from many manufacturers and are usually more expensive than salt hydrates\(^1,14\).

Advantages

Paraffin waxes are congruent melting materials and show no tendency to segregate. They are also chemically stable although Lane\(^4\) reports slow oxidation when exposed to oxygen requiring closed containers. Sharma et al.\(^11,12\) found that commercial grade paraffin wax is stable even after 1500 cycles of melting and cooling. Further, sue to congruent melting, paraffins have no tendencies to super cool, so nucleating agents are not needed\(^1,14\).

Paraffin waxes are safe and non-corrosive\(^7,8\). They are compatible with all metal containers and easily incorporated into heat storage systems\(^4\). It has been reported that paraffins have tendency to infiltrated plastic containers and thus soften some plastics\(^1\). Paraffin qualifies as heat of fusion storage materials due to their availability in a large
temperature range. Due to cost consideration, however, only technical grade paraffins may be used as PCMs in latent heat storage systems.

**Disadvantages**

In their solid state paraffins have low thermal conductivity and thus are not suitable for high heat transfer rates. Velraj et al.\textsuperscript{13} reports that this problem can be alleviated by the use finned containers and metallic fillers or through combination latent/sensible storage systems. Aluminum honeycombs has been found to improve system performance and crystallization time was reduced by a factor of 4 to 7\textsuperscript{14}. Due to high volume changes during phase change from solid to liquid paraffins present a challenge for suitable container design\textsuperscript{15}. Paraffins are flammable but this can be taken care of by selecting proper container\textsuperscript{7}. Lane\textsuperscript{1} also reports that paraffins can contract enough to pull away from the walls of the storage container, thereby, greatly decreasing heat storage capacity. Paraffins have melting ranges\textsuperscript{3} of up to 43 °C. Paraffins being a mixture of hydrocarbon chains, a solid-solid phase transformation in commercial grade paraffins immediately before melting stores a great amount of the latent heat capacity of the material\textsuperscript{3}. Abhat et al.\textsuperscript{7} reported the thermophysical properties of selected paraffins as shown in Table 1-1 along-with their melting point, latent heat of fusion and groups. Phase change temperature and latent heat of fusion of straight chain paraffins from 14-24 carbons is listed in Table 1-2. Paraffins are categorized as: (i) Group I, most promising; and (ii) Group II, moderately promising\textsuperscript{19}.

**1.3 Non-Paraffins**

Lane\textsuperscript{1} and Abhat\textsuperscript{8} have done a thorough investigation of classifying a number of organic materials such as esters, glycols and alcohols. This materials category is very broad and
encompasses generally flammable materials which can not be used at elevated temperatures.

Table 1-1. The thermophysical properties of some paraffins collected by Abhat et al. 7

<table>
<thead>
<tr>
<th>Paraffin</th>
<th>Distribution of C-Atoms</th>
<th>Phase change temperature (°C)</th>
<th>Latent heat of fusion (kJ/kg)</th>
<th>Thermal conductivity (W/m·K)</th>
<th>Density (kg/m³) Solid (20 °C)</th>
<th>Liquid (70 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5913(6)</td>
<td>C₁₃-C₂₄</td>
<td>22-24</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>900</td>
<td>760</td>
</tr>
<tr>
<td>Octadecane</td>
<td>C₁₈</td>
<td>28</td>
<td>244</td>
<td>0.15 (solid)</td>
<td>814</td>
<td>774</td>
</tr>
<tr>
<td>6106(8)</td>
<td>C₁₆-C₂₈</td>
<td>42-44</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>910</td>
<td>765</td>
</tr>
<tr>
<td>P116(b)</td>
<td></td>
<td>45-48</td>
<td>210</td>
<td>-</td>
<td>817</td>
<td>786</td>
</tr>
<tr>
<td>5838(6)</td>
<td>C₂₀-C₃₃</td>
<td>48-50</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>912</td>
<td>769</td>
</tr>
<tr>
<td>6035(6)</td>
<td>C₂₂-C₄₅</td>
<td>58-60</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>920</td>
<td>795</td>
</tr>
<tr>
<td>6403</td>
<td>C₂₃-C₄₅</td>
<td>62-64</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>915</td>
<td>790</td>
</tr>
<tr>
<td>6499(6)</td>
<td>C₂₁-C₅₀</td>
<td>66-68</td>
<td>189</td>
<td>0.21 (solid)</td>
<td>930</td>
<td>830</td>
</tr>
</tbody>
</table>

(a) Manufacturer of technical grade paraffins 5913, 6106, 5838, 6035 and 6499: Ter Hell Paraffin Hamburg, FRG.
(b) Manufacturer of Paraffin P116: Sun Oil Company, USA.
(c) “-” implies data is not sufficient.

Table 1-2 Phase change temperature and latent heat of fusion for pure paraffins.

<table>
<thead>
<tr>
<th>Number of carbon atoms</th>
<th>Phase change temperature (°C)</th>
<th>Latent heat of fusion (kJ/kg)</th>
<th>Group (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>5.5</td>
<td>228</td>
<td>I</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>205</td>
<td>II</td>
</tr>
<tr>
<td>16</td>
<td>16.7</td>
<td>237.1</td>
<td>I</td>
</tr>
<tr>
<td>17</td>
<td>21.7</td>
<td>213</td>
<td>II</td>
</tr>
<tr>
<td>18</td>
<td>28.0</td>
<td>244</td>
<td>I</td>
</tr>
<tr>
<td>19</td>
<td>32.0</td>
<td>222</td>
<td>II</td>
</tr>
<tr>
<td>20</td>
<td>36.7</td>
<td>246</td>
<td>I</td>
</tr>
<tr>
<td>21</td>
<td>40.2</td>
<td>200</td>
<td>II</td>
</tr>
<tr>
<td>22</td>
<td>44.0</td>
<td>249</td>
<td>II</td>
</tr>
<tr>
<td>23</td>
<td>47.5</td>
<td>232</td>
<td>II</td>
</tr>
<tr>
<td>24</td>
<td>50.6</td>
<td>255</td>
<td>II</td>
</tr>
</tbody>
</table>

(a) Group: I, most promising; II, promising; III, less promising.
Some of the salient features of materials belonging to this category are – (i) High heat of fusion, (ii) Low flash point, (iii) Poor thermal conductivity, (iv) Toxicity, and (v) Unstable at elevated temperatures. Table 1-3 lists the properties and heat of fusion of various fatty-acids compiled by Abhat et al\textsuperscript{8} and Lane\textsuperscript{1}.

Table 1-3. Melting temperature and heat of fusion data for fatty-acids.\textsuperscript{1,8}

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Melting point (°C)</th>
<th>Latent heat (kJ/kg)</th>
<th>Group*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH$_3$COOH</td>
<td>16.7</td>
<td>164</td>
<td>I</td>
</tr>
<tr>
<td>Polytetraethylene glycol (600)</td>
<td>HOOC$_2$H$_4$OH</td>
<td>20-23</td>
<td>146</td>
<td>I</td>
</tr>
<tr>
<td>Capric acid</td>
<td>CH$_3$(CH$_2$)$_3$COOH</td>
<td>36</td>
<td>152</td>
<td>–</td>
</tr>
<tr>
<td>Elaidic acid</td>
<td>CH$_3$CH$_2$CH$_2$COOH</td>
<td>47</td>
<td>218</td>
<td>I</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>CH$_3$(CH$_2$)$_4$COOH</td>
<td>49</td>
<td>178</td>
<td>II</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>CH$_3$(CH$_2$)$_14$COOH</td>
<td>52.5</td>
<td>178</td>
<td>–</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>CH$_3$(CH$_2$)$_16$COOH</td>
<td>59</td>
<td>191</td>
<td>–</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>CH$_3$(CH$_2$)$_14$COOH</td>
<td>59</td>
<td>199</td>
<td>–</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>CH$_3$(CH$_2$)$_16$COOH</td>
<td>59</td>
<td>199</td>
<td>–</td>
</tr>
<tr>
<td>Acetamide</td>
<td>CH$_3$CONH$_2$</td>
<td>81</td>
<td>241</td>
<td>I</td>
</tr>
<tr>
<td>Methyl formate</td>
<td>(CH$_3$O)NH$_2$</td>
<td>102</td>
<td>242</td>
<td>I</td>
</tr>
</tbody>
</table>

* Group I: most promising; Group II: promising; Group III: less promising; – insufficient data.

1.4 Salt Hydrates

Salt hydrates are basically inorganic salts with specific number of water molecules forming crystalline solid of general formula AB.nH$_2$O. Solid-liquid transformation of salt hydrate involves dehydration of the salt or going to a lower hydrated state with fewer moles of water and accompanied by an aqueous solution.

\[
\text{AB.nH}_2\text{O} \rightarrow \text{AB.mH}_2\text{O} + (n-m)\text{H}_2\text{O}
\]

\[
\text{AB.nH}_2\text{O} \rightarrow \text{AB} + n\text{H}_2\text{O}
\]

Advantages

Cheaper and easy availability is the most desirable characteristic of salt hydrates relative to other PCMs. Most commonly found salt hydrates are CaCl$_2$.6H$_2$O and Na$_2$SO$_4$.10H$_2$O\textsuperscript{1}. They have a high heat of fusion accompanied by lower volume changes
relative to other PCMs. They have high thermal conductivity which reduces the heat storage system size.

**Disadvantages**

Except Ca\((\text{NO}_3)_2\cdot6\text{H}_2\text{O}\), most of the salt hydrates suffer from severe segregation problems. At melting point, the lower hydrate does not have enough water to dissolve itself and thus segregates to the bottom of the unit. Due to segregation, there is a decrease of 73\% in \(\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}\) heat of fusion after 1000 melt/freeze cycles\(^8\). Salt hydrates have poor nucleating properties which lead to supercooling due to delay in crystallization. This can be taken care of by using proper nucleating agents. Salt hydrates are very corrosive especially with metallic containers\(^8\). Table 1-4 shows thermal properties of salt-hydrates.

Table 1-4. Thermal properties of salt hydrates\(^3, 4, 8, 9,16,17\)

<table>
<thead>
<tr>
<th>Name</th>
<th>Melting Point (ºC)</th>
<th>Density (kg/m³)</th>
<th>Thermal Conductivity (W/m K)</th>
<th>Latent Heat (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO(_3\cdot3\text{H}_2\text{O})</td>
<td>8</td>
<td>n.a.</td>
<td>n.a.</td>
<td>253</td>
</tr>
<tr>
<td>NH(_4)Cl\cdot\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O})</td>
<td>11</td>
<td>n.a.</td>
<td>n.a.</td>
<td>163</td>
</tr>
<tr>
<td>K(_2)H(_2)O\cdot6\text{H}_2\text{O})</td>
<td>14</td>
<td>n.a.</td>
<td>n.a.</td>
<td>108</td>
</tr>
<tr>
<td>NaCl\cdot\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O})</td>
<td>18</td>
<td>n.a.</td>
<td>n.a.</td>
<td>286</td>
</tr>
<tr>
<td>K(_2)F(_4)\cdot\text{H}_2\text{O})</td>
<td>18</td>
<td>n.a.</td>
<td>n.a.</td>
<td>330</td>
</tr>
<tr>
<td>K(_2)H(_2)O\cdot4\text{H}_2\text{O})</td>
<td>18.5</td>
<td>1447(^{10\text{C}}), 1455(^{18\text{C}})</td>
<td>n.a.</td>
<td>231</td>
</tr>
<tr>
<td>Mg(\text{NO}_3)_2\cdot6\text{H}_2\text{O})</td>
<td>25</td>
<td>1730(^{10\text{C}}), 1211</td>
<td>n.a.</td>
<td>148</td>
</tr>
<tr>
<td>LiBO(_2\cdot8\text{H}_2\text{O})</td>
<td>25.7</td>
<td>n.a.</td>
<td>n.a.</td>
<td>289</td>
</tr>
<tr>
<td>FeBr(_3\cdot6\text{H}_2\text{O})</td>
<td>27</td>
<td>n.a.</td>
<td>n.a.</td>
<td>105</td>
</tr>
<tr>
<td>CaCl(_2\cdot6\text{H}_2\text{O})</td>
<td>29 - 30</td>
<td>1562(^{15\text{C}}), 1802(^{24\text{C}})</td>
<td>0.561(^{81\text{C}}), 1.008(^{92\text{C}})</td>
<td>170 - 192</td>
</tr>
<tr>
<td>LiNO(_3\cdot3\text{H}_2\text{O})</td>
<td>30</td>
<td>n.a.</td>
<td>n.a.</td>
<td>189 - 296</td>
</tr>
<tr>
<td>Na(_2)SO(_4)\cdot10\text{H}_2\text{O})</td>
<td>32</td>
<td>1485(^{14\text{C}})</td>
<td>0.544</td>
<td>251 - 254</td>
</tr>
<tr>
<td>Na(_2)CO(_3)\cdot10\text{H}_2\text{O})</td>
<td>33 - 36</td>
<td>1442</td>
<td>n.a.</td>
<td>247</td>
</tr>
<tr>
<td>KFe(\text{SO}_4)_2\cdot12\text{H}_2\text{O})</td>
<td>33</td>
<td>n.a.</td>
<td>n.a.</td>
<td>173</td>
</tr>
</tbody>
</table>
1.5 Eutectics

A eutectic is a congruent melting/freezing solid of two components. It always solidifies as an intimate mixture of crystals which arrests segregation. Components can be metallic or non-metallic. Table 1-5 lists thermal properties for metallic eutectic mixtures. Table 1-6 lists thermal properties of organic and inorganic eutectics.

Table 1-5. Thermal properties of metallic eutectic mixtures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point (°C)</th>
<th>Latent heat (kJ/kg)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium–gallium antimony eutectic</td>
<td>29.8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Gallium</td>
<td>30.0</td>
<td>80.3</td>
<td>I</td>
</tr>
<tr>
<td>Cerrobend eutectic</td>
<td>61</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bi–Cd–In eutectic</td>
<td>70</td>
<td>25</td>
<td>I</td>
</tr>
<tr>
<td>Bi–Pb–In eutectic</td>
<td>96</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bi–Pb eutectic</td>
<td>125</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Group I, most promising; group II, promising; group III, less promising; — insufficient data.

Table 1-6. Thermal properties of organic and inorganic eutectics.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (wt %)</th>
<th>Melting point (°C)</th>
<th>Latent Heat of fusion (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃ + NaCl + KCl + H₂O</td>
<td>31+13+16+40</td>
<td>4</td>
<td>234</td>
</tr>
<tr>
<td>NaSO₄ + NaCl + NH₄Cl + H₂O</td>
<td>32+14+12+42</td>
<td>11</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cu₂Cl₂(H₂O)₆ + (CaH₂)₂O</td>
<td>26.5+73.5</td>
<td>12</td>
<td>97.9</td>
</tr>
<tr>
<td>Na₂SO₄ + NaCl + H₂O</td>
<td>37+17+46</td>
<td>18</td>
<td>n.a.</td>
</tr>
<tr>
<td>Na₂S₂ + MgSO₄ + H₂O</td>
<td>25+21+54</td>
<td>21-24</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cu₂H₂O₃ + Cu₂(OH)₂O₂</td>
<td>34+66</td>
<td>24</td>
<td>147.7</td>
</tr>
<tr>
<td>Ca(NO₃)₂ + 4H₂O + Mg(NO₃)₂ + 6H₂O</td>
<td>47+53</td>
<td>30</td>
<td>136</td>
</tr>
<tr>
<td>NH₄CONH₂ + NH₄NO₂</td>
<td>–</td>
<td>46</td>
<td>95</td>
</tr>
<tr>
<td>Mg(NO₃)₂ + 6H₂O + NH₄NO₃</td>
<td>61.5+38.4</td>
<td>52</td>
<td>125.5</td>
</tr>
<tr>
<td>Mg(NO₃)₂ + 6H₂O + MgCl₂ + 6H₂O</td>
<td>58.7+41.3</td>
<td>59</td>
<td>132.2</td>
</tr>
<tr>
<td>Mg(NO₃)₂ + 6H₂O + Al(NO₃)₃ + 9H₂O</td>
<td>53+47</td>
<td>61</td>
<td>148</td>
</tr>
<tr>
<td>Mg(NO₃)₂ + 6H₂O + MgBr₂ + 6H₂O</td>
<td>59+41</td>
<td>66</td>
<td>168</td>
</tr>
<tr>
<td>Naphthalene + Benzoic Acid</td>
<td>67.1+32.9</td>
<td>67</td>
<td>123.4</td>
</tr>
<tr>
<td>AlCl₃ + NaCl + ZrCl₂</td>
<td>79+17+4</td>
<td>68</td>
<td>234</td>
</tr>
</tbody>
</table>
1.6 Polyalcohols

Polyalcohols store/release heat energy when they undergo phase transition from a lower temperature heterogeneous structure to high temperature cubic structure\(^{24}\). The polyalcohols, amines and other families of compounds have two crystallographic forms. The high temperature phase was designated as ‘phase I’ and the low temperature phase as ‘phase II’ by the pioneering researchers such as Timmermann\(^{22}\), Nitta\(^{23}\), and others. Chandra et al\(^{24}\) have modified these designations to account for the presence of additional phases in binary and ternary systems. He recommended that the high temperature phase for pure or solid solutions be designated as “\(\gamma\) phase” applicable to pure polyalcohols only. The change in nomenclature is significant in the low temperature phase regions which are labeled as “\(\alpha\) or \(\beta\) phase” to cover the entire region in multi-component systems. We will use Chandra’s designation in this work.

Due to large enthalpies of transformation associated with polyalcohols, interest has been growing in this area of phase change materials for heat storage. Early investigations were limited to pure polyalcohols only. Murilla and Breed\(^{25}\) were the first to evaluate the feasibility of thermal applications of selected PCMs on passive temperature control of satellites. Benson\(^{26}\) and colleagues, with grants from DOE, conducted thermal analyses of different PCMs. From their initial experiments they realized that for polyalcohols to be effective in thermal energy storage, phase transition temperatures needed to be adjusted. Their experiments on PE-PG, PE-NPG and PG-NPG revealed that transition temperatures can be changed by mixing of two polyalcohols. In order to decrease the phase transition temperature of high temperature transitions (PE, TRIS), this was the essential
requirement. Benson’s work also highlighted the presence of undercooling in most polyalcohols.

For understanding of binary mixtures, phase diagrams are constructed with temperature and composition being state variables. The development of binary phase diagram for polyalcohols is very important to understand the dependence of phase transition temperature on solute composition. This understanding and knowledge gained from binary phase diagrams can be used for evaluating similar systems and ternary systems for thermal energy storage.

These materials have the advantage of low volume change, no liquid leaking issues and no degradation of material. On the other hand, polyalcohols have low latent heat, high phase change temperatures and high cost. Wang reports a heat storage system where different polyalcohols were combined to adjust the solid-solid phase transformation temperature. Most prominent polyalcohols are Pentaerythritol, Pentaglycerine, and Neopentylglycol. Table 1-7 lists thermal properties of polyalcohols.

Table 1-7. Thermal properties of various polyalcohols.

<table>
<thead>
<tr>
<th>Material</th>
<th>Transition Temperature, °C</th>
<th>Latent Heat of Transition, kcal/mol</th>
<th>Melting Temperature, °C</th>
<th>Latent Heat of Fusion, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentaerythritol (PE)</td>
<td>188</td>
<td>9.87</td>
<td>~ 260</td>
<td>1.2</td>
</tr>
<tr>
<td>Pentaglycerine (PG)</td>
<td>89</td>
<td>5.53</td>
<td>200</td>
<td>1.3</td>
</tr>
<tr>
<td>Neopentylglycol (NPG)</td>
<td>43</td>
<td>3.26</td>
<td>~ 126</td>
<td>1.1</td>
</tr>
<tr>
<td>2-Amino-2-Methyl-,3-Propanediol (AMPL)</td>
<td>84</td>
<td>5.63</td>
<td>~ 116</td>
<td>0.79</td>
</tr>
<tr>
<td>Hydroxymethyl-Aminomethane (TRIS)</td>
<td>134</td>
<td>7.82</td>
<td>172</td>
<td>0.79</td>
</tr>
</tbody>
</table>
1.7 References

7. Abhat A., “Investigation of physical and chemical properties of phase change materials for space heating/cooling applications”, Proc. Of the Internationals solar energy congress, New Delhi, India
28. Master of Science Thesis by John Hansen, UMI number 1386827
Chapter 2

Background

2.1 Crystal Structure of Pentaerythritol (PE)

Plastic crystals generally have ordered layered structure or chain structure at room temperature with different molecular arrangement in the structure. In pentaerythritol unit cell, there is strong hydrogen bonding within the layers and weak van der waal force between the layers. It has 5 carbons and 4 O-H-O bonds in the molecule.

Figure 2-1. Structure of PE molecule (a) and Molecular arrangement of atoms in PE molecule (b).

The lattice parameters for low and high temperature phases of PE are shown in Table 2-1. Nitta and Watanbe\textsuperscript{7} were the first to determine the crystal structure of PE. Later on, Eilerman and Rudman\textsuperscript{1} refined the PE structure and determined atom positions in the unit cell. At room temperature, PE crystallizes as body-centered tetragonal structure, I4- space group. The unit cell (Figure 2-2) contains two molecules and the molecules possess S4
symmetry. Molecules are arranged in parallel planes (001) and held together by hydrogen bonds.

Table 2-1. Lattice parameters of Pentaerythritol (PE) \(^3\)

<table>
<thead>
<tr>
<th>Structure and Lattice Parameters of Low temperature phase PE</th>
<th>Structure and Lattice Parameters of High temperature phase PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal</td>
<td>Cubic</td>
</tr>
<tr>
<td>(a_0 = 6.0576 \AA)</td>
<td>(a_0 = 8.999 \AA)</td>
</tr>
<tr>
<td>(c_0 = 8.7798 \AA)</td>
<td></td>
</tr>
<tr>
<td>At 25 °C</td>
<td>At 189 °C</td>
</tr>
</tbody>
</table>

Figure 2-2 \(^9\). Crystal structure of PE at room temperature. On the left: view of (001) plane; on the right: view of (100) plane. Legend: carbon-black, oxygen-red, hydrogen-white/blue, hydrogen bonds are delineated by blue dashed lines. The unit cell is demarcated by solid lines.

The central carbon atoms of the molecules are at 0,0,0 and \(\frac{1}{2},\frac{1}{2},\frac{1}{2}\), each molecule having 4-fold symmetry. The (100) projection shows the layering of molecules in the unit cell.
with a period of $c_0/2 = 4.469 \text{ Å}$. The neighboring molecule linkage in the sheet/layer is mainly hydrogen bonding via interaction of hydroxyl (-OH) groups. Four hydroxyl groups, one from each molecule, form a bridge of hydrogen atoms with a length of 2.71 Å. Intermolecular dimensions from literature are shown in Table 2-2.

Table 2-2. Intermolecular dimensions of PE at room temperature

<table>
<thead>
<tr>
<th>Selected Intermolecular Dimensions</th>
<th>Lattice</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>C-O</td>
<td>C-H1</td>
</tr>
<tr>
<td>0.94</td>
<td>1.43</td>
<td>1.09</td>
</tr>
<tr>
<td>0.75</td>
<td>1.422</td>
<td>0.95</td>
</tr>
<tr>
<td>0.94</td>
<td>1.45</td>
<td>0.94</td>
</tr>
<tr>
<td>0.933</td>
<td>1.422</td>
<td>1.07</td>
</tr>
</tbody>
</table>

The data from Ref. [4 and 6] were determined from neutron diffraction, while the data from Refs. [20 and 5] from X-ray diffraction. One can also notice that the length of OH bond from Refs. [20] differs markedly from the data of others. Apparently, as pointed in Ref. [5], this value is erroneous, as a result of improper weight placed on the least-squares coordinates for hydrogen atom. One C-C-C angle in a molecule is 107.33˚ and the other is 110.55˚. Upon heating the PE crystal, there is anisotropic expansion along the c-axis. There is decrease in the ordering of the unit cell from layers to non-rigid molecular shape due to rotation about C-O and C-C bonds, or both. With increase in temperature, the hydrogen bonding gets weaker in the layers and thus allows rearrangement of molecules which leads to phase change. It has been established that this phase change is a first-order transformation.
The adjustment in lattice dimensions and crystal structure due to heating through the transition temperature to evaluate the possible crystallographic relationships between low and high temperature phases were investigated by Chandra and Barrett. 

Figure 2-3. Schematic showing transformation of four tetragonal PE cells to one large face centered cell (FCC). Relative positions of molecular center in BCT compared with those in FCC Pentaerythritol near the transition temperature. Cross-hatched circles are in the plane of the paper, open circles are in the first layer behind the paper in each phase.

The unit cell of body-centered tetragonal (BCT) PE projected on (001) plane is shown in Figure 2-3. Circles with horizontal hatched lines represent the positions of molecular centre, which are at the centre of tetragonal units cells, 0,0,0 positions –and at the
positions ½, ½, ½, in the centre of each cell (body centered position). The symmetry and size of each molecule is not to scale. The cell dimensions at 180˚C are \(a_0 = b_0 = 6.100 \text{Å}\) and \(c_0 = 8.939 \text{ Å}\) just under the transformation temperature to \(\gamma\) phase.

On the same Figure 2-3, is superimposed a possible transformed face centered cubic (FCC) structure of PE just above the transformation temperature, based on x-ray results. As PE gets heated through 188˚C, where the BCT structure transforms to FCC, the distance between the neighboring molecules increases in the tetragonal phase along a and b axes \((a_0 = b_0 = 6.100 \text{ Å})\) and is plotted in the plane of the paper and the c-axis is normal to it and all molecules in the plane of the paper are crosshatched.

Now, if the tetragonal plane (001) starts morphing to FCC, the molecules in this plane can move short distances from the tetragonal positions to FCC positions in the same plane, resulting in a FCC square with edge dimension of approximately 9Å. The centers of molecules shown as circles for the tetragonal phase are not cross-hatched are in the plane body center of the paper a distance \(a_{0\text{tet}}/2 = 4.47\text{Å}\) below the plane of the paper. If this plane transforms to cubic it becomes a plane \(a_{0\text{cubic}}/2 = 4.5\text{Å}\) below the plane of the paper, indicated by open FCC circles. Dimensions used in the figure are \(c_{0\text{tet}} = 8.939\text{Å}\) at 180˚C, which expands to \(c_{0\text{cubic}} = a_{0\text{cubic}} = 9.000\text{Å}\) at 189˚C, only 0.69% expansion.

However, the distance between coordinates 0, 0, 0, and 1, 1, 0 in the tetragonal PE at 180˚C is \((a_0^2 + b_0^2 + c_0^2)^{1/2} /2 = 6.2118\text{Å}\); this becomes 6.3636Å in the cubic phase at 189˚C, a 2.4% increase, which accompanies the 9.5% increase in volume per molecule on heating through the transformation. These dimension changes accompanying the transformation may account for the crystal break-up and re-orientation that was shown by the Laue photographs of Nitta and Watanbe\(^7\) when a tetragonal crystal of PE was heated.
through the cubic phase range. Single crystal studies have also been performed in which
dynamic phase changes occurring in PE crystals when heated through the transformation
temperature were observed by optical microscopy; pyramidal outgrowth of the high
temperature phase on (002) plane of the cleaved PE single crystal phase II has been
observed at the transition temperature.
The complexity of liberation and translation movements of molecules is undoubtedly
very large in the cubic phase compared with those of the tetragonal phase. As a result,
layering is not maintained, cubic phase is “plastic”, “not layered” and evidence indicated
that the molecules are not rigid. The question of statistical preference of molecular
orientation in the cubic cell was addressed by Nitta and Watanbe\textsuperscript{7} who attempted to
match the intensities of the reflection from powder sample to ten different models, and
with very few Debye rings that are available at such high temperatures (because of the
extremely high x-ray temperature factor) it would seem that x-ray powder diffraction data
can not yield details of the orientation preferences.

2.2 Crystal Structure of Neopentylglycol (NPG)

Hydrogen bonded NPG crystal has been investigated by Murrill and Breed\textsuperscript{8} and Benson\textsuperscript{9}
et al. throughout 1970s. Timmermann\textsuperscript{10} in 1961 established low temperature phase of
NPG to be layer type monoclinic. Zannetti\textsuperscript{11} and Frank\textsuperscript{12} et al. also found the monoclinic
structure with space group P2\textsubscript{1}/C. Nakano also reported monoclinic structure but used an
alternate space group P2\textsubscript{1}/n with different lattice constants. Figure 2-5 shows the NPG
molecule and atomic arrangement of NPG with 5 carbons and 2 O...H...O bonds. High
temperature phase is disordered isotropic cubic. Chandra et al.\textsuperscript{13} during investigation of binary phase diagram for polyalcohols involving NPG as one component found discrepancies in indexing of the patterns using accepted Zannetti’s JCPDS file. It was found that the undercooled $\gamma$ phase was retained below the temperature range in which it was stable. The Bragg peaks from the undercooled phase overlapped with some peaks of the $\alpha$ phase. This caused uncertainties in the intensities and indices of the Bragg peaks of the room temperature crystal structure of this important thermal energy storage material. These difficulties prompted re-determination of the NPG room temperature structure by Chandra et al\textsuperscript{13}.

The re-determined structure reported by Chandra et al.\textsuperscript{13} is monoclinic, \(M = 104.15\) amu, space group \(P2_1/n\) (an alternate setting of \(P2_1/c\)-C52h, space group No. 14), \(a = 5.979\) (1)Å, \(b = 10.876(2)\)Å, \(c = 10.099(2)\)Å, \(b = 99.78\) (1)°, \(V = 647.2\) (2)Å\(^3\) at 20 (±1)°C, \(D_x = 1.069\) g.cm s\(^{-3}\) for \(Z = 4\). This study by Chandra et al.\textsuperscript{13} used advanced single crystal x-ray diffraction analyses, cell parameters, bond lengths, atom positions and other structural factors were determined.

The NPG molecule drawing is shown in Figure 2-5. Non-hydrogen atoms, represented by thermal vibration ellipsoids, drawn to encompass 50\% of their electron density and hydrogen is represented by arbitrary small diameter sphere. Non-hydrogen atoms,
represented by thermal vibration ellipsoids, drawn to encompass 50% of their electron density and hydrogen is represented by arbitrary small diameter sphere. The bond lengths and angles are given in Table 2-3.

Table 2-3. Bond Lengths and Bond Angles in Crystalline monoclinic NPG

<table>
<thead>
<tr>
<th>Type</th>
<th>Length, Å</th>
<th>Type</th>
<th>Length, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-C1</td>
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<td>O2-C3</td>
<td>1.410(4)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.514(5)</td>
<td>C2-C4</td>
<td>1.522(6)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.517(4)</td>
<td>C2-C5</td>
<td>1.528(5)</td>
</tr>
<tr>
<td>O1-H1</td>
<td>1.06(4)</td>
<td>O2-H2</td>
<td>0.84(5)</td>
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<table>
<thead>
<tr>
<th>Type</th>
<th>Angle, °</th>
<th>Type</th>
<th>Angle, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1C1O2</td>
<td>113.63(3)</td>
<td>C1:C2C5</td>
<td>109.6(3)</td>
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<tr>
<td>C1C2C3</td>
<td>109.9(2)</td>
<td>C3C2C5</td>
<td>107.3(3)</td>
</tr>
<tr>
<td>C1C2C4</td>
<td>107.8(3)</td>
<td>C4C2C5</td>
<td>112.0(3)</td>
</tr>
<tr>
<td>C3C2C4</td>
<td>110.2(3)</td>
<td>C2C3C2</td>
<td>112.9(3)</td>
</tr>
<tr>
<td>C1O1H1</td>
<td>117(2)</td>
<td>C3O2H2</td>
<td>102(2)</td>
</tr>
</tbody>
</table>

Figure 2-5. Non-hydrogen atoms, represented by thermal vibration ellipsoids, drawn to encompass 50% of their electron density and hydrogen is represented by arbitrary small diameter sphere.

The low temperature structure (α phase) of NPG has pairs of tetrahedral molecules joined via O…H bonds to form bimolecular chains producing a highly anisotropic structure. The
arrangement of molecules in NPG is quite different from the arrangement of their homologues, such as Pentaerythritol (PE), which has layered structure. The linear chains of NPG form zig-zag, alternating hydrogen bonds and the chains are Van der Waal bonded to the neighboring chains. Computer generated projections of the molecules in the a-b, b-c, and a-c planes in the space group P21/n are given in Figure 2-6, with the unit cell outlined. There are inversion centers at the mid-points of each unit cell edge, at the corners of the unit cell and at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. There are two fold screw axes parallel to the x-axis, normal to the paper. Pairs of NPG molecules can be viewed as bonded together by strings of hydrogen bonds; O-H…O. the average donor-oxygen to acceptor-oxygen contact distance is 2.703Å and the average hydrogen to acceptor-oxygen distance, shown by dashed lines in Figure 2-6, is 1.765Å.

These intermolecular hydrogen bond distances are quite similar to those found in PE. Four dashed lines (O-H…O bonds) form a rectangle in a chain that lies parallel to the x-axis. In Figure 2-6. (a), such a rectangle is centered at $x,y,z = 1/2,1/2,0$ and is labeled $R_1$ (an identical one to $R_2$). Rectangle $R_3$ that is centered at $1,0,1/2$ (and the identical one $R_4$) lies in a plane also parallel to the x-axis, and is related to $R_2$ by the screw axes of symmetry that pass through point $S$ of Figure 2-6 (a). The chain through the $R_3$ and $R_4$ lies in a plane separated by $b/2$ from the plane containing $R_1$ and $R_2$. Figure 2-6. (b) and (c) show hydrogen bond dashed lines as seen by viewing along the x-axis and z-axis, respectively.

The NPG plastic crystals undergo $\alpha \rightarrow \gamma$ phase transformation at $\sim 41^\circ C$. The structure of the $g$ phase has been determined as orientationally disordered FCC phase. The Guinier film patterns of the $\gamma$ phase, taken In the symmetric mode, showed only the 111 and 200
reflections. These characteristic reflections matched FCC structure and are typical of other homologues polyalcohols such as Pentaerythritol (PE)\textsuperscript{15}. The lattice parameters of the $\gamma$ FCC phase measured at 45, 50, 56 °C are 8.845(3), 8.8479(1), and 8.555(1) Å, respectively.

Figure 2-6. Orientation of hydrogen bonded molecules in the unit cell of Neopentylglycol

The Guinier film patterns obtained in the symmetric mode showed another reflection of (222) but of very weak intensity. The absence of other FCC reflections is due to orientational disorder in the isotropic $\gamma$ phase; the low temperature $\alpha$ phase chain structure is no longer maintained. Molecular orientation in the $\gamma$ phase of NPG could not
be determined because very few reflections were available for analyses. However, AC impedance studies by Helms et al.\textsuperscript{16} showed dielectric loss during heating through the room temperature to 81°C; three orders of magnitude increase in the conductivity is observed at 81°C suggesting molecular reorientation and the diffusion in the $\gamma$ phase of the NPG.

The large solid-state latent heat storage capacity of 13.6 kJ mol\textsuperscript{-1} further suggests vibrational/rotational motion in the $\gamma$ phase. Intermolecular hydrogen bonding has been found to exist in NPG above and below the transition temperature. Structural studies on similar molecules of other polyalcohols with FCC high temperature structures revealed that there is a possible reorientation of the molecule about its center of gravity and intramolecular rotation, may very well apply to NPG molecules. This reorientation process in the $\alpha$ phase becomes prominent just below the transition temperature resulting in progressive breaking of intermolecular hydrogen bonds. Intermolecular hydrogen bonding has been found to exist in NPG above and below the transition temperatures\textsuperscript{9}. A cubic modification of the NPG molecule at high temperature is shown in Figure 2-7. This model suggests that some possible proposed orientation of neighboring molecules on a (001) face of the FCC unit cell, orientations that would permit rotation if intermolecular hydrogen bonds such as the O$_1$-H…O$_2$ bonds (a dotted line in the Figure 2-7). The assumptions are that the carbon atoms C$_1$, C$_2$, C$_3$ and C$_4$ lie on the cube face.
Figure 2-7. Suggested packing of the NPG molecules in the orientationally disordered $\gamma$ phase showing projection on the 001 plane.

(001) of the unit cell. The bond C$_2$-O$_1$ rotates as the generator of a cone whose axis is an extension of C$_1$-C$_2$, and similarly O$_2$-C$_3$ rotates synchronously about an extension of C$_3$-C$_4$ as an axis, keeping the hydrogen bond O$_1$-H…O$_2$ at a constant length of 2.72Å. Similar rotations at bond C$_6$-O$_3$ would occur about the axis C$_5$-C$_6$ that is inclined at 45° to the plane of the drawing. Intramolecular hydrogen bonds also absorb infrared energy but motions of these are not indicated in Figure 2-7$^{13}$.

2.3 Crystal Structure of Pentaglycerine (2-hydroxymethyl-2methyl-1,3-propanediol)

Pentaglycerine with 5 carbons and 3 O…H…O bonds are shown in Figure 2-9. Rudman et al.$^1$ in 1983 established PG crystal structure. At room temperature, PG has a body centered tetragonal crystal structure with space group I4, Z = 2. There is a phase
transition to orientationally disordered FCC structure at about 353 K and it remains in this phase till melting at about 460 K.

The low temperature phases are rigid crystals which are held together by hydrogen bonds between OH of neighboring molecules. The transition to FCC phase is accompanied with large enthalpy related to breaking of hydrogen bonds. This takes place as the molecule is going from an ordered phase to disordered phase. The transition entropy is the measure of the disorder in the high temperature phase. Depending on the molecular symmetry, in PG there are 48 orientations allowed in the FCC phase. The entropy corresponding to this orientational disorder is \( R \ln(48) = 32.2 \text{ JK}^{-1}\text{mol}^{-1} \). This is supplemented by conformational disorder which does not depend on symmetry. Assuming the molecule has tetrahedral shape, the total entropy of 59.6 \text{ JK}^{-1}\text{mol}^{-1} calculated matches well with the experimentally determined entropy of 59.3 \text{ JK}^{-1}\text{mol}^{-1}. This match is quite impressive but it has to be kept in mind that there are assumptions behind this: Three configurations for one methylol group, fully excited configurations and independence of the three methylol groups in the molecule.
Further, there have been reports in the literature that PG might have a monoclinic structure at room temperature\textsuperscript{17}. We think that PG has body-centered tetragonal structure at room temperature, based on the following facts –

(A) X-ray powder diffraction pattern of PG does not show monoclinic peaks instead, it matches very close to Pentaerythritol (PE) suggesting that it has a similar structure (body-centered tetragonal)

(B) PE-PG phase diagram\textsuperscript{18} shows isomorphous region over the complete composition region suggesting iso-structural molecules which show complete miscibility into each other.

Table 2-4. Lattice Parameters for PG\textsuperscript{18,19,20}

<table>
<thead>
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<th>Phase</th>
<th>Parameters</th>
<th>Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>a (Å)</td>
<td>c (Å)</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>6.054 (2)</td>
<td>8.866 (3)</td>
<td>25 C</td>
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<td>25 C</td>
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<tr>
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<td>6.052 (2)</td>
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<td>γ</td>
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<td></td>
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<td>100 C</td>
</tr>
<tr>
<td></td>
<td>8.866 (8)</td>
<td></td>
<td>83 C</td>
</tr>
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</table>

Table 2-4 lists lattice parameters of Pentaglycerin (PG) as determined by various authors. Suenaga et al.\textsuperscript{17} reported the dependence of thermo physical properties of the homologous polyols on number of –OH groups. As the number of –OH groups increases in each molecule, the molar volume of the high temperature phase decreases and that of low temperature phase increases. The temperature, enthalpy and entropy of transition also depend systematically on the number of OH groups. Dissociation of hydrogen bonds and the intermolecular motional degrees of freedom thereby enhanced would play an essential
role in the phase transition. The transition entropy increases with increased number of methylol groups, indicating a large contribution arising from the conformational degrees of freedom of molecule on passing through the phase transition.

2.4 Pentaerythritol (PE)-Neopentylglycol (NPG) Phase Diagram

The phase transitions in polyols such as PE, PG and NPG are significant because it involves large enthalpy change that can be used as heat storage medium. Low temperature ordered phase to high temperature disordered plastic phase transitions are of first order and occur at temperatures well below the melting/fusion temperatures. These energetic transitions are accompanied by a large entropy change of solid-solid transition compared to solid-liquid transition\(^{14}\). Benson et al.\(^{9}\) first reported the thermophysical properties of PE, PG and NPG and their mixtures. Chandra et al.\(^{21}\) reported the adjustment of transformation temperatures and effects of dopants in the crystal structural properties of these polyalcohols. Chandra et al.\(^{21}\) prepared their samples by melting the required amounts of PE and NPG in a closed test tube and slowly cooling the melt to room temperature. To attain equilibrium the cooled mass was placed in a freezer \(-25^\circ\text{C}\) for a minimum of 12 hours. These powders were then compacted in disk form of approximately \(\frac{3}{4}\)“ diameter, with the thickness varying from \(1/8\)“ to \(3/16\)“ so that undercooled phases were precipitated by application of pressure which supplied the strain energy for the transformation, in a manner described by Barrett\(^{22}\). The authors based their phase diagram on DSC and high temperature Guinier diffractometry experiments. Chandra et al.\(^{14}\) investigated PE-NPG binary phase diagram for 0-30 mol% NPG. They reported that there is little solubility of NPG in PE and there are two distinct phases present in the system at 19°C; monoclinic (β) NPG and body centered tetragonal (α) PE.
The phase transitions were established based on peak heights in XRD by examining (011) reflection for monoclinic and (002) reflection for tetragonal phase. High temperature Guinier XRD showed reflection from $\alpha$ and $\beta$ phases at room temperature. At about 41˚C, the pattern showed transformation of $\beta$ phase to high temperature $\gamma$ phase but the reflections from the new phase were not immediately observed and indexed. Only the patterns obtained at high temperatures, showed the presence of overlapped peaks of $\alpha$ and $\gamma$ reflections. Above 41˚C, $\alpha$ and $\gamma$ phases are stable and DSC thermal analyses suggests that $\gamma$ phase eventually dissolves in $\alpha$ phase. At about 188˚C, PE transforms to its high temperature FCC phase $\gamma'$ and stays same till melting. As an example, the phase transition scheme for PE-20mol%NPG was reported as

$$\alpha + \beta \rightarrow \alpha + \gamma \rightarrow \alpha \rightarrow \alpha + \gamma' \rightarrow \gamma' \rightarrow \text{Liquid}$$

As the temperature increases, there is a gradual increase in ‘c’ parameter of the $\alpha$ unit cell and NPG solubility in PE increases at higher temperatures.

Teisseire et al.\textsuperscript{23} investigated PE-NPG phase diagram over the complete composition range. The samples were prepared by mixing the PE and NPG powder in a glass cell which was subjected to heating in a furnace till melting was achieved. Overheating was avoided which leads to sample decomposition and sample were finally allowed to slowly cool to room temperature. They used XRD Guinier-Simon camera which allows the continuous evolution of the diffraction pattern of a sample with temperature to be filmed. The sample for XRD was prepared in Lindmann tubes to prevent sublimation of the sample constituents at higher temperatures. DSC data is tabulated in Table 2-5. Barrio et al.\textsuperscript{24} also worked on PE-NPG system and tried to explain some peaks reported by
Teisseire et al.\textsuperscript{23}. They stated that there is another invariant transition happening in PE-NPG system at 343 K due to the existence of intermediate phase. Hence, they modified the PE-NPG diagram reported by Teisseire et al. according to the authors; new measurements were performed using a highly sensitive thermal device with sample masses smaller than those used by Teisseire et al. in order to decrease the temperature gradients.
Table 2-5. Temperatures recorded from DSC experiments on the binary NPG-PE system.

<table>
<thead>
<tr>
<th>X_{PE} (mol%)</th>
<th>T_1 °C</th>
<th>T_2 °C</th>
<th>T_3 °C</th>
<th>T_4 °C</th>
<th>T_5 °C</th>
<th>T_6 °C</th>
<th>T_7 °C</th>
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<td></td>
<td>185</td>
<td>185</td>
<td>250</td>
<td>250</td>
<td></td>
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</tbody>
</table>

T_1 °C, temperature for NPG transition and eutectoid invariant;
T_2 °C, peritectic invariant; T_3 °C, metatectic invariant
T_4 °C, beginning of cubic transition; T_5 °C, end of cubic transition
T_6 °C, beginning of melting,
T_{solidus} T_7 °C, end of melting, T_{liquidus}

The experimental PE-NPG phase diagram constructed/proposed by the authors is shown in Figure 2-8.
Also, in-situ XRD measurements were taken at different temperatures in order to complete the PE-NPG phase diagram. Solubility boundaries of PE and NPG were determined from X-ray diffraction patterns from the evolution of characteristic reflections of each phase versus composition. According to Barrio et al.\textsuperscript{24}, there is a new intermediate cubic phase, called \( C_3 \), which is also FCC and the presence of this phase necessitates the establishment of new invariant transformation at 353 K. using thermal and crystallographic characterizations, a new and complex phase diagram (Figure 2-10) was reported for PE-NPG system. As reported, this phase diagram is characterized by the presence of –

- Five invariant lines, temperatures and concentration values of which are reported in Table 2-6.
- The existence of an intermediate cubic phase was established in a narrow composition range towards NPG.

Table 2-6. Compositional limits (F, G, and H) and the temperatures of the different invariant lines in PE-NPG phase diagram\textsuperscript{24}.

<table>
<thead>
<tr>
<th>Invariant</th>
<th>X</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Metatectic</td>
<td>.25-.3</td>
<td>.4-.45</td>
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<tr>
<td>Peritectic ((T_{P1}))</td>
<td>0.15-0.2</td>
<td>0.3-0.35</td>
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<tr>
<td>Peritectic ((T_{P2}))</td>
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<td>Eutectoid</td>
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<tr>
<td>Eutectoid</td>
<td>&lt;0.02</td>
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Table 2-7. PE$_x$NPG$_{1-x}$ transition properties.

<table>
<thead>
<tr>
<th>X$_{PE}$</th>
<th>Phase Change Temperature, K</th>
<th>Enthalpy of Transformation, kJ/mol</th>
<th>Specific Heat, J/mol.K</th>
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<tr>
<td>0.00</td>
<td>326.00</td>
<td>12.60</td>
<td>287.00</td>
</tr>
</tbody>
</table>

Benson et al.\textsuperscript{9} measured the transformation temperatures of PE-NPG system which are tabulated in Table 2-7.

### 2.5 Pentaglycerine (PG)-Neopentylglycol (NPG) Phase Diagram

Pentaglycerine (PG) and Neopentylglycol (NPG) exhibit plastic crystal phases at high temperatures in which there is relative loss of order and thus these phases are also known as Orientationally disordered crystals (ODIC). The low temperature PG and NPG rearrange their molecules into a cubic phase at higher temperatures, where some hydrogen bonding which is responsible for the rigid low temperature structure are broken. Barrio et al.\textsuperscript{19} was the first to propose a phase diagram for the binary mixture of PG-NPG system. In their work, they used thermal analysis and X-ray powder diffraction techniques to characterize the changes taking place in the mixtures. Samples were prepared by mixing the two pure chemicals in desired proportions and then melting them in the furnace followed by slow cooling to room temperature.
PG and NPG, both may be considered a derivative of Pentaerythritol (PE). PG is obtained by substituting one \(-\text{CH}_2\text{OH}\) group with a methyl (-\text{CH}_3) group. In a similar manner, NPG involves substitution of two \(-\text{CH}_2\text{OH}\) groups with two methyl groups. Phase transitions in PG and NPG have been characterized as first order transitions\(^9,18\). The first hypothesis for crystal to plastic transition was made by Nitta\(^7\) for PE, where he proposed that hydrogen bonds which maintain the molecules rigidly in the ordered solid crystal phase are broken at the transition temperature permitting the molecular vibration and rotation, so that the molecules can be considered as spherical in the plastic form.

Infrared absorption studies done by Benson et al.\(^9\) further strengthen this argument that the \(-\text{OH}\) stretching vibrations corresponding to hydrogen bond is present in PE, PG, and NPG for the low temperature phase. Upon heating, the vibration frequency band of \(-\text{OH}\) increases at temperature close to the transition temperature. These shifts are known to be characteristic of hydrogen bond breakage. Based on these facts, same phase transformation mechanism can be applied to PG and NPG compounds.

Because of chemical bond similarity of PG and NPG with PE, structural studies done on PE can be used to investigate these molecules. PG is iso-structural with PE (body-centered tetragonal structure with I4 space group) and same hydrogen bonding is found except one link is open in the PG structure. This means that PG has strong intermolecular hydroxyl hydrogen bonding in the layers parallel to the \((001)\) plane\(^9\). The interlayer bonds are weak Van der Waals forces.

The same structural study of NPG also indicates that the arrangement of hydrogen bonds around the center of symmetry is similar to that of PE. For example, the hydrogen bond
distance O...O is 2.710 Å in PE \(^1\); 2.714 Å in PG \(^2\) and between 2.65 Å and 2.75 Å in NPG\(^2\).

The phase diagram solubility boundaries/limits at room temperature were determined from Bragg’s angles variation with the concentration of PG. (021) and (011) reflections
of monoclinic phase were studied. Using this method, solubility boundary of PG in NPG was established – 0.07 mol fraction of PG: NPG $0.83$PG $0.07$

In the same manner, evolution of (002) and (110) reflections corresponding to body centered tetragonal phase with respect to concentration established the NPG solubility in PG at 0.58 mol fraction of PG; NPG $0.42$PG $0.58$

At 356 K, just above the crystal to plastic phase transition temperature of PG, only cubic reflections were recorded. The DSC pattern at such a point only shows melting which signifies complete miscibility. Table 2-8 shows the characteristic temperatures concerning the NPG$_{1-x}$PG$_x$ alloys.

Table 2-8. Characteristic temperatures concerning the NPG$_{1-x}$PG$_x$ alloys.$^{19}$

<table>
<thead>
<tr>
<th>X$_{PG}$</th>
<th>$T_\text{tr start}$, K</th>
<th>$T_\text{tr finish}$, K</th>
<th>$T_\text{solidus}$, K</th>
<th>$T_\text{liquidus}$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>313.2 ± 1.0</td>
<td>-</td>
<td>398.2 ± 1.0</td>
<td>-</td>
</tr>
<tr>
<td>0.04</td>
<td>306.3 ± 1.0</td>
<td>309.0 ± 1.0</td>
<td>388.4 ± 1.7</td>
<td>392.0 ± 1.6</td>
</tr>
<tr>
<td>0.08</td>
<td>301.9 ± 2.0</td>
<td>306.8 ± 2.0</td>
<td>382.9 ± 1.7</td>
<td>386.8 ± 1.8</td>
</tr>
<tr>
<td>0.1</td>
<td>298.8 ± 1.0</td>
<td>305.8 ± 1.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>298.1 ± 1.0</td>
<td>304.9 ± 1.5</td>
<td>380.9 ± 2.1</td>
<td>383.0 ± 2.1</td>
</tr>
<tr>
<td>0.2</td>
<td>298.8 ± 1.0</td>
<td>303.6 ± 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>298.0 ± 1.0</td>
<td>301.8 ± 1.3</td>
<td>379.6 ± 2.0</td>
<td>382.0 ± 2.0</td>
</tr>
<tr>
<td>0.26</td>
<td>297.6 ± 1.0</td>
<td>300.4 ± 1.2</td>
<td>380.9 ± 1.9</td>
<td>385.7 ± 1.9</td>
</tr>
<tr>
<td>0.27</td>
<td>297.6 ± 1.1</td>
<td>302.4 ± 1.1</td>
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<td></td>
</tr>
<tr>
<td>0.3</td>
<td>297.6 ± 1.1</td>
<td>307.8 ± 1.0</td>
<td>382.4 ± 1.8</td>
<td>390.2 ± 1.7</td>
</tr>
<tr>
<td>0.37</td>
<td>298.3 ± 0.5</td>
<td>309.0 ± 2.0</td>
<td>386.1 ± 1.8</td>
<td>393.1 ± 2.0</td>
</tr>
<tr>
<td>0.4</td>
<td>298.5 ± 1.5</td>
<td>310.4 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.42</td>
<td>301.0 ± 1.1</td>
<td>315.6 ± 1.2</td>
<td>390.7 ± 1.7</td>
<td>398.0 ± 1.9</td>
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<tr>
<td>0.46</td>
<td>304.8 ± 1.01</td>
<td>317.7 ± 1.0</td>
<td>395.7 ± 2.0</td>
<td>405.4 ± 1.6</td>
</tr>
<tr>
<td>0.5</td>
<td>307.2 ± 1.3</td>
<td>318.6 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>311.5 ± 1.0</td>
<td>323.4 ± 1.6</td>
<td>400.9 ± 1.7</td>
<td>409.8 ± 1.80</td>
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<tr>
<td>0.57</td>
<td>312.7 ± 1.1</td>
<td>325.9 ± 1.3</td>
<td>404.3 ± 2.1</td>
<td>415.6 ± 1.4</td>
</tr>
<tr>
<td>0.6</td>
<td>314.1 ± 1.2</td>
<td>326.6 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.62</td>
<td>318.5 ± 1.0</td>
<td>330.3 ± 1.0</td>
<td>412.8 ± 1.6</td>
<td>421.2 ± 1.5</td>
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<tr>
<td>0.67</td>
<td>320.4 ± 2.0</td>
<td>334.4 ± 1.0</td>
<td>422.9 ± 1.8</td>
<td>429.8 ± 2.1</td>
</tr>
<tr>
<td>0.7</td>
<td>323.1 ± 1.0</td>
<td>335.5 ± 1.0</td>
<td></td>
<td>435.9 ± 1.9</td>
</tr>
<tr>
<td>0.8</td>
<td>330.2 ± 1.0</td>
<td>340.6 ± 1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.81</td>
<td>332.0 ± 1.1</td>
<td>340.5 ± 1.0</td>
<td>435.4 ± 2.1</td>
<td>441.4 ± 2.2</td>
</tr>
<tr>
<td>0.88</td>
<td>339.8 ± 1.1</td>
<td>345.2 ± 1.2</td>
<td>446.6 ± 2.2</td>
<td>450.4 ± 2.1</td>
</tr>
<tr>
<td>0.9</td>
<td>341.6 ± 1.0</td>
<td>346.9 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>353.5 ± 1.0</td>
<td>-</td>
<td>459.2 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>
Benson et al. also obtained PG-NPG thermal measurements using DSC and reported their data as shown in Table 2-9. On the basis of thermal and crystallographic measurements, PG-NPG phase diagram is depicted in Figure 2-11.

Table 2-9. $\text{PG}_x\text{NPG}_{1-x}$ transition properties (x in mol%).

<table>
<thead>
<tr>
<th>$X_{\text{PG}}$</th>
<th>Phase Change Temperature, K</th>
<th>Enthalpy of Transformation, kJ/mol</th>
<th>Specific Heat, J/mol.K</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.00</td>
<td>362.00</td>
<td>16.70</td>
<td>330.00</td>
</tr>
<tr>
<td>87.50</td>
<td>350.00</td>
<td>15.70</td>
<td>349.00</td>
</tr>
<tr>
<td>75.00</td>
<td>335.00</td>
<td>12.20</td>
<td>343.00</td>
</tr>
<tr>
<td>60.00</td>
<td>320.00</td>
<td>11.70</td>
<td>290.00</td>
</tr>
<tr>
<td>50.00</td>
<td>313.00</td>
<td>9.96</td>
<td>268.00</td>
</tr>
<tr>
<td>40.00</td>
<td>299.00</td>
<td>8.41</td>
<td>292.00</td>
</tr>
<tr>
<td>25.00</td>
<td>297.00</td>
<td>8.16</td>
<td>265.00</td>
</tr>
<tr>
<td>12.50</td>
<td>300.00</td>
<td>7.03</td>
<td>296.00</td>
</tr>
<tr>
<td>0.00</td>
<td>321.00</td>
<td>12.60</td>
<td>287.00</td>
</tr>
</tbody>
</table>

2.6 Pentaglycerine (PG)-Pentaerythritol (PE) Phase Diagram

Pentaerythritol (PE) and Pentaglycerine (PG) phase was investigated by Barrio et al. Thermal analysis and X-ray Guinier-Simon method was used by the authors to characterize PE-PG alloys from room temperature to liquid phase. The alloys were prepared by melting the desired composition in a furnace and slow cooling to room temperature.

PE and PG are iso-structural, both at room temperature (body centered tetragonal) and high temperature phases (FCC). Low temperature phase of PE is characterized by strong intermolecular hydroxyl hydrogen bonding between molecule and eight of its neighbors.
in a layer parallel to the (001) plane. The interlayer bonds are weak and due to Van der Waals forces. PG has similar bonding scheme to PE except that one link is open, due to substitution by -CH$_2$OH group in the PE molecule for a –CH$_3$ group in the PG molecule. I4 symmetry of PG requires the presence of a statically disordered molecule since the
required site symmetry, 4, is not present in PG molecule as in PE. As reported previously, the crystal to plastic transformation in PE and PG are first order transitions. Nitta suggested correlation between the hydrogen bond breaking at higher temperatures permitting rotation and molecular vibration leading to plastic phase. Benson et al. measured infrared absorption for PE and indicated that all the hydrogen bonds are broken at the transition temperature. Taking into account the enthalpy variations for the crystal-plastic phase transition in PE in which there are four hydrogen bonds for each molecule, the maximum energy value for one bond is about 10 kJmol⁻¹. This result also matches the enthalpy variation for the crystal to plastic phase transition in PG, in which there are two hydrogen bonds for each molecule on average.

Bragg’s angles reflection were analyzed for establishing the solubility regions of PE and PG. The absence of splitting in these reflections (002) and the continuous variation of Bragg’s angles with composition suggest total miscibility at 293 K. It was found that ‘a’ parameter of PE showed 0.55% expansion and ‘c’ parameter showed a contraction of 1.45% throughout the system. Thus, it was concluded that taking into account the estimated error, the system behave as quasi-ideal from a crystallographic point of view. The difference in evolution of ‘a’ and ‘c’ is due to strong hydrogen bonds in (001) plane and weak interlayer Van de Waals forces. The temperatures obtained from thermal analysis are in Table 2-10. Benson et al. also obtained PG-NPG thermal measurements using DSC and reported their data as shown in Table 2-11.  

Figure 2-12 shows the experimental phase diagram of PE-PG. PE-PG phase diagram is characterized by a very narrow plastic to liquid domain, which has a maximum width of about 3 K and a wide crystal to plastic equilibrium domain with a maximum width of
about 44 K for the central compositions. Calculated phase diagram is based on Oonk’s method which uses the concept of Equal Gibbs Curve (EGC). The phase diagram shows two domains of complete miscibility; one at lower temperature with tetragonal structure.

### Table 2-10. Characteristic temperatures of PEₙPG₁₋ₓ

<table>
<thead>
<tr>
<th>Xₑ</th>
<th>Tₑstart, K</th>
<th>Tₑfinish, K</th>
<th>Tₑsolidus, K</th>
<th>Tₑliquidus, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>353.5 ± 1.0</td>
<td>-</td>
<td>459.1 ± 1.0</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>360.4 ± 1.0</td>
<td>369.7 ± 11.2</td>
<td>461.1 ± 1.9</td>
<td>462.0 ± 1.0</td>
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<tr>
<td>0.2</td>
<td>367.3 ± 1.0</td>
<td>393.6 ± 2.0</td>
<td>468.0 ± 1.0</td>
<td>469.9 ± 1.0</td>
</tr>
<tr>
<td>0.3</td>
<td>372.6 ± 1.4</td>
<td>410.0 ± 1.0</td>
<td>474.6 ± 1.4</td>
<td>476.8 ± 1.0</td>
</tr>
<tr>
<td>0.4</td>
<td>380.3 ± 1.4</td>
<td>422.6 ± 1.9</td>
<td>480.6 ± 1.1</td>
<td>483.4 ± 2.8</td>
</tr>
<tr>
<td>0.5</td>
<td>386.3 ± 2.4</td>
<td>430.4 ± 2.1</td>
<td>487.9 ± 1.5</td>
<td>491.0 ± 1.3</td>
</tr>
<tr>
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<td>437.6 ± 1.6</td>
<td>495.1 ± 2.0</td>
<td>498.0 ± 1.0</td>
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<tr>
<td>0.7</td>
<td>409.1 ± 1.9</td>
<td>444.2 ± 1.4</td>
<td>502.1 ± 3.4</td>
<td>504.6 ± 1.0</td>
</tr>
<tr>
<td>0.8</td>
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<td>449.9 ± 2.9</td>
<td>509.1 ± 1.0</td>
<td>511.5 ± 1.6</td>
</tr>
<tr>
<td>0.9</td>
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<td>453.8 ± 1.0</td>
<td>518.1 ± 1.0</td>
<td>520.0 ± 1.0</td>
</tr>
<tr>
<td>1</td>
<td>460.7 ± 1.0</td>
<td>-</td>
<td>534.5 ± 1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2-11. PEₙPG₁₋ₓ transition properties.

<table>
<thead>
<tr>
<th>Xₑ</th>
<th>Phase Change Temperature, K</th>
<th>Enthalpy of Transformation, kJ/mol</th>
<th>Specific Heat, J/mol.K</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.00</td>
<td>460.00</td>
<td>36.80</td>
<td>387.00</td>
</tr>
<tr>
<td>86.10</td>
<td>442.00</td>
<td>31.80</td>
<td>387.00</td>
</tr>
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<td>72.60</td>
<td>422.00</td>
<td>28.80</td>
<td>394.00</td>
</tr>
<tr>
<td>57.00</td>
<td>401.00</td>
<td>21.30</td>
<td>393.00</td>
</tr>
<tr>
<td>50.00</td>
<td>397.00</td>
<td>22.30</td>
<td>417.00</td>
</tr>
<tr>
<td>37.00</td>
<td>381.00</td>
<td>21.60</td>
<td>411.00</td>
</tr>
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<td>22.70</td>
<td>373.00</td>
<td>18.60</td>
<td>381.00</td>
</tr>
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<td>11.20</td>
<td>361.00</td>
<td>17.40</td>
<td>321.00</td>
</tr>
<tr>
<td>0.00</td>
<td>355.00</td>
<td>16.70</td>
<td>337.00</td>
</tr>
</tbody>
</table>
and another one at higher temperature plastic phase with cubic structure. Finally, the authors concluded that the plastic alloys behavior can be considered as ideal.

Figure 2-12. Phase Diagram of the PE-PG system. ( - Calculated; . . . – EGC curve; - - Experimental)
2.7 Basic Phase Rule

As propounded by Willard Gibbs, the phase rule is fundamental to the study of phase/equilibrium diagrams. Only a brief introduction is given here to help understand interpret and construct phase diagrams. The phase rule expresses the relationship, at equilibrium, of the number of phases, \( P \), with the number of components, \( C \), and the number of degrees of freedom, \( F \). The rule may be written as follows –

\[
P + F = C + 2 \tag{2-1}
\]

The phase is defined as the homogenous art of the system, bounded by surfaces, and in principle, can be separated mechanically. Phases generally show compositional variations.

The number of components is defined as the smallest number of independently variable constituents necessary for the statement of the compositions of all the phases in the system, for example, the number of constituent metals.

The number of degrees of freedom of the equilibrium state is the number of conditions that can be altered independently without changing the state of the system, or which have to be specified to define completely the state of the system. In equation 2-1, it has been assumed that only temperature, pressure and composition are the only externally controllable variables that influence the phase equilibria.

In ternary systems, two compositions need to be defined/specified to define the system. In systems where pressure is assumed as constant, the phase rule reduces to

\[
P + F = C + 1 \tag{2-2}
\]
Applying this reduced ‘phase rule’ to ternary system with $C = 3$, gives

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tbody>
<tr>
<td>P</td>
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</tr>
<tr>
<td>F</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

### 2.8 Ternary Space Model

To represent the complete ternary phase system, a ternary space model is required wherein the composition requires two dimensions and temperature is third dimension. The model that fits this description is a triangular prism.

![Triangular space model for ternary systems.](image)

In this model, the vertical sides of the prism represent three binary systems, $AB$, $BC$, and $AC$ that make up the ternary system $ABC$.

The composition triangle is represented by an equilateral triangle with lines parallel to its sides. Three corners represent three components and the length of each side of the triangle is divided into 100 equal parts where each part represents 1% on the composition scale in each binary system.
For example, as shown in Figure 2-14, consider plotting the alloy composition in which A is 40%, B is 20% and C is 40%. Starting from A, a length Az corresponding to 40% C is marked along AC and then length Ax corresponding to 40% A is marked along AB. The composition point of the alloy lies at the intersection, y, of lines yz and yx.
2.9 References

Chapter 3

Experimental Methods

3.1 Differential Scanning Calorimeter

Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes:

Here \( \frac{dH}{dt} \) is the heat flow measured in mcal / sec. The heat flow difference between the sample and the reference is:

\[
\Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}}
\]

and can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence \( \Delta dH/dt \) is positive. Other endothermic processes include helix-coil transitions in DNA, protein denaturation, dehydrations, reduction reactions, and some decomposition reactions. In an exothermic process, such as crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions, the opposite is true and \( \Delta dH/dt \) is negative.
The calorimeter consists of a sample holder and a reference holder as shown in Figure 3-1. Both are constructed of platinum to allow high temperature operation. Under each holder is a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. The difference in the power to the two holders, necessary to maintain the holders at the same temperature, is used to calculate $\Delta dH/dt$. A schematic diagram of a DSC is shown in Figure 3-2. A flow of nitrogen gas is maintained over the samples to create a reproducible and dry atmosphere. The nitrogen atmosphere also eliminates air oxidation of the samples at high temperatures. The sample is sealed into a small aluminum pan. The reference is usually an empty pan and cover. The pans hold up to about 10 mg of material.

During the heating of a sample, for example, from room temperature to its decomposition temperature, peaks with positive and negative $\Delta dH/dt$ may be recorded; each peak corresponds to a heat effect associated with a specific process, such as crystallization or melting.
Figure 3-2. (a) A General schematic of a DSC. The triangles are amplifiers that determine the difference in the two input signals. The sample heater power is adjusted to keep the sample and reference at the same temperature during the scan and (b) Typical DSC scan. The heat capacity of the sample is calculated from the shift in the baseline at the starting transient. Glass transitions cause a baseline shift. Crystallization is a typical exothermic process and melting a typical endothermic process, $\Delta H_n$ is calculated from the area under the peaks. Few samples show all the features shown in this thermogram.
The question arises as to what kind of information is obtainable from a DSC curve. The first and most direct information is the temperature at which a certain process occurs, for example, the melting point of a polymer. The temperature at which a reaction, such as decomposition, may start is another important parameter. The peak temperature is associated with the temperature at which maximum reaction rate occurs.

A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, $T_g$. This is the temperature at which amorphous (non-crystalline) polymers are converted from a brittle, glasslike form to a rubbery, flexible form. This is not a true phase transition but one that involves a change in the local degrees of freedom. Above the glass transition temperature certain segmental motions of the polymer are comparatively unhindered by the interaction with neighboring chains. Below the glass transition temperature, such motions are hindered greatly, and the relaxation times associated with such hindered motions are usually long compared to the duration of the experiment. The operative definition of glass transition temperature is that at this temperature, or within a few degrees, the specific heat, the coefficient of thermal expansion, the free volume, and the dielectric constant (in the case of a polar polymer) all change rapidly. Since the mechanical behavior of polymers changes markedly at the glass transition temperature, it is an important characteristic of every polymer. In the DSC experiment, $T_g$ is manifested by a drastic change in the base line, indicating a change in the heat capacity of the polymer (Figure 3-3). No enthalpy is associated with such transition (for which reason it is also called a second order transition); therefore, the effect in a DSC curve is slight and is observable only if the
instrument is sensitive enough. The second direct information obtainable from DSC curves is the enthalpy associated with certain processes.

![Diagram of Heat flux and Glass transition](image)

**Figure 3-3.** Glass transition. If there are sloping baselines before and after the glass transition, extrapolate the baselines forwards and backwards (as shown by dotted lines) and take the baseline shift when the transition is about 63% complete (as shown by arrows).

### 3.2 Theory

The integral under the DSC peak, above the baseline, gives the total enthalpy change for the process:

\[
\int \left( \frac{dH}{dt} \right)_{\text{sample}} \, dt = \Delta H_{\text{sample}} \quad \text{Equation 3-1}
\]

Assuming that the heat capacity of the reference is constant over the temperature range covered by the peak, \( \Delta H_{\text{reference}} \) will cancel out because the integral above the baseline is taken. Therefore, equation 2 is also valid when the integral is taken from the DSC plot of \( \Delta dH/dt \). Heat capacities and changes in heat capacity can be determined from the shift in the baseline of the thermogram. The heat capacity is defined as:
\[ C_p = \left( \frac{dq}{dT} \right)_p = \left( \frac{dH}{dT} \right)_p \]

Equation 3-2

The temperature scan rate is:

\[ \text{scan rate} = \frac{dT}{dt} \]

Using the chain rule:

\[ C_p = \left( \frac{dH}{dT} \right) = \frac{dH}{dt} \cdot \frac{dt}{dT} \]

Equation 3-3

where \( \frac{dH}{dt} \) is the shift in the baseline of the thermogram and the last derivative is just the inverse of the scan rate. For differential measurements, we determine the difference in the heat capacity of the sample and the reference:

\[ \Delta C_p = C_p(\text{sample}) - C_p(\text{reference}) \]

\[ \Delta C_p = \Delta \left( \frac{dH}{dT} \right) = \Delta \frac{dH}{dt} \cdot \frac{dt}{dT} \]

Equation 3-4

The units of the heat flow are mcal sec\(^{-1}\) and the temperature scan rate is usually expressed as °C min\(^{-1}\). So to be consistent with units you must multiply by 60 sec min\(^{-1}\):

\[ \Delta C_p = \left( \frac{\text{mcal}}{\text{sec}} \right) \cdot \left( \frac{\text{min}}{\text{°C}} \right) \cdot \left( \frac{60 \text{ sec}}{\text{min}} \right) \]

Equation 3-5

3.3 Working Principle

In a heat flux DSC system, the sample and reference pans are placed on raised constantan (45% Ni – 55% Cu) platforms. The heat is transferred through these platforms and measured by area thermocouples, which are made from chromel wafers. The differential heat flow to the sample and reference is measured using thermal equivalent of Ohm’s law.
\[
\frac{dQ}{dt} = \frac{\Delta T}{R_D} \quad \text{Equation 3-6}
\]

where \( \frac{dQ}{dt} \) is the heat flow, \( \Delta T \) is temperature difference between sample and reference pans, and \( R_D \) is the resistance of thermoelectric (constantan) disk.

In order to account for the extraneous heat flow within the sensor or between the sensor pan, TA instruments apply \( T^\text{zero} \) technology. Mathematically, it is represented as

\[
Q = -\frac{\Delta T}{R_r} + \Delta T_o \left( \frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{dt} - C_r \frac{d\Delta T}{dt} \quad \text{Equation 3-7}
\]

where, \(-\Delta T/R_r\) represents the conventional DSC heat flow,

\( \Delta T = T_s - T_r \)

\( \Delta T_o(1/R_s - 1/R_r) \) accounts for the additional heat flow due to the imbalance in the sample and reference thermal resistances,

\( \Delta T_o = T_o - T_s \)

\((C_r - C_s) \frac{dT_s}{dt}\) represents the heat flow due to the thermal capacitances imbalance, and

\(-C_r \frac{d\Delta T}{dt}\) accounts the difference in the sample and reference sensor heating rate. This term has significant influence during enthalpy related transitions.

The inclusion of additional terms allows for the accurate measurement of baseline.
3.4 X-ray Diffractometry

3.4.1 Bragg-Brentano Diffractometry

Powder X-ray diffraction was used for investigating the structural properties of polyalcohols. An in-situ setup was employed to study the phase changes in the binary system with temperature.

In this technique, an x-ray of known wavelength is focused on the unknown sample. This monochromatic radiation is diffracted by the sample which is measured by an electronic pulse counter. This device converts incoming diffracted x-rays into the pulses of electric current. This counter number is directly proportional to the intensity of the x-ray beam.

The essential features of a diffractometer are shown in Figure 3-4. A powder sample C, either in the form of flat sample or in a quartz capillary, is placed on table H. x-ray source S is normal to the plane of the paper and is hence parallel to the diffractometer axis O. X-rays diverged from the sample pass through slit F and enter the pulse counter G. A and B are special slits for collimating the incident and diffracted beam. The receiving slits are supported on the carriage E, which may be rotated about the axis O and its angular position is given by $2\theta$. the supports E and H are mechanically coupled such that a rotation of the counter by $2x$ degrees leads to a sample rotation of $x$ degrees. The counter is driven constantly at an angular velocity through increasing values of $2\theta$. 
The diffractometer used in this study was a PANalytical X’pert PRO X-ray Diffraction System. A Ni-filter was used to obtain a Cu Ka beam at 40 kV and 40 mA. The scan covered a range from 10˚ to 70˚ in steps of 0.02˚ with 2 second counts at each step. A Si standard was mixed in all the samples which act as an internal standard for calibrating the instrument and aligning the x-ray spectra with JCPDS files. A photograph of the TTK-450 sample stage for in-situ powder x-ray diffraction is shown in Figure 3-5. In addition to that, capillary method was used to measure x-ray diffraction data. Because of the high vaporization at elevated temperatures, the specimen composition might be altered. To prevent the loss of specimen due to evaporation, a very small amount of specimen is sealed inside a 1mm quartz capillary and loaded in to the custom-made fixture for the capillary. Heating of the capillary is done by a tubular heater which utilizes air. An external thermocouple monitors the capillary temperature. A photograph of the capillary setup is shown in Figure 3-6.
Figure 3-5. Actual view of the sample holder for the in-situ x-ray measurement for obtaining the crystallographic data. Specimen is placed in the sample holder and real-time temperature is controlled with an in-built thermocouple.

Figure 3-6. A picture of the capillary method setup for obtaining x-ray diffraction of the specimen at elevated temperatures without altering the composition.
3.4.2 Guinier High Temperature Diffractometry\textsuperscript{1}

Some parts of the PE-NPG phase diagram was determined using in-situ high temperature, high resolution Guinier x-ray diffractometry equipped with a Seeman-Bohlin focusing geometry using a Huber-Guinier x-ray diffraction system with a high temperature film attachment. Film technique allows the step-wise in-situ recording of diffraction patterns at different temperatures. Figure 3-7 shows the focusing geometry of this type of camera. It is a cylindrical camera with the specimen and film arranged on the surface of the cylinder. Camera is placed on position ‘C’ with ‘D’ as specimen position. Focal point ‘F’ of the monochromatic beam acts as a virtual source of divergent radiation. The diffracted rays from the sample/specimen are focused on the film for all hkl reflections. The requirement for this camera is that the film should be placed on a circle passing through the specimen and the focal point ‘F’.

![Figure 3-7. Schematic of Guinier x-ray diffractometer.](image)

Guinier camera provides a twice the resolution than Debye-Scherer camera for the same exposure time. This type of camera covers only a limited range of $2\theta$ which makes it a very useful tool for observing complex patterns.\textsuperscript{2}.
A Germanium crystal monochromator was used to obtain Cu Kα₁ radiation. Cassette holder was advanced using a Research Inc. Microstar controller model 838D which also controlled the in-situ furnace temperature. Around nine to twelve patterns were obtained on one film. A modified furnace was used to heat the sample in the quartz capillaries. The Guinier diffractometer was interfaced with a Microvax II DEC computer. The capillary was sealed with high temperature stable epoxy to prevent loss of sample due to heating. This is very important in case of polyalcohols which have high vapor pressure and sealing the capillary prevents compositional inhomogeneity.

3.5 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance, or NMR as it is abbreviated by scientists, is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin.

The following features lead to the NMR phenomenon:

1. A spinning charge generates a magnetic field. The resulting spin-magnet has a magnetic moment (µ) proportional to the spin.

2. In the presence of an external magnetic field (B₀), two spin states exist, +1/2 and -1/2. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field, Figure 3-8.

3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small, Figure 3-9. The following
Figure 3-8. Spin energy states with the application of external magnetic field.

The diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to $B_x$ a formula for the energy difference is given (remember $I = 1/2$ and $\mu$ is the magnetic moment of the nucleus in the field).

Figure 3-9. Energy as a function of induced external Magnetic Field.

Strong magnetic fields are necessary for NMR spectroscopy. The international unit for magnetic flux is the Tesla (T). The earth's magnetic field is not constant, but is approximately $10^{-4}$ T at ground level. Modern NMR spectrometers use powerful magnets.
having fields of 1 to 20 T. A Varian 500MHz NMR instrument shown in Figure 3-10 was used for recording NMR spectra from the specimens.

![Varian 500MHz NMR instrument at UNR.](image)

**3.5.1 Quantitative Proton NMR (qNMR)**

To begin with, the NMR spectrometer must be tuned to a specific nucleus, in this case the proton. The actual procedure for obtaining the spectrum varies, but the simplest is referred to as the continuous wave (CW) method. A typical CW-spectrometer is shown in the following diagram. A solution of the sample in a uniform 5 mm glass tube is oriented between the poles of a powerful magnet, and is spun to average any magnetic field variations, as well as tube imperfections. Radio frequency radiation of appropriate energy is broadcast into the sample from an antenna coil (colored red). A receiver coil surrounds the sample tube, and emission of absorbed rf energy is monitored by dedicated electronic devices and a computer. An NMR spectrum is acquired by varying or sweeping the
magnetic field over a small range while observing the rf signal from the sample. An equally effective technique is to vary the frequency of the rf radiation while holding the external field constant.

All protons do not give one peak, the peak position of proton resonance, chemical shift, depends on the immediate molecular environment of the proton. In each molecule, the electron(s) surround the proton in covalent compounds and ions. Since electrons are charged particles, they move in response to the external magnetic field ($B_o$) so as to generate a secondary field that opposes the much stronger applied field. This secondary field shields the nucleus from the applied field, so $B_o$ must be increased in order to achieve resonance (absorption of rf energy).

Samples are dissolved in a deuterated solvent such as D$_2$O because deuterium ions are invisible to the NMR equipment which is tuned to proton frequency.

In NMR, chemical shifts are usually referred in units of parts per million (ppm). The most significant feature of qNMR is the direct proportionality of the signal intensity to the number of protons contributing to the resonance. The structures of the chemicals thus become irrelevant. The signal ratio of two different protons can be measured with tremendous precision and the only significant contribution to the measurement uncertainty is the integration of the signals.
For achieving good quantitative NMR (qNMR) results, there are certain basic requirements.

1. Accurately weigh the sample and reference prior to qNMR measurements.
2. Availability of a reference material for internal calibration.
3. The reference substance and sample must not interact/react with each other or solvent.
4. The relevant signals which are selected for measurement must be clearly separated from each other and from other signals.
5. Appropriate instrument settings must be in place to avoid any loss of intensity due to incomplete relaxation.

Figure 3-11. Schematic of NMR instrument."
3.5.2 Preparation of standard and test solution

Stock solution of Internal Standard Maleic acid (10.00 mg/0.6ml) was prepared. 166.00 mg of Maleic acid was weighed accurately and mixed with 10 mL of Deuterated water, D$_2$O in a volumetric flask. The solution is mixed gently for 10 minutes.

Sample for qNMR was prepared by accurately weighing 10.00 mg of sample powder and adding 0.6 ml of stock solution of Maleic acid.

3.5.3 NMR data Calculations

The amount $W_x$ of the unknown component was calculated using the following equations

$$W_x = \frac{I_x}{I_{std}} \frac{N_{std}}{N_x} \frac{M_x}{M_{std}} W_{std}$$  \hspace{1cm} \text{Equation 3-8}

Where $W_x = \text{weight of the unknown sample (mg)}$. 

Figure 3-12. $^1$HNMR spectra of qNMR standards, Maleic Acid in D$_2$O.
\[ I_x = \text{mean Integral value of the analyte } ^1\text{H signal obtained at} \]
\[ 3.44 \text{ ppm for PE; 3.33 ppm for PG; 3.22 ppm for NPG} \]
\[ I_{\text{std}} = \text{Integral value of the } ^1\text{H signal obtained for Maleic Acid at 6.25 ppm} \]
\[ N_{\text{std}} = \text{Number of Protons for the Maleic Acid (}=2) \]
\[ N_x = \text{Number of protons for the analyte in solution (4 for NPG, 8 for PE, and 6 for PG)} \]
\[ M_x = \text{Molecular weight of the analyte (104.15 for NPG, 136.15 for PE, and 120.15 for PG in g/mole)} \]
\[ M_{\text{std}} = \text{Molecular weight of the Standard Maleic Acid (116.07 g/mole)} \]
\[ w_{\text{std}} = \text{weight of the Maleic acid (mg)} \]

NMR was conducted on pure PE, PG and NPG and peaks were identified so that there was no overlapping, Table 3-1. Only CH\(_3\), methyl, peaks were common to PG and NPG.

Table 3-1. NMR peak position of PE, PG and NPG in Deuterated water.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>NMR peaks (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>3.44</td>
</tr>
<tr>
<td>PG</td>
<td>3.33</td>
</tr>
<tr>
<td>NPG</td>
<td>3.22</td>
</tr>
<tr>
<td>D2O</td>
<td>4.66</td>
</tr>
<tr>
<td>Maleic Acid</td>
<td>6.28</td>
</tr>
<tr>
<td>CH3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

3.6 Preparation of Polyalcohol binaries and Ternaries

Sample preparation of polyalcohol binaries needs careful attention due to possibility of undercooling of high temperature phases to room temperature or lower. Therefore, care must be taken to attain thermodynamic equilibrium, which is necessary for characterization of these samples with respect to crystal structure and thermal analyses.
In the present research, procedure delineated by Barrett et al.\textsuperscript{5} was followed. All chemical were obtained from Sigma-Aldrich with 99% purity. Specimens, mixed in respective proportions in a Pyrex glass tube with cap, were melted and slowly cooled to room temperature to provide diffusion homogeneity. To attain equilibrium phases, following procedure was used –

1. The solidified samples were kept in freezer (\textasciitilde -25\degree C) for overnight.

2. The frozen sample was taken out and ground in a mortar and pestle.

3. These ground powders were then compacted into a disk form of approximately \(\frac{3}{4}\)" diameter, with thickness varying from \(\sim 1/8\)" to \(3/16\)" such that undercooled phases get precipitated out by application of strain energy. Place the disks in a freezer for overnight.

4. The frozen disks are again crushed and ground using mortar and pestle into powder form. The samples were then suitably characterized.

5. A portion of the sample was mixed with Silicon powder and placed in 1.0 mm diameter Charles Supper Company’s quartz capillaries, sealed with high temperature epoxy, for high temperature Diffractometry studies.

6. Some portion of the same sample was used for DSC experiments.
### 3.7 References

4. [http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectropy/nmr/nmr1.htm](http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectropy/nmr/nmr1.htm), accessed 26 May 2011.
Chapter 4

PE-NPG Binary System Results and Discussion

Phase transitions in PE-NPG binary system were determined by X-ray diffraction, Guinier high temperature diffractometry and Differential Scanning Calorimetry (DSC). A number of solid solution samples of the binary PE-NPG compositions were investigated to gain understanding of the phase transitions and crystal structure changes related to this system. X-ray diffraction results illustrate the structure changes and their stability over a range of temperature and DSC indicates the actual transition temperatures. Phase boundaries were based on DSC results.

Phase Terminology:

\( \alpha \) = low temperature PE

\( \beta \) = low temperature NPG

\( \gamma' \) = high temperature PE

\( \gamma \) = high temperature NPG

4.1 NPG-rich region – Pure NPG

X-ray diffraction patterns of pure (as received) Neopentylglycol (NPG) were obtained from 25\(^\circ\)C to its melting point (129 \(^\circ\)C). From room temperature to 40\(^\circ\)C, there is pure \( \beta \) phase which is monoclinic structure. At 40\(^\circ\)C, the low temperature monoclinic phase changes to high temperature stable FCC \( \gamma \) phase, when Braggs’ peaks for \( \beta \) phase disappear and new peaks for \( \gamma \) phase appear.
Figure 4-1. X-ray Diffraction Patterns of Pure NPG showing $\beta \rightarrow \gamma$ phase transition.

$\beta \rightarrow \gamma \rightarrow L$

25-40 °C  40-130 °C  130 °C

DSC scan of pure NPG is shown in Figure 4-2. The $\beta$ to $\gamma$ phase transition occurs at around 41°C, depicted by an endotherm. As per DSC data, phase transitions are obtained as follows –

$\beta \rightarrow \gamma \rightarrow L$

25-41 °C  41-129 °C  129 °C

4.2 Dilute Solution of PE in NPG (5 mol% PE)

X-ray diffraction pattern for the PE-5 mol% -NPG 95 mol% is shown in Figure 4-3. The X-ray pattern taken at different temperatures show solid-state transitions and solid-liquid
transitions. The $\beta$ phase (NPG monoclinic structure) Bragg peaks disappear after 41°C and it transforms to high temperature $\gamma$ phase which is face centered cubic in structure. The $\beta$ phase Bragg peaks are not very apparent till 80°C because of overlapping with

![Figure 4-2. DSC scan of pure NPG showing $\beta \rightarrow \gamma$ endothermic phase transition at 43°C.](image)

$\alpha$ PE peaks. From 41°C to 100°C, there is a two phase region, $\alpha + \gamma$, as shown by peaks from both the phases. At around 100°C, all of the $\alpha$ phase transforms to $\gamma$ phase.
Figure 4-3. X-ray Diffraction Patterns of 95NPG-5PE, showing $\beta \rightarrow \gamma$ phase transitions at 41°C. $\alpha + \beta$ is stable from 25-41°C and $\alpha + \gamma$ exists between 41-152°C.

**XRD Phase transitions –**

- $\alpha + \beta$ 41 °C
- $\alpha + \gamma$ 41 °C – 100 °C
- $\gamma$ 100 °C – 134 °C
- $\gamma + L$ 134 °C – 152 °C
- L 152 °C

**DSC Phase transitions –**

- $\alpha + \beta$ 25 °C – 43 °C
- $\alpha + \gamma$ 43 °C – 105 °C
- $\gamma$ 105 °C – 130 °C
- $\gamma + L$ 130 °C – 147 °C
- L 147 °C
Between 100 °C and 134 °C, only γ phase is present. From 134 °C to 152 °C, there is a two phase region comprising of γ phase and liquid phase. Presence of a liquid phase is observed as peak intensity reduction after 134 °C. DSC pattern of this composition, Figure 4-4, shows two endotherms and a broad hump. The first endothermic peak is the transformation of β phase to γ phase at ~ 41°C and the second endotherm represents γ phase going to liquid phase. The broad hump has been interpreted as heat of mixing of α and γ phases. As the composition is changing with increase in temperature and when α phase transforms to γ phase, there is absorption of heat, thus showing an endothermic hump. These phase transition temperatures match very well with the X-ray data.
4.3 Dilute Solution of PE in NPG (10 mol% PE)

Powder X-ray diffraction pattern of 10 mol% PE is shown in Figure 4-5. From the pattern, it is quite evident that the $\beta$ phase Bragg peaks disappear after 41°C and it transforms to high temperature $\gamma$ phase at 41°C which is face centered structure. The $\gamma$ phase Bragg peaks are not very apparent till 90°C because of overlap between $\alpha$-PE peaks and $\gamma_{NPG}$ peaks.

From 41°C to 120°C, there is a two phase region, $\alpha + \gamma$, as shown by peaks from both the phases. At around 120°C, all of the $\alpha$ phase transforms to $\gamma$ phase. Between 120°C and 140°C, only $\gamma$ phase is present. After 140°C, there is $L + \gamma$ phase present till ~155°C. Presence of liquid phase is observed from the peak intensity reduction after 140°C.

<table>
<thead>
<tr>
<th>DSC Phase transitions –</th>
<th>XRD Phase transitions –</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha + \beta$</td>
<td>25°C – 43°C</td>
</tr>
<tr>
<td>$\alpha + \gamma$</td>
<td>43°C – 120°C</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>120°C – 138°C</td>
</tr>
<tr>
<td>$\gamma + L$</td>
<td>138°C – 150°C</td>
</tr>
<tr>
<td>L</td>
<td>150°C</td>
</tr>
<tr>
<td>$\alpha + \beta$</td>
<td>41°C</td>
</tr>
<tr>
<td>$\alpha + \gamma$</td>
<td>41°C – 120°C</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>120°C – 140°C</td>
</tr>
<tr>
<td>$\gamma + L$</td>
<td>140°C – 155°C</td>
</tr>
<tr>
<td>L</td>
<td>155°C</td>
</tr>
</tbody>
</table>
Figure 4-5. In-situ x-ray diffraction patterns of 90NPG-10PE from 25-150°C, showing β → γ phase transition.
Figure 4-6. DSC pattern of 90NPG-10PE with two endothermic peaks and a broad two phase mixing zone. $\beta \rightarrow \gamma$ occurs at ~ $42^\circ$C and $\alpha$ dissolves in to $\gamma$ phase at $120^\circ$C.

### 4.4 Dilute Solution of PE in NPG (15 mol% PE)

X-ray diffraction pattern of 15 mol% PE is shown in Figure 4-7. From the pattern, $\beta$ phase Bragg peaks are observed up to $42^\circ$C. At $42^\circ$C, $\beta$ phase transforms to high temperature face centered cubic $\gamma$ phase. The $\gamma$ phase Bragg peaks are not very apparent till $115^\circ$C because of overlap between $\alpha$–PE peaks and $\gamma_{\text{NPG}}$ peaks.

From $42^\circ$C to $120^\circ$C, there is a two phase region, $\alpha + \gamma$, as shown by peaks from both the phases. At around $120^\circ$C, all of the $\alpha$ phase transforms to $\gamma$ phase. Between $120^\circ$C
and 140 °C, only γ phase is present. After 140 °C, there is liquid + γ phase present till ~155 °C. Liquid phase is observed beyond 140 °C.

Figure 4-7. X-ray diffraction patterns of 85NPG-15PE, showing β → γ phase transition and α + β and α + γ phase regions.
Figure 4-8. DSC pattern of 85NPG-15PE, showing two endothermic peaks and a broad two phase mixing zone. $\beta \rightarrow \gamma$ occurs at ~42°C and $\alpha$ dissolves in to $\gamma$ phase at 120°C.

DSC Phase transitions –

$\alpha + \beta$ 25 °C – 42.7 °C

$\alpha + \gamma$ 42.7 °C – 115 °C

$\gamma$ 115 °C – 138 °C

$\gamma + L$ 138 °C – 167 °C

L 167 °C

XRD Phase transitions –

$\alpha + \beta$ 43 °C

$\alpha + \gamma$ 43 °C – 135 °C

$\gamma$ 135 °C – 150 °C

$\gamma + L$ 150 °C – 160 °C

L 160 °C
### 4.5 Phase Transitions in PE in NPG (20 mol% PE)

X-ray diffraction pattern of 20 mol% PE is shown in Figure 4-9. From the pattern β phase Bragg peaks are observed up to 43°C. At 43°C, β phase transforms to high temperature γ-face centered cubic structure. The γ phase Bragg peaks are not very apparent till 115 °C because of overlap between α–PE peaks and γ\textsubscript{NPG} peaks.

From 43 °C to 140 °C, there is a two phase region, α + γ, as shown by peaks from both the phases. At around 140 °C, all of the α phase transforms to γ phase. Between 140 °C and 150 °C, only γ phase is present. After 150 °C, there is liquid + γ phase present till ~155 °C. Presence of liquid phase is observed due to peak intensity reduction after 150 °C.

<table>
<thead>
<tr>
<th>DSC Phase transitions –</th>
<th>XRD Phase transitions –</th>
</tr>
</thead>
<tbody>
<tr>
<td>α + β</td>
<td>α + β</td>
</tr>
<tr>
<td>25 °C – 41.52 °C</td>
<td>42 °C</td>
</tr>
<tr>
<td>α + γ</td>
<td>α + γ</td>
</tr>
<tr>
<td>41.52 °C – 115 °C</td>
<td>42 °C – 145 °C</td>
</tr>
<tr>
<td>γ</td>
<td>γ</td>
</tr>
<tr>
<td>115 °C – 145 °C</td>
<td>145 °C – 160 °C</td>
</tr>
<tr>
<td>γ + L</td>
<td>L</td>
</tr>
<tr>
<td>154 °C – 172 °C</td>
<td>&gt; 160°C</td>
</tr>
</tbody>
</table>
Figure 4-9. X-ray diffraction patterns of 80NPG-20PE from 25 - 160°C, showing $\beta \rightarrow \gamma$ phase transition. Between 140-150°C, only $\gamma$ phase is stable.
4.6 Phase Transitions in 75 mol% NPG - 25 mol% PE

X-ray diffraction pattern of 25 mol% PE is shown in Figure 4-11. From the pattern, β phase Bragg peaks are observed up to 40°C. At 40°C, β phase transforms to high temperature γ phase which is face centered cubic structure. There is overlap between α–PE and γNPG Bragg peaks till 125 °C. From 40 °C to 140 °C, there is a two phase region, α + γ, as shown by peaks from both the phases. At around 140 °C, all of the α phase transforms to γ phase which is stable up to 155 °C. Liquid phase appears after about 150°C. All of γ phase transforms to liquid at temperatures > 170 °C.
Figure 4-11. X-ray diffraction patterns of 75NPG-25PE. $\beta \rightarrow \gamma$ occurs at ~ 42°C and $\alpha + \gamma$ is stable from 42-140°C when $\alpha$ dissolves into $\gamma$ phase. $\gamma$ exists between 140-155°C.
Figure 4-12. DSC pattern of 75NPG-25PE sample. The first peak is $\beta \rightarrow \gamma$ transition, broad hump is $\alpha + \gamma$ mixing, small hump between -110-155°C is $\gamma$ phase; last peak is for melting (165°C).

DSC Phase transitions –  
- $\alpha + \beta$ 25 °C – 41.4 °C 
- $\alpha + \gamma$ 41.4 °C – 115 °C 
- $\gamma$ 115 °C – 150 °C 
- $\gamma + L$ 150 °C – 175 °C 
- $L$ > 165 °C

XRD Phase transitions – 
- $\alpha + \beta$ 43 °C 
- $\alpha + \gamma$ 43 °C – 160 °C 
- $\gamma$ 160 °C – 170 °C 
- $L$ > 165 °C
4.7 Phase Transitions in 70 mol% NPG - 30 mol% PE

X-ray diffraction pattern of 30 mol% PE is shown in Figure 4-13. β phase Bragg peaks are observed up to 40˚C after which the phase transforms to high temperature γ phase. From 40 °C to 140 °C, there is a two phase region, α + γ, as shown by peaks from both the phases. All of the α phase transforms to γ phase at around 160 °C. Between 160 °C and 165 °C, only γ phase is present. Liquid phase is observed at > 175 °C.

DSC Phase transitions –

<table>
<thead>
<tr>
<th>Transition</th>
<th>± °C</th>
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<tbody>
<tr>
<td>α + β</td>
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<tr>
<td>α + γ</td>
<td>41.7 - 112</td>
</tr>
<tr>
<td>γ</td>
<td>112 - 170</td>
</tr>
<tr>
<td>γ + L</td>
<td>170 - 180</td>
</tr>
<tr>
<td>L</td>
<td>180</td>
</tr>
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</table>

XRD Phase transitions –

<table>
<thead>
<tr>
<th>Transition</th>
<th>± °C</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>α + γ</td>
<td>43 - 160</td>
</tr>
<tr>
<td>γ</td>
<td>160 - 175</td>
</tr>
<tr>
<td>γ + L</td>
<td>175 - 180</td>
</tr>
<tr>
<td>L</td>
<td>180</td>
</tr>
</tbody>
</table>

4.8 Discussion of Results - Pure NPG to 30 % PE-NPG

A partial phase diagram is constructed by combining DSC and XRD results for the Pure NPG to 30 %PE as shown in Figure 4-15. The first solid state phase transition, β → γ, was shown by both DSC and XRD techniques and the temperatures were in agreement with each other. The second solid-solid phase transformation, α → γ, was not detected by DSC may be due to low transitional energies. The XRD pattern indicated that this phase transformation occurs by the absence of 002 (PE) peaks from the next higher temperature scan in the XRD sequence. The third transformation is solid-liquid which is appropriately
Figure 4-13. X-ray diffraction patterns of 70NPG-30PE at different temperatures, showing phase transitions and stable phases.
Figure 4-14. DSC pattern of 70NPG-30PE, with very similar transitions to 75NPG-25PE.

Figure 4-15. Partial phase diagram for the Pure NPG to 30% PE marked with different zones based on experimental data from XRD.
defined by DSC scans. The results from this region will be compiled with the rest of the region to construct a full equilibrium phase diagram for PE-NPG system.

Key changes in this region can be summarized as follows –

1. There is no solubility of PE in NPG and vice-versa at room temperature. This is because of the fact that PE has a body-centered tetragonal structure and NPG is monoclinic. For complete solubility, compounds should have similar crystal structures as governed by Hume Rothery rules\(^1\).

2. From XRD and DSC measurements, \(\beta \rightarrow \gamma\) phase transformation occurs between \(41-43 \, ^\circ\text{C}\). A two phase region is observed above the invariant \(43^\circ\text{C}\) transformation line.

3. Single \(\gamma\) phase region is observed on the NPG rich side of the phase diagram. Around \(129-130 \, ^\circ\text{C}\), \(\gamma\) phase transforms to become liquid phase.

4. The solidus and liquidus temperatures increase as the amount of PE increases. These boundaries are located on the phase diagram using DSC measurements.

### 4.9 Phase Transitions in 65 mol% NPG - 35 mol% PE

X-ray diffraction pattern of 35 mol% PE is shown in Figure 4-16. \(\beta\) phase is stable up to \(40^\circ\text{C}\), whence it transforms to the high temperature FCC \(\gamma\) phase. Characteristic \(\gamma\) phase Bragg peaks show clearly after \(125^\circ\text{C}\) when there is no more overlap between \(\alpha\)–PE and \(\gamma_{\text{NPG}}\) peaks. Temperatures between \(40 \, ^\circ\text{C}\) to \(140 \, ^\circ\text{C}\), show a two phase region, \(\alpha + \gamma\). At \(~160 \, ^\circ\text{C}\), all of the \(\alpha\) phase transforms to \(\gamma\)’ phase. Between \(170 \, ^\circ\text{C}\) and \(190 \, ^\circ\text{C}\), both
Figure 4-16. In-situ x-ray diffraction patterns of 65NPG-35PE at different temperatures showing phase transitions. \( \gamma + \gamma' \) region was observed between 170-190°C. Both high temperature phases co-exist at high temperatures.

DSC Phase transitions –

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha + \beta )</td>
<td>25 °C – 41.8 °C</td>
</tr>
<tr>
<td>( \alpha + \gamma )</td>
<td>41.8 °C – 168 °C</td>
</tr>
<tr>
<td>( \gamma + \gamma' )</td>
<td>168 °C – 180 °C</td>
</tr>
<tr>
<td>( \gamma + L )</td>
<td>180 °C</td>
</tr>
</tbody>
</table>

XRD Phase transitions –

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha + \beta )</td>
<td>25 °C – 42 °C</td>
</tr>
<tr>
<td>( \alpha + \gamma )</td>
<td>42 °C – 170 °C</td>
</tr>
<tr>
<td>( \gamma + \gamma' )</td>
<td>170 °C – 190 °C</td>
</tr>
<tr>
<td>( \gamma + L )</td>
<td>190 °C</td>
</tr>
</tbody>
</table>

\( \gamma \) and \( \gamma' \) phases are present. After 190 °C, predominantly \( \gamma' \) phase is present up to ~205 °C.
Figure 4-17. DSC pattern of 65NPG-35PE sample. The first peak is $\beta \rightarrow \gamma$ transition; the second hump is for the heat of mixing of $\alpha + \gamma$; third peak is $\alpha \rightarrow \gamma'$ transition of PE at ~168°C. $\gamma + \gamma'$ phase is stable between 170-190°C

4.10 Phase Transitions in 60 mol% NPG - 40 mol% PE

X-ray diffraction pattern of 40 mol% PE is shown in Figure 4-18. The low temperature $\beta$ phase starts to transform to the high temperature $\gamma$ phase at ~42°C. The Bragg peaks for the $\gamma$ phase peaks overlapped with the $\alpha$-phase at lower temperatures, (up to ~ 100°C).

From 40 °C to 166 °C, there is a two phase region, $\alpha + \gamma$, as shown by peaks from both the phases. At around 166 °C, all of the $\alpha$ phase transforms to $\gamma$' phase. Between 170 °C and 190 °C, both $\gamma$ and $\gamma'$ phases are present. After 190 °C, only $\gamma'$ phase is present up to ~205 °C.
Figure 4-18. In-situ x-ray diffraction patterns of 60NPG-40PE, showing $\gamma + \gamma'$ phase between 170-190°C. At temperatures > 190°C, only $\gamma'$ phase exists till melting.

DSC Phase transitions –

$\alpha + \beta$  25 °C – 41.7 °C  
$\alpha + \gamma$  41.7 °C – 170 °C  
$\gamma + \gamma'$  172 °C – 190 °C

XRD Phase transitions –

$\alpha + \beta$  25 °C – 42 °C  
$\alpha + \gamma$  42 °C – 170 °C  
$\gamma + \gamma'$  170 °C – 190 °C  
$\gamma + L$  190 °C
Figure 4-19. DSC pattern of 60NPG-40PE observed $\alpha \rightarrow \gamma'$ transition; $\gamma + \gamma'$ phase was stable between 170-190°C.

### 4.11 Phase Transitions in 50 mol% NPG - 50 mol% PE

Guinier x-ray diffraction pattern of 50 mol% PE is shown in Figure 4-20. We deduce that the $\beta$ phase is stable up to ~23°C and it transforms to high temperature $\gamma$ between 23-49°C.

From 23 °C to 169 °C, there is a two phase region, $\alpha + \gamma$, as shown by peaks from both the phases. At around 169 °C, all of the $\alpha$ phase transforms to $\gamma'$ phase. Between 169 °C and 194 °C, both $\gamma$ and $\gamma'$ phases are present. After 194 °C, only $\gamma'$ phase is present up to ~208 °C.
Figure 4-20. Guinier xrd scan of 50NPG-50PE composition shows the presence of peaks from $\gamma$ and $\gamma'$ phases between 170-190°C.

DSC Phase transitions –

$\alpha + \beta$ 25 °C – 41.9 °C
$\alpha + \gamma$ 41.9 °C – 173.8 °C
$\gamma + \gamma'$ 173.8 °C – 190 °C
$\gamma' + L$ 190 °C – 240 °C

XRD Phase transitions –

$\alpha + \beta$ 25 °C – 40 °C
$\alpha + \gamma$ 40 °C – 169 °C
$\gamma + \gamma'$ 169 °C – 194 °C
$\gamma + L$ 194 °C - 208 °C
4.12 Phase Transitions in 40 mol% NPG - 60 mol% PE

DSC scan of 40NPG-60PE is shown in Figure 4-22. From 41.1°C to 145 °C, there is a two phase region, $\alpha + \gamma$, as shown by a broad heat of mixing endothermic peak from 50°C to 110°C, immediately followed by this endotherm, is an exothermic dip due to $\gamma$ phase dissolving into $\alpha$ phase and releasing heat. At around 173.7 °C, all of the $\alpha$ phase transforms to $\gamma'$ phase. After 173.7°C only $\gamma'$ phase is present.
Figure 4-22. DSC plot of 40NPG-60PE shows heat of mixing and $\beta \rightarrow \gamma$ transition.

Phase transitions –

$\alpha + \beta \quad 25 \degree C - 41.1 \degree C$

$\alpha + \gamma \quad 41.1 \degree C - 173.7 \degree C$

$\gamma' \quad 173.7 \degree C - 190 \degree C$

### 4.13 Phase Transitions in 30 mol% NPG - 70 mol% PE

Guinier x-ray diffraction pattern of 50 mol% PE is shown in Figure 4-23. At 78°C, $\beta$ phase has transformed to high temperature $\gamma$ phase. After 165 °C, $\gamma$ phase peaks are not observed which means that $\gamma$ phase has dissolved into $\alpha$ phase. From 165°C to 188°C,
only $\alpha$ phase peaks were observed. After 188 $^\circ$C, $\alpha$ transforms to $\gamma'$ phase. Between 188 $^\circ$C and 213 $^\circ$C, both $\alpha$ and $\gamma'$ phases are present.

Figure 4-23. In-situ high temperature Guinier diffraction pattern of 30NPG-70PE, showing phase transitions (work done in Dr. Chandra’s group at UNR).

4.14 Phase Boundaries in the composition range 35% PE - 70% PE

Samples in the composition range with 35 to 70 mol% PE were investigated for this purpose.

(A) Transition and Stability at 35% PE

XRD data for this composition is shown in Figure 4-16. At room temperature, there is a two phase region of $\alpha$ phase of PE and $\beta$ phase of NPG. XRD shows Bragg reflection from both phases. Around 40-45 $^\circ$C, $\beta$ phase of NPG transforms to high temperature FCC $\gamma$ phase of NPG with (111) and (200) reflections. Therefore, it can be concluded that $\beta \rightarrow$
Figure 4-24. DSC plot of 30NPG-70PE show following transitions. $\beta \rightarrow \gamma$, $\alpha + \gamma$ heat of mixing; $\gamma \rightarrow$ dissolving into $\alpha$, and $\alpha \rightarrow \gamma'$.

DSC Phase transitions –

- $\alpha + \beta$ 25 °C – 40.8 °C
- $\alpha + \gamma$ 40.8 °C – 175 °C
- $\alpha + \gamma'$ > 175 °C

XRD Phase transitions –

- $\alpha + \beta$ 25 °C – 40.8 °C
- $\alpha + \gamma$ 40.8 °C – 154 °C
- $\alpha + \gamma'$ 154 °C – 188 °C
- $\alpha + \gamma'$ 188 °C – 213 °C

$\gamma'$ at 45 °C. The reflections are not very clear just above the transition temperature of 45 °C because of overlapping with PE peaks. Around 85 °C, $\gamma$ (111) peaks are distinct. From 45 °C to 170 °C, there is a two phase $\alpha + \gamma$ region. At 170 °C, Bragg reflections from $\gamma'$
phase of PE appear. Low temperature PE phase $\alpha \rightarrow \gamma'$ transformation takes place. Between 170 – 190 °C, both $\gamma$ and $\gamma'$ phases coexist as shown by the Bragg reflection from the XRD patterns.

(B) Transition and Stability at 40% PE

XRD data for 40% PE is shown in Figure 4-18. As seen in the XRD patterns at 25, 38 and 42 °C, the Bragg reflections from $\beta$ phase NPG disappear after 42 °C which means that $\gamma$ phase NPG has appeared but the Bragg reflections are overlapped with 002 reflection of $\alpha$ phase PE. After 65 °C, $\gamma$ phase NPG reflections can be seen. This means that $\beta \rightarrow \gamma$ phase transition takes place at around 42 °C. From 42 °C to 170 °C, there are no crystal structure changes in the system are observed. This establishes $\alpha + \gamma$, two phase region from 42 °C to 170 °C. At around 170 °C the $\alpha$ phase transforms to $\gamma'$ phase which has FCC crystal structure. This is very clear from the absence of 002 $\alpha$-phase Bragg reflections at and after 170 °C. Between 170 °C to 190 °C, Bragg reflections from $\gamma$ and $\gamma'$ are clearly visible from the XRD pattern. Thus, this composition reveals a very interesting $\gamma + \gamma'$ equilibrium region.

DSC plots of both 35% and 40% PE are very similar. From the thermal data, $\beta \rightarrow \gamma$ transformation takes place at around 41 °C for both compositions. The second endotherm has been assigned to $\alpha \rightarrow \gamma'$ transformation which occurs at 168 °C for 35% PE and 172 °C for 40% PE compositions.

(C) Transition and Stability at 50% PE

XRD data for 50% PE is shown in Figure 4-19. As seen in the XRD patterns at 25, 38 and 42 °C, the Bragg reflections from $\beta$ phase NPG disappear after 42 °C which means
that \(\gamma\) phase NPG has appeared but the Bragg reflections are overlapped with (002) reflection of \(\alpha\)-phase PE. After 65°C, \(\gamma\)-phase NPG reflections can be seen. This means that \(\beta \rightarrow \gamma\) phase transition takes place at around 42 °C. From 42 °C to 170 °C, no crystal structure changes in the system are observed. This establishes \(\alpha + \gamma\), two phase region from 42 °C to 170 °C. At around 170 °C, the \(\alpha\)-phase transforms to \(\gamma'\) phase which has FCC crystal structure. This is very clear from the absence of (002) \(\alpha\)-phase Bragg reflections at and after 170 °C. Between 170 °C to 190 °C, Bragg reflections from \(\gamma\) and \(\gamma'\) are clearly visible from the XRD pattern. Thus, this composition reveals a very interesting \(\gamma + \gamma'\) equilibrium region.

\textit{(D) Transition and Stability at 60% PE}

DSC plots of both 50% and 60% PE are very similar. From the thermal data, \(\beta \rightarrow \gamma\) transformation takes place at around 41°C for both compositions. The second endotherm has been assigned to \(\alpha \rightarrow \gamma'\) transformation which occurs at 168 °C for 35% PE and 172 °C for 40% PE compositions.

\subsection*{4.15 Discussion of Results from 35\% PE to 70\% PE}

XRD and thermal data from this composition range has been analyzed and mapped. XRD can correctly determine the structure changes taking place at different temperatures for a particular composition. Solid-solid transitions are thus easily observed by XRD. Thermal analysis is best suited for solid-liquid transformations. Thus, a partial phase diagram is mapped for this composition range as shown in Figure 4-25.

The first phase transformation of \(\beta \rightarrow \gamma\) occurs at around 41°C, which was observed in both XRD and DSC plots at same temperatures. At around 170 °C, there is an invariant
eutectoid temperature boundary. The interesting features of this mid-composition range from 35% to 70% PE are as follows –

1. At around 41°C, $\beta \rightarrow \gamma$ transformation takes place and $\alpha + \gamma$ phase get stable up to around 170 °C. Below 41°C, $\alpha + \beta$ phases are stable which means both compounds have no solubility into each other.

2. From 41 °C to 170 °C, $\alpha + \gamma$ phases are stable and at around 170 °C $\alpha \rightarrow \gamma'$ transformation takes place.

3. For compositions between 35% PE and 40% PE, $\gamma' + \gamma$ phases are stable up to ~ 190-200 °C. There is a possible eutectoid reaction occurring at ~ 35-40 %PE.

Figure 4-25. Partial phase diagram of PE-NPG from 35% PE to 70% PE.
4.16 PE-rich Region – Pure Pentaerythritol

X-ray diffraction patterns of pure (as received) Pentaerythritol (PE) were obtained from 25 °C to melting point. In Figure 4-26, from room temperature to 185°C, there is pure α phase which has body centered tetragonal structure. Between 185°C and 190°C, the low temperature α phase changes to high temperature stable FCC γ' phase, when Bragg peaks for α phase disappear and new peaks for γ' phase appear.

\[
\alpha \rightarrow \gamma
\]

25-185 °C  185-190 °C

DSC scan of pure PE is shown in Figure 4-27. The α to γ' phase transition occurs at around 189°C, depicted by an endotherm. As per DSC data, phase transitions are obtained as follows –

\[
\alpha \rightarrow \gamma' \rightarrow L
\]

25-185 °C  189 °C  ~ 260 °C

X-ray diffraction patterns of pure (as received) Pentaerythritol (PE) were obtained from 25 °C to melting point. In Figure 4-26, from room temperature to 185°C, there is pure α phase which has body centered tetragonal structure. Between 185°C and 190°C, the low temperature α phase changes to high temperature stable FCC γ phase, when Bragg peaks for α phase disappear and new peaks for γ phase appear.

\[
\alpha \rightarrow \gamma
\]

25-185 °C  185-190 °C
Figure 4-26. XRD scans of pure PE at different temperatures between 25°C to 190°C showing a $\alpha \rightarrow \gamma'$ transition at $\sim 188$°C.

DSC scan of pure PE is shown in Figure 4-27. The $\alpha$ to $\gamma'$ phase transition occurs at around 189°C. As per DSC data, phase transitions are obtained as follows –

$$\alpha \rightarrow \gamma' \rightarrow L$$

$25-185$ °C  $189$ °C  $\sim 260$ °C
Figure 4-27. DSC scan of pure PE with $\alpha \rightarrow \gamma'$ occurring at ~ 188°C and melting at 260°C (The large peak at the melting side is due to the aluminum pan bursting under pressure at high temperature).

4.17 Discussion of Results for PE-NPG binary phase diagram

XRD, Guinier XRD and DSC methods are used to plot the complete PE-NPG phase diagram. The dynamic crystal structure changes are best captured by X-ray method. Thermal data analysis was not able to reveal the $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ phase transitions. Further, x-ray technique was instrumental in mapping the phase boundaries at higher temperatures.

The salient features of this equilibrium diagram shown in Figure 4-28 are – Six different phase transitions are occurring in this binary. Below 41°C, it was observed that there is
not much solubility of PE in NPG, but NPG has limited solubility in PE (from 0 – 5 mole%). The low temperature phases, $\alpha$ and $\beta$ are not very miscible due to difference in their crystal structures. $\beta$ phase is monoclinic while $\alpha$ phase is body-centered tetragonal at room temperature. At ~ 41°C, $\beta \to \gamma$ transition takes place. On the NPG side of the phase diagram, above 41°C, we observe $\alpha \to \gamma, \alpha \to \gamma', \gamma \to \gamma'$ phase transitions occurring. On the PE side, above 41°C, we observe $\gamma \to \alpha, \alpha \to \gamma', \gamma \to \gamma'$ phase transitions occurring. There is a two phase region comprising $\alpha + \gamma'$ phases which are low and high temperature phases of PE. At around 192°C, there is a eutectoid at ~ 35 mol% PE where $\gamma' \to \alpha + \gamma$. The high temperature $\gamma'$ phase transforms into $\alpha + \gamma$ phases upon cooling. An interesting feature of this phase diagram was the establishment of $\gamma + \gamma'$ phase region in the upper mid-compositional range of the phase diagram. On the NPG rich side of the phase diagram, a peritectic reaction was observed where $\gamma' + L \to \gamma$ transformation has been observed.
Figure 4-28. Re-determined experimental phase diagram of PE-NPG system.
Table 4-1. Comparison of Experimental data from this work with literature.

<table>
<thead>
<tr>
<th>Invariant Equilibria</th>
<th>Mole % PE</th>
<th>Temperature (˚C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metatectic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ → L + Q</td>
<td>55</td>
<td>173</td>
<td>Teisseire et al. [5]</td>
</tr>
<tr>
<td><strong>Eutectoid</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ' → α + γ</td>
<td>50</td>
<td>170</td>
<td>This work</td>
</tr>
<tr>
<td><strong>Metatectic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ → L + Q</td>
<td>40-45</td>
<td>165</td>
<td>Barrio et al. [4]</td>
</tr>
<tr>
<td><strong>Peritectic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L + Q → C₁</td>
<td>36.5</td>
<td>163.5</td>
<td>Teisseire et al. [5]</td>
</tr>
<tr>
<td><strong>Peritectic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ' + L → γ</td>
<td>35</td>
<td>192</td>
<td>This work</td>
</tr>
<tr>
<td><strong>Peritectic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃ + L → C₁</td>
<td>15-20</td>
<td>145</td>
<td>Barrio et al. [4]</td>
</tr>
</tbody>
</table>

*Note:* C₂ = γ', Q = α, L = Liquid

A comparison of the various invariant equilibria is tabulated in Table 4-1. Comparing the data from this work with Ref.[4] and Ref.[5], it has been observed that a eutectoid occurs at around 192˚C, γ' → γ + α, but both the cited references show a metatectic reaction, γ' → L + Q.

As reported by Chandra et al. ²(1990), the lattice parameters of α and γ phases for 20 mol% NPG is shown in Figure 4-29. The lattice parameters of α-phase in α + β region show slight increase in c-direction with very little increase in a-direction. As the temperature was increased, the α + β region transforms to α + γ region above ~ 38˚C and there was an increase in the c-parameter of the α phase while the a-parameter did not increase much. In the temperature range of 40-97˚C, there was non-linear increase in the c-parameter at different temperatures. They also reported that between 40-100˚C, there
were small changes in composition with increases in temperature but between 100-133°C; small changes in temperature cause large changes in compositions.

Figure 4-29. Lattice Parameter changes in the \( \alpha \), \( \gamma \) and \( \gamma' \) phases with the increase in temperature in the PE-20mol% NPG. \( \alpha + \gamma \) region shows non-linear compositional changes with change in temperature.\(^3\)

The lattice expansion behavior of 20 mol% NPG was observed to be very similar to pure PE.\(^3\) The volume expansions in the \( \gamma' \) phase are \( 2.2 \times 10^{-4} \) /°C which is more than pure PE (\( 1.57 \times 10^{-4} \) /°C). The volume changes in the \( \alpha \), \( \gamma \) and \( \gamma' \) phases is shown in Figure 4-30. The NPG rich \( \gamma \)-phase transformed to \( \alpha \)-phase at \( \approx 140 \)°C which further transformed to \( \gamma' \)-phase at higher temperatures, \( \gamma \rightarrow \alpha \rightarrow \gamma' \). There was 10.8% volume expansion observed during this transformation.
Figure 4-30. Volume expansions in the, $\gamma$ and $\gamma'$ phases for PE-20 mol%NPG. The $\gamma$ and $\gamma'$ phases have greater expansions than the $\alpha$ phase.

In this study, we also observed the change in lattice parameters of the $\gamma$ phase in PE-NPG binary system\(^3\). As shown in Figure 4-31, we observed that as the amount of NPG decreases in the alloy, the lattice parameters change very rapidly with increases in temperature.
The thermal analysis of PE-NPG system revealed some interesting features. It should be kept in mind that DSC interpretation is very difficult without XRD data. In this study also, x-ray data was used to interpret the DSC results.
Figure 4-32. Progressive DSC scans of NPG rich binaries ranging from 0 to 50 mol% PE.
Figure 4-33. Progressive DSC scans of PE rich binaries from 50 to 100 mol% PE.
The DSC traces of the PE-NPG binary system are shown in Figure 4-32 and Figure 4-33. It was observed that there is a negative exothermic dip (depicted with blue-hashed area) in the PE-rich binaries after $\beta \rightarrow \gamma$ transition at 41˚C. After this transition, $\gamma$ phase starts dissolving into the $\alpha$ phase. The heat thus released due to continuous $\gamma \rightarrow \alpha$ transition leads to a negative dip because of heat released during the process. As the temperature increases, the amount of $\gamma$ phase decreases in the $\alpha + \gamma$ region. The continuous $\gamma \rightarrow \alpha$ transformation goes on till ~ 140˚C. The negative dip was observed till 40 mol% NPG binaries on the PE side as shown in Figure 4-33. The area has been hashed for visual recognition. The enthalpies of transformation for $\alpha \rightarrow \gamma'$ are shown in Figure 4-35.

DSC traces for NPG rich binaries show $\beta \rightarrow \gamma$ transition at around 42˚C. For composition ranging from 60 to 95 mol% NPG, a broad continuous endotherm was observed which has been interpreted as continuous $\alpha \rightarrow \gamma$ transition preceded by $\beta \rightarrow \gamma$ transition. As the temperature increases, more and more $\alpha$ transforms to $\gamma$ phase with continuous heat absorption from ~ 40˚C to 100˚C. This is in contrast to exothermic dip observed in PE rich binaries. The continuous broad endotherm has been marked with red-hashes for visual recognition.

Barrio et al.\textsuperscript{4} have interpreted the continuous endotherm as an invariant reaction. The results in this work match with Teisseire \textit{et al.}\textsuperscript{5} but with some exception in the mid-composition range of the PE-NPG system. In this work, a mixed region with $\gamma$ and $\gamma'$ was observed but Teisseire \textit{et al.} described a similar region as L + $\alpha$ phase. The Bragg peaks of $\alpha$ phase clearly disappear and new $\gamma'$ peaks appear, so we interpret it as $\gamma + \gamma'$ region. Further, on the NPG rich side of the phase diagram, the peritectic reaction temperature was observed at $\gamma$ phase extends up to 180˚C.
Enthalpy measurements of the phase transitions were measured for the PE-NPG binary system. Figure 4-34 shows the combined plot for the PE-NPG system. Solid-solid transformations, $\alpha \rightarrow \gamma'$ for PE and $\beta \rightarrow \gamma$ for NPG are displayed. It is observed that $\beta \rightarrow \gamma$ phase transition enthalpy increases with increase in NPG amount. Enthalpy of transition for $\alpha \rightarrow \gamma'$ decreases with increase in NPG content.
The free energies $\Delta G$ for fusion and solid-solid transition are shown in Figure 4-36 equation used to calculate free energies are $\text{3}^3$

- NPG (fusion), $\Delta G = 4715 - 11.8T$
- NPG (transition), $\Delta G = 13600 - 43.4T$
- PE (fusion), $\Delta G = 5012 - 9.42T$
- PE (transition), $\Delta G = 41300 - 90.2T$
Figure 4-35. The variation of $\Delta H_t$ as a function of temperature for $\alpha \rightarrow \gamma'$ transition of the NPG-PE system

Figure 4-36. $\Delta G$ for solid-solid and solid-liquid transitions for NPG and PE.
4.18 References

1 L.H. Van Vlack, Elements of Materials Science and Engineering, Addison-Wesley, 1985
3 D. Chandra, “Crystal Structure and thermal studies on solid-state energy storage materials”, Report number:19X-SC644V/DE-AC05-84 OR21400
Chapter 5

Results and Discussion of Ternary PE-PG-NPG system

Nomenclature and Assumptions for Construction of Ternary Phase Diagrams

Binary thermodynamic and crystallographic phase diagram data of PE-PG, PG-NPG, and PE-NPG were assembled from the literature. We used the literature data of PG-NPG\(^1\) and PE-PG\(^2\). In evaluating the PE-NPG we found discrepancies which are discussed in the background section. In this study, redetermination studies of the phase diagram were performed, and are reported in Figure 4-28. The construction of the ternary phase diagram was performed by first making the ternary triangle and superimposing the above mentioned three binary phase diagrams as shown in Figure 5-1. This method has been used by many researchers\(^15\).

The phase designations are primarily based on the type of crystal structures for PE (C\(_5\)H\(_{12}\)O\(_4\)) and PG (C\(_5\)H\(_{12}\)O\(_3\)) have the same BCT (low temperature layered) crystal structure and solid solutions of any combination of PE and PG are assigned as “\(\alpha\)-phase” in any of the three binary phase diagrams. In addition, the same nomenclature was used in the ternary phase diagram as well as in the ternary phase diagram in which three components varied in any concentration. The NPG (C\(_5\)H\(_{12}\)O\(_2\)) has bimolecular chained monoclinic structure and this low temperature phase is assigned as “\(\beta\)-phase.” Each of these compounds exhibit a solid state phase transition from \(\alpha\) or \(\beta\) \(\rightarrow\) \(\gamma\) (high temperature phases). All these three compounds exhibit the same orientationally disordered FCC type cubic crystal structure and are designated as \(\gamma\) and \(\gamma\_T\) phases; the \(\gamma\) phase rich in NPG and
and $\gamma_T$ solid solution of high-temperature phase of PE-PG and PG-NPG. As far as the binary phase equilibria is concerned, one can observe: ($\alpha+\beta$), ($\alpha+\gamma$), ($\alpha+\gamma_T$), ($\beta+\gamma_T$), (L+$\gamma$), (L+$\gamma_T$),(L+$\gamma_T$). In the ternary system one can expect similar binary

Figure 5-1. Schematic of the arrangement of binary phase diagrams around the Gibbs triangle to project the binary phases. In this work, PE-PG\textsuperscript{2}, PG-NPG\textsuperscript{1} and PE-NPG (this work) binaries are used to investigate PE-PG-NPG ternary system. The data generated in the study will be used in conjunction with the binaries to determine the ternary phase equilibria.
phase equilibria, as well as three phase equilibria, such as: ($\alpha+\beta+\gamma$), ($\alpha+\beta+\gamma'$), ($\alpha+\beta+\gamma_T$),

($L+\alpha+\gamma_T$) and other combinations. These three phase regions are found in the “tie triangle” in the ternary phase diagrams. It is important to point out that low temperature phases can equilibrate with the liquid phases, for example, ($\alpha+L$), ($\beta+L$) phase stability is possible in the ternary system. It should be noted that in the binary systems; only the $\gamma$ phases are in equilibrium with the liquid phases, and not $\alpha$ or $\beta$ phases. The overall scheme of phase transitions is shown in Figure 5-2.

**Justification of $\gamma_T$ assumption:**

The high temperature phases of all three components in this ternary system have FCC crystal structure. Lattice parameters of the $\gamma_{NPG}$ is $8.8\text{\ Å}$ at $43^\circ\text{C}$ ($\beta \rightarrow \gamma_{NPG}$ transition)$^3$, $\gamma_{PG}$ lattice parameter is $8.87\text{\ Å}$ ($\alpha \rightarrow \gamma_{PG}$ transition at $\sim 88^\circ\text{C}$)$^4$ and that of $\gamma_{PE}$ is $8.84\text{\ Å}$ ($\alpha \rightarrow \gamma_{PE}$ transition at $\sim 188^\circ\text{C}$)$^5$. Since the lattice parameter of the FCC phases is so close, we have assumed that high temperature phase of PE-PG and PG-NPG will be referred as $\gamma_T$. NPG high temperature phase has not been included in $\gamma_T$ because in PE-NPG binary system high temperature phase of PE and NPG exist separately with a very small region of $\gamma_{PE} + \gamma_{NPG}$.

**Development of Ternary Phase Diagrams:**

Three perpendicular lines were drawn from center of each base in the Gibbs triangle; these are designated along the line joining the pure PE vertex point to the point 50/50 PG-NPG. In a similar manner the other two line are constructed; these are designated based
Figure 5-2. Phase designations used to construct the ternary isothermal PE-PG-NPG Phase diagrams in this study. (b) The ternary compositional plot shows all the sample compositions used in this study.

Table 5.1. PE-PG-NPG sample compositions in mole% used in this study.

<table>
<thead>
<tr>
<th>PE-PG-NPG</th>
<th>α-Phase → γ_T</th>
<th>β-Phase (NPG-rich) → γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-PG</td>
<td>(PE or PG rich)- All compositions</td>
<td></td>
</tr>
<tr>
<td>PG-NPG</td>
<td>α-Phase (PG-rich) → γ_T</td>
<td></td>
</tr>
<tr>
<td>NPG-PG</td>
<td>α-Phase (PE-rich) → γ_T</td>
<td></td>
</tr>
</tbody>
</table>

Legend:
- PE (BCT)
- PG (BCT)
- NPG (Mono)

Note: Liq. Phase can co-exist with either α, β or any of the γ phases in ternaries.
Ternary compositions are labeled from 1 through 44 in the Gibbs triangle; key samples were selected and samples were made. In general, the results are presented based on the point of origin, for example, "PE line," "PG line," NPG line," and other lines.

<table>
<thead>
<tr>
<th>Point No.</th>
<th>PE</th>
<th>PG</th>
<th>NPG</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
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</tr>
<tr>
<td>41</td>
<td>50</td>
<td>30</td>
<td>20</td>
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</tbody>
</table>
points: 1 to 11, 12 to 22, and 22 to 33 along the lines, there are other compositions that were used for checking the phase boundaries.

5.1 In-situ x-ray Diffraction, DSC and NMR Along “NPG Line”

The point numbers in the Gibbs triangles correspond to the compositions of PE-PG-NPG as shown in the Table 5.1. Selected results from ternary compositions prepared at points 2, 4, 6, 7, 8, 10, and 11 are presented in this section in Figure 5-1.

Besides the PE, PG, and NPG Lines, other sample compositions were selected in which one component was kept constant and the other allowed to vary or vice versa. We start from at the data of Point No. 1 (pure NPG), from Chapter 4; the results are presented in Figure 4.1 and Figure 4.2 As a starting point, the phase transitions for pure NPG were found, as follows:

$$\alpha \text{ Phase} \rightarrow \gamma \text{ Phase} \rightarrow \text{Liq.}$$

\[ \sim 316K \quad \sim 403K \]

5.1.1 Solid Solution 10PE-10PG-80NPG (at Point No.2):

Now we focus our attention to the ternary system rich in NPG component. To interpret the ternary composition X-ray patterns, binary phase diagrams were taken into consideration. As mentioned previously in chapter 2, due to structural similarities, PE-PG make solid solution phases at all temperatures. X-ray patterns of PE and PG overlap almost completely and peak positions are right next to each other for all 20 positions. So, the solid solution of PE-PG at low temperatures is denoted as $\alpha$ in the X-ray patterns. PG-NPG has considerable solubility after 22°C at which it transforms to high temperature $\gamma_{PG/NPG}$ phase for compositions ranging from 10%-40% PG\(^1\). So, the solid solution of PG-
NPG at high temperatures is denoted as $\gamma_T$ in the X-ray patterns. For the composition 10PE-10PG-80NPG (at Point No.2) in-situ XRD data was obtained at several temperatures ranging from $25^\circ$C (298K) to $80^\circ$C (353K) and presented in Figure 5-3. The XRD pattern at $25^\circ$C clearly shows presence of $\alpha$ and $\beta$ phases stable between $25^\circ$ to $35^\circ$C; with predominance of the $\beta$ phase, as expected. Then the $\beta$ phase transforms to the high temperature $\gamma_T$ phase that coexists with (small amounts) of the $\alpha$ phase (rich in PG-PE) up to $\sim80^\circ$C (353K). The PG and NPG make a complete solid solution, $\gamma_T$ should be expected after $\sim43^\circ$C. The $\gamma_T$ (111) Bragg Peaks and $\alpha$ (101) Bragg peaks overlap so these peaks can not be distinguished at low temperatures except that the $\alpha$ (101) peak has broadened which indicates the presence of another peak; possibly $\gamma_T$ (111). Thermal analyses were also performed on the sample (at Point No.2) and the DSC scan is shown in Figure 5-4.
Figure 5-3. X-ray data for point 2, obtained from 25°C to 80°C. β phase transforms to γ-phase at around 40°C.
Figure 5-4. DSC scan of point 2, showing $\beta \rightarrow \gamma$ phase transition and heat of mixing in the two phase region.

Figure 5-5. NMR spectra of point 2 shows the chemical shift peaks from PE-PG-NPG components. It is a NPG rich composition.
This pattern is labeled in three zones, $\alpha+\beta$, $\alpha+\gamma$, and $\alpha+\gamma_T$; there is a first order transition at $\sim43^\circ$C of $\beta\rightarrow\gamma$, then there is continuous transformation between $\alpha$ and $\gamma$ (in effect phase mixing) that occurs from $\sim47^\circ$ to $65^\circ$C which is indicated by the hump in the scan in the range and has an enthalpy of $31.74$ J/g in this ternary. Then $\gamma$ phase transitions to $\gamma_T$ phase at $65^\circ$C. Finally the melt occurs at $140^\circ$C. The phases were assigned based on the XRD data. The phase transitions for the 10PE-10PG-80NPG (#2) sample are shown:

$$\alpha + \beta \rightarrow \alpha + \gamma_T \rightarrow CT(\alpha \leftrightarrow \gamma_T) \rightarrow L$$

$$316K \sim 321K - 358K \sim 413K$$

$$\Delta H^\circ = 61.13 \text{J/g} \quad \Delta H^\circ = 61.13 \text{J/g} \quad \Delta H^\circ = 31.74 \text{J/g}$$

CT=Continuous Transitions

In order to obtain the activity of the individual molecules in the phases NMR experiments were performed for each of these compositions. For the composition 10PE-10PG-80NPG (point No.2) the NMR spectra is shown in Figure 5-5. The details of interpretations of the patterns are explained in the experimental section in Chapter No.3; here we show the intensity of the PE, PG, and NPG that show the thermodynamic activity peaks of the molecules. In this case, the NPG peak has the highest signal intensity, as expected, and the composition of the three component solution obtained from NMR is slightly higher than the actual mole fraction. The NMR data further confirms the presence of all three components in the solid solution even though due to overlapping patterns in NMR, PE and PG cannot be distinguished.

### 5.1.2 Solid Solution 20mol.% PE-20mol.% PG-60mol.% NPG (at Point No.4):

The sample at Point No. 4 in the Gibbs triangle is shown in Figure 5-1. This is also NPG rich sample with 10% more concentration of the PE and PG. The in-situ XRD patterns
taken at various temperatures are shown in Figure 5-6 and Figure 5-7. The XRD patterns in the Figure 5-6 are taken using Anton Parr heating stage TTK 450 in the PANalytical X-ray diffractometer; whereas the patterns in Figure 5-7 are taken using the capillary X-ray air-heating system also mounted on the PANalytical machine. The reasons to obtain these two sets of data is to check effect of vaporization of more volatile component in the large volume heating stage of the Anton Paar stage (see Figure 3-5 and 3-6). The glass capillaries are sealed with a small amount of sample in a very volume, so there is no evaporation of the volatile component from the solid solution. The capillary method is very effective >100°C temperatures for these applications. In this section the low temperature data is shown in Figure 5-6, and higher temperature data up to 155°C is shown in Figure 5-7. Using the XRD data (Figure 5-6) one can see α+ β phase stability from 25°C to 40°C. Above this 40°C, the β→γ and coexist with the α phase of NPG is stable and after 40°C. As this sample (at Point No.4) has greater PG in the solution as compared to the sample (at Point No.2), at high NPG concentrations there is phase transformation at around 40°C as per PG-NPG binary phase diagram,. The γT peak and α (101) Bragg peaks overlap so these peaks can not be easily distinguished at low temperatures, but the existence of γT phase is determined by the overlapped Brags indicated by the (101) broadened peak. Above 40°C, α and γT phases are stable up to 70°C and after that α + γT becomes the stable phase. After this temperature γT Bragg peaks disappear and only α phase peaks can be seen. Thus in this case, the α phase is stable up to melting temperature of 175°C.
Figure 5-6. X-ray diffraction data for point 4 showing $\beta \rightarrow \gamma$ transition between 40-45°C. $\alpha$ (101) peak has a slight hump due to $\gamma_T$ (111) peak overlap.
In order to determine the thermal events, DSC analyses Figure 5-8 were also performed and they showed two sharp endothermic peaks and a broad hump.

![Graph showing XRD data](image)

Figure 5-7. High temperature capillary XRD data for point 4. From 25°C to 110°C, \( \alpha + \gamma \) two phase region is stable. After 110°C, \( \gamma_T \) phase disappears and only \( \alpha \) remain stable till liquid temperature of 185°C.

Since it is a ternary mixture, PE, PG and NPG interact with each other, the DSC peaks are labeled as per current XRD data in Figure 5-6 and Figure 5-7. The DSC data shows \( \alpha \) and \( \beta \) phase are stable up to \( \sim 38 \) °C, which is in reasonable agreement with the XRD data. At \( \sim 38 \) °C, a first order \( \beta \rightarrow \gamma \) transformation takes place at \( \sim 38 \) °C. From \( \sim 41 \) °C to \( \sim 125 \) °C, there are continuous phase transitions between \( \alpha \), \( \gamma \) and \( \gamma_T \) due to
Figure 5-8. DSC scan of point 4 shows $\beta \rightarrow \gamma$ phase transition and heat of mixing in the two phase region. High temperature capillary XRD data shows peak evolution at high temperatures and based on that some DSC transitions are proposed.

Figure 5-9. NMR peak intensities show relative abundance of the three molecules in Point No. 4 composition. Maleic acid is used as reference standard.
changes in composition in the two phase region. Based on PE-PG binary phase diagram, there may be $\alpha \rightarrow \gamma_T$ transformation at around 130°C and both high temperature phases, $\gamma_T$, might be stable till complete melting occurs at ~ 175°C.

These DSC results are summarized as follows (Point #4):

$$\alpha + \beta \rightarrow \alpha + \gamma \rightarrow \text{CT}(\alpha \leftrightarrow \gamma) \rightarrow \text{CT}(\alpha \leftrightarrow \gamma_T) \rightarrow \alpha + \gamma + \gamma \rightarrow \gamma + \gamma_T \rightarrow \text{L > 448K}$$

$$\Delta H^\circ = 23.94 \text{J/g}$$

CT=Continuous Transitions

The concentration of the NPG, PG, and PE are shown in NMR spectra of this composition (point No.4) (Figure 5-9). The NPG peak has the highest signal intensity indicating NPG rich mixtures. NMR further confirms the presence of all three components even though due to overlapping patterns in XRD, PE and PG can not be distinguished.

5.1.3 Solid Solution - 30 mol% PE - 30 mol% PG - 40 mol% NPG (at Point No.6):

This sample has considerable amount of PE and PG. The in-situ XRD patterns taken at from 25°C to 40°C show $\alpha + \beta$ phases are stable up to 40°C. The $\beta \rightarrow \gamma$ occurs ~40°C in a similar manner to the other two previous samples (at Points 2 and 4). As there is PG component in this mixture, so as per PG-NPG binary phase diagram, at 40% NPG concentration there is phase transition occurs at a different temperature, at ~ 32°C. PG and NPG make a complete solid solution, $\gamma_{\text{PG/NPG}}$ above ~ 32°C. The $\gamma_T$ peak and $\alpha$ (101) Bragg peaks overlap so these peaks cannot be distinguished at low temperatures but
the $\alpha$(101) and $\gamma_T$ (111) peak are overlapped and thus broadened. In the 45° to 80°C region, the $\alpha$ and $\gamma_T$ phases are stable.

Figure 5-10. XRD scans for point 6 from 25-80°C. $\beta \rightarrow \gamma$ transition takes place at around 40°C and $\alpha + \gamma_T$ are stable between 60-80°C.
Thermal analyses by DSC, shows low intensity endothermic peaks at ~30°C and a broad hump between 550 to 1500°C indicating heat of mixing of the α and the γ\(_T\) phases due to changes in compositions. Note that the XRD data show α and β phase are stable up to ~40°C, and it is proposed that α and γ\(_T\) phases remain stable up to ~150°C. Also, the high temperature phase, γ\(_T\), might be stable till complete melting occurs at ~200°C. (Point #6)

\[
\alpha + \beta \rightarrow \alpha + \gamma \rightarrow CT(\alpha \Leftrightarrow \gamma) \rightarrow CT(\alpha \Leftrightarrow \gamma_T) \rightarrow \alpha + \gamma + \gamma_T \rightarrow \gamma_T + L \rightarrow \gamma_T + L (> 498K)
\]

\(\Delta H^\circ = 23.94 J / g\) \(\Delta H^\circ (s \rightarrow L)\) not measured but appears high

CT=Continuous Transitions

The NMR spectra of this composition are shown in Figure 5-12. As seen, PE has the highest signal intensity indicating that PE is the dominating component.

### 5.1.4 Solid Solution - 33.3%NPG-33.3%PE -33.3%PG (at Point No.7):

The solid solution at the center of the Gibbs triangle was sample No.7 that has an equimolar composition of 33.3 mol % each of PE, PG, and NPG. In-situ XRD patterns are shown in Figure 5-13 (25-80°C-Diffractometer) and Figure 5-14 (25-205°C-Capillary method). Figure 5-13 shows small amounts of β phase present in the α+β mixtures (indicated by low intensity (002) and (021) Bragg peaks) that are stable from 25°C to 35°C. The Bragg peaks of β phase disappear at temperatures greater than 35°C. At 40°C and above, it is possible that the γ phase Braggs are overlapped with the α-phase peaks. As there is PG component in this mixture, as per PG-NPG binary phase diagram, at 40%
Figure 5-11. DSC scan of point 6 shows mixing of two phase zone from ~50-140°C. 
\( \beta \rightarrow \gamma \) transition takes place at ~40°C and complete melting at 200°C.

\[ \Delta H = 83.86 \text{ J/g} \]

Figure 5-12. NMR spectra of point 6 shows the presence of PE, PG and NPG molecules wherein PE and NPG relative activity is more than PG.
Figure 5-13. XRD scans at different temperatures for equimolar composition of point 7. Small amount of $\beta$ phase is present till 35°C and it disappears at 40°C due to $\beta \rightarrow \gamma$ transformation.
NPG concentration there is phase transformation at ~32°C; as PG and NPG make a complete solid solution, the $\gamma_T$ should be expected after ~32°C. The $\gamma_T$ peak and $\alpha$(101) Bragg peaks overlap, so these are difficult to detect at low temperatures except that the $\alpha$(101) peak has broadened which indicates the presence of another peak. Capillary technique was used to characterize this composition at higher temperatures up to liquid state. Due low resolution of the capillary method, the Bragg peaks are broader. Between 110°C and 150°C, $\gamma_T$ (111) Bragg peaks disappear and only $\alpha$ (101) peaks remain, indicating only $\alpha$ phase is stable it goes to the liquid phase. The DSC Figure 5-15 shows endothermic transitions at ~30°C and a broad hump of continuous transitions, (as seen in the other samples) from ~50° to 160°C. It is proposed that $\alpha$ and $\gamma_T$ phases remain stable until ~160 °C. Above 160°C, as shown by XRD scans Figure 5-14, high temperature phase, $\gamma_T$ remains stable until complete melting occurs at ~200°C. The transitions from DSC may be summarized as follows (Point #7):

$$
\alpha + \beta \rightarrow \alpha + \gamma \rightarrow \text{CT}(\alpha + \gamma_T) \rightarrow \text{CT}(\alpha + \gamma + \gamma_T) \rightarrow \gamma + \gamma_T \rightarrow L (>463K)
$$

($\sim 303K$) ($\sim 350K-393K$) ($\sim 393K-413K$) ($\sim 413K-458K$)

$\Delta H^o = 61.13J/g$ $\Delta H^o = 27.62J/g$

CT=Continuous Transitions

The NMR spectra Figure 5-16 for this composition shows high PE signal intensity indicating that PE is the dominating component.

5.1.5 Solid Solution 30% NPG-35% PE -35% PG (at Point No.8):

The stable phases and phase transitions are shown in the in-situ XRD patterns (Figure 5-17) shows very similar results to that of the composition at Point No.7 showing $\alpha+\beta$
phases stable up to 35°C and $\alpha+\gamma_{PG/NPG}$ for temperatures greater than 40°C. The DSC data (Figure 5-18) scan is also showing a broad endotherm and results may be summarized as follows (Point #8):

$$\alpha+\beta \rightarrow \alpha+\gamma \rightarrow \text{CT}(\alpha+\gamma_T) \rightarrow \text{CT}(\alpha+\gamma+\gamma_T) \rightarrow \gamma+\gamma_T \rightarrow L (\sim 473K)$$

$$\sim 303K \quad \sim 323K - 383K \quad \sim 383K - 413K \quad > 413K$$

$$\Delta H^o = 61.13 J/g \quad \Delta H^o (s \rightarrow L) \text{not measured.}$$

CT=Continuous Transitions

The NMR spectra is also shown in Figure 5.19.
Figure 5-15. DSC data of point 7 has a big two-phase endothermic mixing zone ranging from 55°C to 165°C. Melting occurs at 205°C.

Figure 5-16. NMR spectra shows relative amounts of PE, PG and NPG in equi-molar composition of point 7. NPG has a reduced NMR peak, suggesting possible change of crystal structure.
Figure 5-17. XRD scans from 25°C - 80°C of point 8 composition. Very small amount of β phase is evident from a small peak at β 2θ position for (021). α+β phase is stable up to 35°C and α+γ for temperatures greater than 60°C.
Figure 5-18. DSC scan of point 8 composition shows a wide mixing zone from ~55-160°C. $\alpha + \beta$ phase transition to $\alpha + \gamma$ at around 40°C complete liquid state occurs at ~180°C, lower than point 7 (205°C).

Figure 5-19. NMR spectra shows reduced NPG amount, possibly due to solid solution formation.
5.1.6 **Solid Solution 10% NPG-45% PE -45% PG (at Point No.10):**

Sample at point No. 10 shows \( \alpha \)-phase (BCT) from 25\(^\circ\)C to 100\(^\circ\)C as shown in XRD patterns (Figure 5-20). This is the first time that the \( \beta \) phase of NPG was not detected at room temperature, exhibiting similar behavior to that of 50%PE-50%PG. The DSC pattern is different as well (Figure 5-21), the transitions appear to be more complex. The \( \alpha \rightarrow \gamma_T \) transitions start at 110\(^\circ\)C and end at 160 \(^\circ\)C, and the melting occurs ~210\(^\circ\)C. The NMR results for this composition are shown in Figure 5-22 (Point No. 10).

\[
\begin{align*}
\alpha & \rightarrow \alpha + \gamma_T \rightarrow \gamma_T \rightarrow \gamma_T + L \rightarrow L(\sim 493K) \\
(-358K) & \sim (358K - 475K) \sim (475K - 493K) \\
\Delta H^o &= 138.29 J/g \quad \Delta H^o = 23.02 J/g
\end{align*}
\]

These NMR results further confirm the presence of all three components even though due to overlapping patterns in XRD PE and PG cannot be distinguished.
Figure 5-20. XRD scans from 25-80°C of point 10 shows only α peak at all temperatures. This point is very similar to 50PE-50PG, point 11, in the XRD pattern.
Figure 5-21. DSC scan of point 10 shows a double endothermic hump, very similar to 50PE-50PG. Endoderm at 100-175 °C is due to $\alpha \rightarrow \gamma_T$ phase transition. Liquid state occurs at ~225°C.

Figure 5-22. Very small peak of NPG in point 10 NMR spectra. This point is very similar to point 11, except there is very small NPG peak at 3.22 ppm
5.1.7 Solid Solution Binary of 50% PE - 50% PG (at Point No.11):

The last point on the NPG line is a sample with binary composition (at Point No. 11) 50% PE - 50% PG. In-situ XRD patterns show the Bragg peaks of $\alpha$ (BCT) phase throughout the temperature regime, from 25$^\circ$C to 80$^\circ$C, Figure 5-23. The DSC data in Figure 5-24 shows a rather broad peak (with a shoulder on the right), starting from ~110$^\circ$C and ending at 160$^\circ$C indicating that there is $\alpha + \gamma_T$ two phase region until it fully transforms to $\gamma_T$. From Figure 2-13, in the PE-PG phase diagram, it can be seen that from ~112$^\circ$C to 160$^\circ$C there is $\alpha + \gamma_T$ phase region at 50/50 PE/PG composition. From ~160$^\circ$C to 230$^\circ$C, $\gamma_T$ is stable, and the $\gamma_T$ phase transforms to liquid state at 230$^\circ$C. The NMR spectra in Figure 5-25 of this composition shows PE has the highest signal intensity indicating that PE is the dominating component. NMR further confirms the presence of both components even though due to overlapping patterns in XRD, PE and PG can not be distinguished.

In summary the phase transitions for the 50/50 PE/PG sample are as follows (Point #11):

$$
\begin{align*}
\alpha & \rightarrow \alpha + \gamma_T \\
(\sim 383K - \sim 413K) & \rightarrow \gamma_T \\
(\sim 413K - \sim 463K) & \rightarrow \gamma_T \\
(~ 463K - \sim 483K) & \rightarrow L (> \sim 483K)
\end{align*}
$$

Overall $\Delta H'' = 196.17 J/g$ and $\Delta H''_{L} = 45.34 J/g$

Two phase regions of $\alpha + \gamma_T, L + \gamma_T$

5.2 In-situ x-ray Diffraction, DSC and NMR of the Ternary S-S Along “PE Line”

In a similar manner as discussed for the “NPG line” samples the data for the samples at points 14, 16, 18, 20, and 22 are presented in this section.

5.2.1 Solid Solution Ternary of 80% PE - 10% PG - 10% NPG. (at Point No.14):
At this time we focus on the pure PE, and PE rich ternary samples along the "PE line"

For the pure PE sample, the XRD patterns (25°C up to 185°C) show α (BCT) phase only, and at 190°C the γ phase Bragg peaks appear in the XRD pattern. (Figure 5-264-26). The DSC pattern in Figure 4-27 confirms this for pure PE. We will not discuss this further as these transitions are well known.

Let us consider solid solution 80%PE-10%PG-10%NPG (Point No. 14). The XRD patterns (Figure 5-26) taken at various temperatures, from 25 °C onwards, the majority α phase Bragg peaks, and minor amounts of β peaks are observed up to 135°C. At 155°C, another peak starts emerging along α (101) peak. Since there is PG component in this mixture, so as per PE-PG binary phase diagram, PE and PG make complete solid solution, γT should be expected. Capillary technique was used to characterize this composition at higher temperatures up to liquid state. Due to intensity losses and multiple diffractions in capillary technique, Bragg peaks are broader. Between 155°C and 185°C, γT (111) Bragg peaks are present along side α (101) peaks remain, indicating only α phase is stable till liquid state. From 185°C upwards, γT (111) Bragg peaks are present and stays till 240°C (liquid state).

To summarize, the structural data show α + γT region between 155° to 165°C and reactions are as follows (Point No.14):

\[
\begin{align*}
\alpha + \beta^* & \rightarrow \alpha + \gamma \quad \rightarrow \gamma + \gamma_T \quad \rightarrow \gamma_T \quad \rightarrow \gamma_T + L \rightarrow L (> 508K) \\
(300K - 318K) & \quad (318K - 448K) \quad (488K - 508K)
\end{align*}
\]

Two phase region \(\alpha + \gamma \quad \beta^*\) – minor phase
Figure 5-23. In-situ x-ray scans of point 11 from 25-80°C. Only α phase was observed between 25-80°C.
Figure 5-24. DSC plot of point 11. The double hump peaks are due to $\alpha \rightarrow \gamma_T$ and the transition occurring over a range of temperature and is accompanied by rapid composition change of the phases.

Figure 5-25. NMR spectra of point 11 shows only PE and PG peaks, PE being relatively more than PG.
Figure 5-26. In-situ x-ray patterns of point 14; α phase is stable till 175°C and then γ_T appears at 155°C is stable till melting at 255°C.

DSC data is shown in Figure 5-27 and Figure 5-28 shows the NMR data, and we derive the following conclusions from these data:

\[
\alpha + \beta \rightarrow (\alpha + \gamma_{PE|PG} \rightarrow \gamma_{PE|PG}) \rightarrow L
\]

\[
(start @ \sim 428K \quad end @ \sim 438K) \sim 503K
\]

overall \ \Delta H^o = 196.17 J/g \ \Delta H_L^o = 45.34 J/g

It should be noted that in the NMR plot the PE has the highest signal intensity indicating that PE is the dominating component. NMR (Figure 5-28) further confirms the presence
Figure 5-27. DSC plot of point 14 shows very small endothermic peak at $\beta \rightarrow \gamma$ transition of $\sim 41^\circ$C. $\gamma_T$ appears at 165°C.

Figure 5-28. NMR spectra of point 14 suggest very small PG relative to PE and NPG.
of all three components even though due to overlapping patterns in XRD, PE and PG can not be distinguished.

5.2.2 Solid Solution Ternary of 60% PE-20% PG -20% PE (at Point No.16):

In-situ XRD patterns, Figure 5-29, taken from 25 °C to 40°C show that the β phase of NPG is stable up to 40°C, at which β phase of NPG transforms to γ phase. Since there is PG component in this mixture, so as per PG-NPG binary phase diagram, PG and NPG make a complete solid solution, γ of all three should be expected after ~ 32°C. The γT peak and α (101) Bragg peaks overlap so these peaks cannot be distinguished at low temperatures except that the α (101) peak has broadened which indicates the presence of another peak. There is very small amount of γT phase in the mixture. After 60°C, α and γT phases are stable for the tested range of 25°C to 80°C. Figure 5-30 shows the DSC scan with one sharp and one small endothermic peak. Since it is a ternary mixture, PE, PG and NPG interact with each other and some transitions are proposed based on the binary phase diagrams (PE-PG, PE-NPG and PG-NPG) and current XRD data. α and β phase are stable up to ~ 39 °C. At ~ 39 °C, β → γ transformation takes place. From ~ 39 °C to 60 °C, α and γ are stable and a broad hump occurs due to heat of mixing of two phases. The double hump indicates the transition of γ phase to γT phase. Based on PE-PG binary phase diagram, it is proposed that there is α → γT transformation at 165°C and γT is stable till 185 just below the melting point of 205 ~ 250 °C. An NMR spectrum is shown in Figure 5-31. The in-situ XRD data composition of 60%PE-20%PG -20%PE (at Point No. 16) lead us to conclude the following:
Figure 5-29. In-situ xrd patterns of point 16 taken at different temperatures from 25-80°C. Very small β phase peak (021) can be seen that transitions to γ phase at ~ 40°C.
Figure 5-30. DSC plot of point 16 shows $\beta \rightarrow \gamma$ at $\sim 41^\circ C$. A small endothermic hump at 50-90$^\circ C$ is interpreted as mixing of $\alpha$ and $\gamma$. The sharp peak at $\sim 180^\circ C$ is $\alpha \rightarrow \gamma_T$.

Figure 5-31. NMR of point 16 shows very small abundance of PG and NPG in this PE rich composition.
5.2.3 Solid Solution Ternary of 40%PE-30%PG-30%PE (at Point No.18):

The sample at Point No. 18 has a composition of 40%PE-30%PG-30%PE. Figure 5-32 shows XRD patterns (similar to the patterns in Figure 5-29 for Point 16) at various temperatures and we conclude the following phase transitions, which are very similar to the DSC scans with three endothermic peaks.

The DSC data shows (Figure 5-33) shows two endothermic reactions, and one large continuous phase transition between 80\(^\circ\)C to 170\(^\circ\)C. The ternaries with NPG rich components exhibit very complex reactions, and in this case as the temperature is increased the \(\alpha\) phase (largely PE with high solid-solid phase (\(\alpha \rightarrow \gamma_T\)) transition temperature of 188\(^\circ\)C (~461K), and melting point of 269\(^\circ\)C remains stable and some \(\gamma_T\) is expected to dissolve, and later precipitate out yielding a three phase region in the ternary, however this speculation., so the proposed reactions are:

Summary for Point #18:

\[
\alpha + \beta \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma_T \rightarrow \alpha + \gamma + \gamma_T \rightarrow \gamma + \gamma_T
\]

\((-318K-358K)(\sim 358K-408K)(\sim 408K-443K)(\sim 443K-497K)\)

Data > 443K not available.
Figure 5-32. In-situ x-ray patterns of point 18 from 25-80°C. α and γ are stable after 40°C.
Figure 5-33. DSC plot of point 18 shows two endothermic peaks between 0-75°C. The second peak is interpreted as $\beta \rightarrow \gamma$ at ~41°C. The broad hump is possibly mixing of two phases.

Figure 5-34. NMR spectra of point 18 shows PE is dominating the ternary system.
An NMR spectrum of point 18 is shown Figure 5-34.

5.2.4 Solid Solution 20 mol% PE – 40 mol% PG – 40 mol% NPG (at Point No.20):

The sample at Point No. 20 (Sample 20) has a composition of 20%PE-40%PG-40%NPG, the thermal ramping behavior of the ternaries are expected to show more complex reactions. However, the structural features in the XRD patterns taken at various temperatures (Figure 5-35) show predominantly $\alpha + \beta$ phases stable. It should be noted that the $\beta$ phase amount is very small in this case, and when the patterns are compressed it is difficult to observe these very low intensity peak. From 25°C to 40°C, $\beta$ phase of NPG is stable and after 40°C Bragg peaks from this phase disappear. At 40°C, $\beta$ phase of NPG transforms to $\gamma$ phase. Since there is PG component in this mixture, so as per PG-NPG binary phase diagram, PG and NPG make a complete solid solution, $\gamma_T$ should be expected after $\sim$ 75°C. The $\gamma_T$ peak and $\alpha$ (101) Bragg peaks overlap so these peaks can not be distinguished at low temperatures except that the $\alpha$ (101) peak has broadened which indicates the presence of another peak. After 40°C, $\alpha$ and $\gamma$ phases are stable and above 75°C, $\alpha$ and $\gamma_T$ are stable for the tested range of 25°C to 80°C. We propose that the reactions are as follows based on the XRD data: The DSC scan with two endothermic peaks and a broad endothermic hump which represents heat of mixing of two phases (Figure 5-36). Since it is a ternary mixture, PE, PG and NPG interact with each other and some transitions are proposed based on the binary phase diagrams (Point #20):

$$\alpha + \beta \rightarrow (CT)\alpha + \gamma \rightarrow (CT)\alpha + \gamma_T \rightarrow (CT)L + \gamma + \gamma_T \rightarrow L + \gamma_T (> 433K)$$

($\sim 223K – \sim 313K$), ($\sim 313K – \sim 353K$), ($\sim 353K – 393K$), ($\sim 393K – 433K$)

CT=Continuous Transition
Figure 5-35. In-situ x-ray patterns of point 20. At 25°C a small β phase peak is observed which transforms to γ. Peak broadening at 80°C can be seen for α (101) peak which show there is γ phase overlapping with α-PE phase.
Figure 5-36. DSC plot of point 20 shows $\beta \rightarrow \gamma$ transition at 41°C and a broad endotherm of mixing of $\alpha + \gamma$ followed by melting.

Figure 5-37. NMR spectra of point 20 is showing PG rich ternary system.
(PE-PG, PE-NPG and PG-NPG) and current XRD data. \( \alpha \) and \( \beta \) phase are stable up to \( \sim 41^\circ C \). At \( \sim 41^\circ C \), \( \beta \rightarrow \gamma \) transformation takes place. From \( \sim 45^\circ C \) to \( 80^\circ C \), \( \alpha \) and binary phase diagrams are stable. It is proposed that \( \alpha \) and \( \gamma_T \) phases remain stable till \( \sim 155^\circ C \). After \( 155^\circ C \), high temperature phase, \( \alpha \) phase dissolves into \( \gamma_T \) which remains stable till complete melting occurs at \( \sim 170^\circ C \). The NMR spectra of this composition are shown in Figure 5-37.

### 5.2.5 Solid Solution 50 mol% PG–50 mol% NPG (at Point No.22)

The reactions for the 50/50 PG/NPG are well known and the XRD, DSC, and NMR plots are shown in Figure 5-38, Figure 5-39 and Figure 5-40. The results are summarized below (Point # 22):

\[
\alpha + \beta \rightarrow \gamma_T \rightarrow L \ (\sim 438K)
\]

(223K – 313K) \( \sim 313K \rightarrow \sim 438K \)

\[ \Delta H^o = 102.61 J / g, \quad \Delta H_L^o = 36.64 J / g \]

### 5.3 In-situ x-ray Diffraction, DSC and NMR of the Ternary S-S Along “PG Line”

So far we have described phase transitions occurring in several samples along “NPG line and PE lines,” these include many ternary compositions as well as some binaries.

The XRD, DSC and NMR will be simply summarized in this section for samples at points, 24, 26, 28, 30, 32 and 33.
Figure 5-38. In-situ x-ray patterns of point 22 show α phase between 25-35°C which transforms to γT between 40-45°C. After 45°C only γT phase is stable.
Figure 5-39. DSC plot of point 22. $\beta \rightarrow \gamma_T$ at 41°C and $\gamma_T$ is stable till melting at 155°C.

Figure 5-40. NMR spectra point 22, showing PG abundance in the equimolar composition of PG-NPG.
5.3.1 A-E. Solid Solution Ternairs and Binaries for the samples at (Points, 24, 26, 28, 30, 32 and 33):

The pure PG sample is well characterized (sample at Point 23) and the following are phase transitions (From Figure 5-41 and Figure 5-42):

\[ \alpha_{PG} (BCT) \rightarrow \gamma_{PG} (FCC) \rightarrow L \]
\[ \sim 358K \sim 473K \]
\[ \Delta H^o = 128.7J/g, \quad \Delta H_{L}^o = 31.37J/g \]

Sample at Point 24 - 5 mol% PE – 90 mol% PG – 5 mol % NPG shows the following transitions (Figure 5-43, Figure 5-44 and Figure 5-45).

\[ \alpha^* + \beta \rightarrow \alpha^* + \gamma_{T} \rightarrow \gamma_{T} \rightarrow L (> 458K) \]
\[ (\sim 328K \sim 333K) \ (\sim 333K \sim 383K) \ (\sim 383K \sim 458K) \]
\[ \Delta H^o = 130.77J/g, \quad \Delta H_{mixing} = 32.97J/g \]

*PG rich

The sample at Point No. 26 (15 mol% PE – 70 mol% PG – 15 mol% NPG):

shows the following reactions transitions (Figure 5-46, Figure 5-47, Figure 5-48 and Figure 5-49)

\[ \alpha^* + \beta \rightarrow \alpha^* + \gamma_{T} \rightarrow \gamma_{T} \rightarrow (L + \gamma_{T} - small region) \rightarrow L \ (> 463K) \]
\[ (~ 223K \sim 333K) \ (\sim 333K \sim 358K) \ (\sim 358K \sim 453K) \ (\sim 353K \sim 463K) \]
\[ \Delta H^o = 145.73J/g, \quad \Delta H_{mixing} = 30.58J/g \]

*PG rich

The Sample at Point No. 28 has a composition of 25%PE-50%PG-20%NPG, and based on the XRD, DSC and NMR data shown in (Figure 5-50, Figure 5-51 and Figure 5-52) we summarize the following:
\[ \alpha^* + \beta \rightarrow (\alpha + \gamma)^* \rightarrow (\alpha + \gamma_T)^* \rightarrow (\gamma_T)^* \rightarrow (L + \gamma + \gamma_T)^* \rightarrow L \ (\text{> 473K}) \]
\[ (-223K \sim 313K) \quad (-313K \sim 358K) \quad (-358K \sim 403K) \quad (-403K \sim 458K) \quad (-458K \sim 473K) \]
\[ \Delta H^o = 103.79 J/g, \quad \Delta H^o = 356.06 J/g \]

*PG rich*

The Sample at Point No. 30 has a composition of 35% PE-30%PG-35%NPG, and based on the XRD, DSC and NMR data shown in (Figure 5-53, Figure 5-54 and Figure 5-55), we summarize the following:

\[ (\alpha + \beta) \rightarrow (\alpha + \gamma) \rightarrow (\alpha + \gamma_T) \rightarrow (\beta + \gamma + \gamma_T)^* \rightarrow (L + \gamma + \gamma_T)^* \rightarrow (L + \gamma_T) \rightarrow L \ (\text{> 483K}) \]
\[ (-223K \sim 308K) \quad (-308K \sim 348K) \quad (-348K \sim 393K) \quad (-393K \sim 438K) \quad (-438K \sim 458K) \quad (-458K \sim 483K) \]
\[ \Delta H^o = 101.77 J/g, \quad \Delta H^o = 47.16 J/g \]

The Sample at Point No. 32 has a composition of 35% PE-30%PG-35%NPG, and based on the XRD, DSC and NMR data shown in Figure 5-56, Figure 5-57 and Figure 5-58; we summarize the following:

\[ (\alpha + \beta) \rightarrow (\alpha + \gamma) \rightarrow (\alpha + \gamma + \gamma_T) \rightarrow (\alpha + \gamma) \rightarrow (L + \gamma_T) \rightarrow L \ (\text{> 488K}) \]
\[ (-223K \sim 308K) \quad (-308K \sim 348K) \quad (-348K \sim 383K) \quad (-383K \sim 428K) \quad (-428K \sim 458K) \quad (-458K \sim 488K) \]

Finally, the last sample 50/50 PE/NPG shows the following based transitions upon Figure 5-59, Figure 5-60 and Figure 5-61 (Point No. 33):

\[ \alpha + \beta \rightarrow \alpha + \gamma \rightarrow \gamma + \gamma_{PE(\text{pure})} \rightarrow L + \gamma_{PE(\text{pure})} \rightarrow L \ (\text{> 488K}) \]
\[ (-223K \sim 313K) \quad (-313K \sim 443K) \quad (-443K \sim 463K) \quad (-463K \sim 488K) \]

In addition to above data that were presented for samples on the PE, PG and NPG lines in the Gibbs triangle, additional DSC data was obtained from ternary samples at points, starting from 34 to 41 (Figure 5-2). The DSC data from Figure 5-62 to Figure 5-69 describe the phase transitions. The DSC patterns are clearly marked with regards to the phase transition sequences, so these will not be discussed any further. These data were helpful on establishing phase boundaries.
Figure 5-41. In-situ X-ray pattern of pure PG, shows $\alpha \rightarrow \gamma_{PG}$ transition at $\sim 88^\circ$C.

Figure 5-42. DSC plot of pure PG showing $\alpha \rightarrow \gamma_{PG}$ transition at $\sim 88^\circ$C and melting at $200^\circ$C.
Figure 5-43. In-situ x-ray pattern of point 24 which is rich in PG and only shows α phase between 25-75°C. At 75°C, $\alpha \rightarrow \gamma_T$. 
Figure 5-44. DSC plot of point 24 showing a broad isotherm between 55-130°C.

Figure 5-45. An NMR spectrum of PG rich point 24.
Figure 5-46. In-situ x-ray pattern of point 26 from 25-80°C. Only α phase is observed till 45°C. At higher temperatures, α + γT is observed.
Figure 5-47. In-situ x-ray pattern of point 26 by capillary method shows the presence of $\gamma_T$ after 155°C till melting.
Figure 5-48. DSC plot of point 26 shows two endotherms, $\alpha \rightarrow \gamma_T$ transition takes place at ~85°C and $\gamma_T$ is stable till melting at 215°C.

Figure 5-49. NMR spectra of PG rich point 26 shows high PG abundance relative to PE and NPG.
Figure 5-50. In-situ x-ray pattern of point 28, showing $\alpha + \beta$ region which transition to $\alpha + \gamma$ at 40°C.
Figure 5-51. DSC scan of point 28 shows a small endothermic hump at ~ 40°C. A broad endotherm is observed from 50-135°C where we propose some transitions based on the binaries.

Figure 5-52. NMR spectra of point 28 showing relative abundance of PG.
Figure 5-53. In-situ x-ray pattern of point 30 at different temperatures. At temperatures higher than 125°C, γT peak appears and could not be seen at lower temperature due to overlap with α (101) peak.
Figure 5-54. DSC plot of point 30 shows small endotherm assigned to $\gamma$ at 41°C. A broad endotherm has been proposed as $\alpha + \gamma$ mixing and $\alpha \rightarrow \gamma_T$.

Figure 5-55. NMR plot of point 30 shows very high intensity relative to PG and NPG.
Figure 5-56. In-situ x-ray pattern of point 32 at different temperatures. At temperatures higher than 45°C, γ peak causes peak broadening of α (101) peak due to overlap. After 40°C, α + γ phase is observed.
Figure 5-57. DSC plot of point 32 shows small endotherm at 41°C for $\beta \rightarrow \gamma$ and the second broad endotherm has been proposed to have multiple phase transformations.

Figure 5-58. NMR spectra of point 32 shows very low intensity of PG due to low PG content.
Figure 5-59. In-situ x-ray pattern of point 33 shows $\beta \rightarrow \gamma$ at ~40°C and $\alpha + \gamma$ is observed between 40-80°C. At higher temperatures only $\alpha$ peaks are observed.
Figure 5-60. DSC plot of point 33, showing $\beta \rightarrow \gamma$ transition at ~40°C. $\alpha \rightarrow \gamma_{\text{PE}}$ and $\gamma \rightarrow \gamma_{\text{PE}}$ at 170°C and 190°C, respectively.

Figure 5-61. NMR spectra of point 33 showing more PE than NPG although it is an equimolar composition.
Figure 5-62. DSC scan of point 35 shows $\alpha + \beta$ region below $\sim 43^\circ$C and then multiple transitions take place, eventually $\gamma_T$ phase goes to liquid at $\sim 220^\circ$C.

Figure 5-63. Point 36 DSC shows only $\alpha$ phase at low temperature which transitions to three phase region of $\alpha + \gamma + \gamma_T$ at $\sim 80^\circ$C.
Figure 5-64. Point 37 DSC has only $\alpha$ phase till 110°C which transforms to $\alpha + \gamma_T$ at around 110°C. A hump in the peak spanning from 100-175°C indicates this transition.

Figure 5-65. DSC scan of point 38 shows $\alpha \rightarrow \alpha + \gamma_T \rightarrow \alpha + \gamma + \gamma_T$, indicated by wide hump from 55-140°C.
Figure 5-66. Point 39 DSC scan has a double peak indicating $\alpha \rightarrow \gamma_T$ and immediately followed by $\beta \rightarrow \gamma$ transition. Three phase region is observed by a wide endothermic hump from 75-130°C.

Figure 5-67. Point 34 DSC shows $\alpha + \beta$ mixing region at ~ -25°C. This is a very unique region where $\alpha + \beta$ composition is rapidly changing with temperature.
Figure 5-68. DSC scan of point 40 is very similar to points 20 and 4. \( \beta \rightarrow \gamma \) transition takes place at \(- 43^\circ C\) which further transforms to \( \alpha + \gamma_T \). Between 80-170\(^\circ\)C, \( \gamma + \gamma_T \) is stable.

Figure 5-69. Point 41 DSC scan shows very weak \( \beta \rightarrow \gamma \) transition takes place at \(- 43^\circ C\) which further transforms to \( \alpha + \gamma_T \). Between 80-160\(^\circ\)C, \( \gamma + \gamma_T \) is stable and a three phase region is observed at \(- 165^\circ C\).
5.4 Summary of NMR data

The mole ratio of each component in the PE-PG-NPG ternary system is calculated using NMR data. Since PE, PG and NPG give identifiable peaks at different chemical shift positions, the respective peaks are integrated to arrive at the mole ratio of each component. Equation 3-8 and Table 3-1 are used to perform the required calculations.

Table 5-2. Sample numbers with original composition and the composition calculated from NMR data at 25˚C.

<table>
<thead>
<tr>
<th>sample #</th>
<th>Formula Composition, mol%</th>
<th>Composition from NMR, mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PE</td>
<td>PG</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>33.3</td>
<td>33.3</td>
</tr>
<tr>
<td>10</td>
<td>45</td>
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<td>40</td>
</tr>
<tr>
<td>22</td>
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<td>50</td>
</tr>
<tr>
<td>28</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>33</td>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5-2 shows the activity of each component in the sample. Using this data, activity plots of the individual components are made as shown in Figure 5-70.
Figure 5-70. Activity data of PE, PG and NPG as determined by NMR.

5.5 Discussion on Polyalcohols and Phase Diagrams

As propounded by Willard Gibbs, the phase rule is fundamental to the study of phase/equilibrium diagrams. Only a brief introduction is given here to help understand interpret and construct phase diagrams. The phase rule expresses the relationship, at equilibrium, of the number of phases, P, with the number of components, C, and the number of degrees of freedom, F. The rule may be written as follows –

\[ P + F = C + 2 \]  

Equation 5-1

The phase is defined as the homogenous part of the system, bounded by surfaces, and in principle, can be separated mechanically. Phases generally show compositional variations.
The number of components is defined as the smallest number of independently variable constituents necessary for the statement of the compositions of all the phases in the system, for example, the number of constituent metals.

The number of degrees of freedom of the equilibrium state is the number of conditions that can be altered independently without changing the state of the system, or which have to be specified to define completely the state of the system. In Equation 5-1, it has been assumed that temperature, pressure and composition are the only externally controllable variables that influence the phase equilibria.

In ternary systems, two compositions need to be defined/specified to define the system. In systems where pressure is assumed as constant, the phase rule reduces to

\[ P + F = C + 1 \]  

Equation 5-2

Applying this reduced ‘phase rule’ to ternary system with \( C = 3 \), gives

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

The composition triangle is represented by an equilateral triangle with lines parallel to its sides. Three corners represent three components and the length of each side of the triangle is divided into 100 equal parts where each part represents 1% on the composition scale in each binary system.

PE-PG phase diagram was developed by Barrio et al.\(^2\). PE and PG are iso-structural both at room temperature (body centered tetragonal)\(^6,7\) and high temperature phases (FCC). Low temperature phase of PE is characterized by strong intermolecular hydroxyl hydrogen bonding between molecule and eight of its neighbors in a layer parallel to the (001) plane\(^8\). The interlayer bonds are weak and due to Van der Waals forces. PG has
similar bonding scheme to PE except that one link is open, due to substitution by -CH$_2$OH group in the PE molecule for a –CH$_3$ group in the PG molecule. I$_4$ symmetry of PG requires the presence of a statically disordered molecule since the required site symmetry, is not present in PG molecule as in PE.

As reported previously, the crystal to plastic transformation in PE and PG are first order transitions. Nitta suggested correlation between the hydrogen bond breaking at higher temperatures permitting rotation and molecular vibration leading to plastic phase. Benson et al. measured infrared absorption for PE and indicated that all the hydrogen bonds are broken at the transition temperature.

Barrio et al. was the first to propose a phase diagram for the binary mixture of PG-NPG system. They used thermal analysis and X-ray powder diffraction techniques to characterize the changes taking place in the mixtures. Samples were prepared by mixing the two pure chemicals in desired proportions and then melting them in the furnace followed by slow cooling to room temperature.

PG and NPG, both may be considered a derivative of Pentaerythritol (PE). PG is obtained by substituting one –CH$_2$OH group with a methyl (-CH$_3$) group. In a similar manner, NPG involves substitution of two –CH$_2$OH groups with two methyl groups. Phase transitions in PG and NPG have been characterized as first order transitions. The first hypothesis for crystal to plastic transition was made by Nitta for PE, where he proposed that hydrogen bonds which maintain the molecules rigidly in the ordered solid crystal phase are broken at the transition temperature permitting the molecular vibration and rotation, so that the molecules can be considered as spherical in the plastic form.
The phase transitions in polyols such as PE, PG and NPG are significant because it involves large enthalpy changes that can be used as heat storage medium. Low temperature ordered phase to high temperature disordered plastic phase transitions are of first order and occur at temperatures well below the melting/fusion temperatures. These energetic transitions are accompanied by a large entropy change of solid-solid transition compared to solid-liquid transition. Benson et al.\textsuperscript{8} first reported the thermophysical properties of PE, PG and NPG and their mixtures. Chandra et al.\textsuperscript{12} reported the adjustment of transformation temperatures and effects of dopants in the crystal structural properties of these polyalcohols. Teisseire et al.\textsuperscript{13} investigated PE-NPG phase diagram over the complete composition range. Barrio et al.\textsuperscript{14} also worked on PE-NPG system and tried to explain some peaks reported by Teisseire et al.\textsuperscript{13}. They stated that there is another invariant transition happening in PE-NPG system at 343 K due to the existence of intermediate phase. Hence, they modified the PE-NPG diagram reported by Teisseire et al. According to the authors, new measurements were performed using a highly sensitive thermal device with sample masses smaller than those used by Teisseire et al. in order to decrease the temperature gradients. According to Barrio et al.\textsuperscript{14}, there is a new intermediate cubic phase, called C\textsubscript{3}, which is also FCC and the presence of this phase necessitates the establishment of new invariant transformation at 353 K. Using thermal and crystallographic characterizations, a new and complex phase diagram () was reported for PE-NPG system.
5.6 **Compilation of DSC data for various Ternary Compositions**

A progression of DSC scans for NPG line is shown in Figure 5-71. The first observation from this plot is the presence of an invariant temperature at around 40-43˚C in which NPG $\beta \rightarrow \gamma$ phase. Also, it is evident from the combined plot that with the decrease of NPG amount in the alloy composition, the melting temperature of the alloy increases from 125˚C for pure NPG to 225˚C for 10 mol% NPG.

A progression of DSC scans for PE line is shown in Figure 5-72. Again, there is a definite eutectoid invariant temperature at around 40-43˚C in which NPG $\beta \rightarrow \gamma$ phase. From the combined plot, alloy melting temperature is decreasing with decrease of PE content in the alloy composition, from ~ 265˚C for pure PE to ~ 160˚C for 20 mol% PE.

Figure 5-73 shows the progressive DSCs for the PG line, from pure PG to no PG in the PE-PG-NPG alloy compositions. It is very clearly seen that with the decrease of PG mole % in the alloy composition, there is increase in the melting temperature of the alloy, from 200˚C for pure PG to ~ 240˚C for 10 mol% PG. Further, there is an invariant temperature from 0-50 mol% PG at around 43˚C.
Figure 5-71. Progression of DSC scans along NPG line marked as black dotted line on the ternary compositional plot.
Figure 5-72. Progression of DSC scans along line PE marked as blue dotted line on the ternary compositional plot.
Figure 5-73. Progression of DSC scans along line PG marked as red dotted line on the ternary compositional plot.
5.7 Development of Isothermal Ternary Phase diagrams of PE-PG-NPG

This study is mainly to develop ternary phase diagrams by using experimental methods. Simple deduction of the ternary diagram from the binaries have been described by many thermodynamics. Oonk and Calvert\textsuperscript{15} showed how to plot ternary isothermal section from binaries (Figure 5-74). The procedure used to develop PE-PG-NPG ternary isothermal sections of the phase diagrams is to arrange the three binaries, namely PE-PG\textsuperscript{2}, PG-NPG\textsuperscript{1}, and PE-NPG (from this work) around the Gibbs triangle. We re-determined the PE-NPG phase diagram in this study due to discrepancies in the literature\textsuperscript{13}.

![Figure 5-74. Ternary system composed of three 1,4-dihalobenzenes forming mixed crystals. Isothermal section (t = 70°C) of ternary (solid-liquid) equilibrium.\textsuperscript{15}](image)

In this study, a template was made with the Gibbs triangle in the middle superimposed by the PE-PG, PE-NPG binary phase diagram to scale. The DSC and XRD data (temperature data) was plotted along with standard phase rule knowledge, incorporating tie triangles.
Some approximations have been made by experience to construct the diagram, where data was lacking. Isothermal sections of PE-PG-NPG at 30°C, 45°C, 80°C, and 205°C have been constructed and shown in Figures 6.1 to 6.5. The 30°C section of PE-PG-NPG was derived by using in-situ XRD data and DSC data.

This section, at 30°C, shows presence of α-phase in equilibrium with α+β phases and α+γT and the α-phase. BCT α covers majority of the PG and PE rich areas of the ternary diagram Figure 5-75. The projection of the pure γ phase on the PG-NPG line was first marked in the vicinity of ~70% NPG, the α+γT and β+γT phase region were also projected from the 30°C on the PG-NPG line of the Gibbs triangle. The boundary between the (α+β) and α region was made using the XRD data of point 2, 4, 6, 7, 8, 10, 11, 14, 16, 20, 22, 23, 24 and 33; the dots with different color indicate the data points. A tie triangle was made to establish α+β+γT region (white region). The regions established, obey the phase rules for the ternaries.

The ternary at 45°C is shown in Figure 5-76. In this case the α-phase is in equilibrium with α+γ phases (γ-rich in NPG), and α+γT. In a similar manner, as described for the 30°C ternary, the α+γT, γT and estimated γ+γT phase regions and finally the tie triangle α+γ+γT were constructed. The dots with different color indicate the data points; the deductions from the DSC are not indicated in the phase diagram for temperature range of 30-80°C. A tie triangle was made to establish α+β+γT region (white region). The isothermal section at 60°C is shown in Figure 5-77. In this case there is a small α-phase is in equilibrium with (a large region) of α+γT phases. A (α+γ) region is also present on the
PE-NPG line of the Gibbs triangle, and a small ($\gamma + \gamma_T$) region in the NPG corner. The tie triangle has $\alpha + \gamma + \gamma_T$.

In a similar manner described for the 60°C ternary diagram, the 80 °C, 140 °C, 160 °C, 205°C, 220°C, 240°C and 280°C isothermal sections were obtained (Figure 5-75 to Figure 5-85). In this case we obtained liquid phase in the PG and NPG region of the ternary diagram; as the PG-NPG diagram shows complete liquid region at 205°C, and the PE-PG shows partial liquid region from 0 - ~ 40% PE, and the PE-NPG diagram shows liquid region between the composition of 70%-100% NPG.

A summary of all the stable phases (single, two, and three phase regions) and their temperature ranges based on the isothermal section of the ternary PE-PG-NPG phase diagrams is presented in Table 5-1. The low temperature solid solution phases (LTSSP) namely ($\alpha$ and $\beta$), and the high temperature solid solution phases (HTSSP) such as $\gamma$ and $\gamma_T$ temperatures are listed. In addition, phase stability regions for the binary ($\alpha + \beta$), ($\alpha + \gamma_T$), ($\gamma_T + \beta$), ($\alpha + \gamma$), ($\gamma + \gamma_T$), ($\alpha + \gamma$), and (L+\gamma) are also listed in Table 5-1. Finally, using the tie triangle rule, the ($\alpha + \beta + \gamma_T$), ($\alpha + \gamma + \gamma_T$), and (L+\gamma+\gamma_T) ternary phases were extrapolated (Table 5-1 and Figures 5-76-5-86). The tie lines could not be placed on the two phase regions of the ternary phase diagram due to lack of extensive data needed for this purpose.

Thus, using experimental data we have constructed the certain isothermal thermal sections of the very complex PE-PG-NPG system. This is expected to lead to new materials for thermal energy storage.
Figure 5-75. Isothermal section at 303K (30°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\alpha$, $\beta$, $\gamma_T$ single phase, $\alpha+\beta$, $\alpha+\gamma_T$, $\beta+\gamma_T$, region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study. Tie triangle $\alpha+\beta+\gamma_T$, was extrapolated.
Figure 5-76. Isothermal section at 318K (45°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The α, γ, γf single phase, α+γ, α+γf, γ+γf, region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and our PE-NPG. Tie triangle α+ γ+γf, was extrapolated.
Figure 5-77. Isothermal section at 333K (60°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\alpha$, $\gamma$, $\gamma_T$ single phase, $\alpha$+$\beta$, $\alpha$+$\gamma_T$, $\gamma$ + $\gamma_T$, region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study. Tie triangle $\alpha$+ $\gamma$ + $\gamma_T$, was extrapolated.
Figure 5-78. Isothermal section at 353K (80°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\alpha$, $\gamma$, $\gamma_T$ single phase, $\alpha+\gamma$, $\alpha+\gamma_T$, $\gamma+\gamma_T$, region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study. Tie triangle $\alpha+\gamma+\gamma_T$, was extrapolated.
Figure 5-79. Isothermal section at 413 K (140°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\alpha$, $\gamma$, $\gamma_T$, L, single phase, $\alpha+\gamma$, $\alpha+\gamma_T$, $\gamma+\gamma_T$, L+$\gamma$, L+$\gamma_T$ region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study. Tie triangles with $\alpha+\gamma+\gamma_T$, and L+$\gamma+\gamma_T$ were extrapolated.
Figure 5-80. Isothermal section at 433K (160°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The α, γ, γT, L, single phase, α+γ, α+γT, γ + γT, L+γ, L+γT region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG and PG-NPG, and PE-NPG from this study. Tie triangles with α+ γ + γT, and L+γ+γT were extrapolated.
Figure 5-81. Isothermal section at 463K (190°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The α, γ, γT, L, single phase, α+γ, α+γT, γ+γT, L+γ, L+γT region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG2 and PG-NPG1, and PE-NPG from this study. Tie triangle L+γ+γT was extrapolated.
Figure 5-82. Isothermal section at 478K (205°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\gamma_T$ and L single phase, L+$\gamma_T$ region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study.
Figure 5-83. Isothermal section at 493K (220°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\gamma_T$, L, and L+$\gamma_T$ region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study. Tie triangles with $\alpha+\gamma+\gamma_T$, and L+$\gamma_T+\gamma_T$ were extrapolated.
Figure 5-84. Isothermal section at 513K (240°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The $\gamma_T$, L, single phase, L+$\gamma_T$ region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s: PE-PG$^2$ and PG-NPG$^1$, and PE-NPG from this study.
Figure 5-85. Isothermal section at 553 K (280°C) of the ternary PE-PG-NPG phase diagram (PD). In-situ XRD and DSC data was used to construct the diagram. The L, single phase region boundaries at the base of the Gibbs triangle were obtained by projections from the three binary PD’s; PE-PG and PG-NPG, and PE-NPG from this study.
Table 1. Phase designations and approximate temperature stability regions for single, two phase, or three phase regions derived form ternary PE-PG-NPG Phase Diagrams.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Stability Temp. Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 188^\circ C$ [PE or PG LTSSP] &quot;LTSSP = Low Temp. Solid Solution (SS) Phase&quot;</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 43^\circ C$ [NPG rich LTSSP] &quot;HTSSP = High Temp. SS Phase&quot;</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$\rightarrow 40^\circ C$ to $\sim 188^\circ C$ [NPG rich HTSSP]</td>
</tr>
<tr>
<td>$\gamma_T$</td>
<td>$\rightarrow 22^\circ C$ to $\sim 188^\circ C$ [PE/PG rich HTSSP]</td>
</tr>
<tr>
<td>$\alpha + \beta$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 40^\circ C$ [PE/PG rich LTSSP+ NPG rich LTSSP]</td>
</tr>
<tr>
<td>$\alpha + \gamma_T$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 188^\circ C$ [PE/PG rich LTSSP+HTSSP]</td>
</tr>
<tr>
<td>$\beta + \gamma_T$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 40^\circ C$ [NPG rich LTSSP+HTSSP]</td>
</tr>
<tr>
<td>$\alpha + \gamma$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 188^\circ C$ [PE/PG rich LTSSP+HTSSP]</td>
</tr>
<tr>
<td>$\gamma + \gamma_T$</td>
<td>$\rightarrow 40^\circ C$ to $\sim 190^\circ C$ [HTSSP's]</td>
</tr>
<tr>
<td>$\alpha + \gamma$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 188^\circ C$ [PE/PG rich LTSSP+HTSSP]</td>
</tr>
<tr>
<td>$L + \gamma$</td>
<td>$\rightarrow 140^\circ C$ to $\sim 190^\circ C$ [L+HTSSP]</td>
</tr>
<tr>
<td>$L + \gamma_T$</td>
<td>$\rightarrow 140^\circ C$ to $\sim 270^\circ C$ [L+HTSSP]</td>
</tr>
<tr>
<td>$\alpha + \beta + \gamma_T$</td>
<td>$\rightarrow 30^\circ C$ to $\sim 43^\circ C$ [LTSSP's+HTSSP] - From Tie triangles</td>
</tr>
<tr>
<td>$\alpha + \gamma + \gamma_T$</td>
<td>$\rightarrow 45^\circ C$ to $\sim 160^\circ C$ [LTSSP+HTSSP's] - From Tie triangles</td>
</tr>
<tr>
<td>$L + \gamma + \gamma_T$</td>
<td>$\rightarrow 140^\circ C$ to $\sim 240$-$250^\circ C$ [L+HTSSP's] - From Tie triangles</td>
</tr>
<tr>
<td>$L$</td>
<td>$\rightarrow &gt; 275^\circ C$ [Complete Phase field]</td>
</tr>
</tbody>
</table>
5.8 References

Chapter 6

Conclusions

6.1 PE-NPG Phase Diagram

Binary phase diagram of PE-NPG has been re-determined. X-ray and DSC characterization has been performed on PE-NPG system. The crystal structure identification plays an important role because the transitions have varying amount of heat absorption, depending on the composition. PE rich binaries show an exothermic dip and NPG rich binaries reveal endothermic continuous transformation regions; these are essentially heat of mixing in a two phase region. The PE-NPG phase diagram shows two eutectoids, $\gamma \rightarrow \alpha + \beta$ at 43°C, and the other $\gamma \rightarrow \alpha + \gamma$ at ~162°C (47 mol% PE); noting that the $\gamma'$ region is denoted as $\gamma_T$ in the ternary diagrams). The peritectic reaction, $L + \gamma' \rightarrow \gamma$ phase occurs at ~192°C and at ~35 mol% PE composition; these results are quite different than noted in latest literature. A major portion of the phase diagram has been constructed using XRD and DSC results. In the mid-composition range from 35 mol% PE to 50 mol% PE, there is a $\gamma + \gamma'$ phase region (between 162°C and ~192°C), indicating two high temperature orientationally disordered high temperature phases, storing different amounts of energy. It was also observed that NPG is more soluble in body-centered tetragonal PE than the PE in monoclinic NPG. Abrupt first order $\alpha \rightarrow \gamma'$ phase transition with volume change from BCT to FCC orientationally disordered phase (Figure 5-8 and Figure 5-9). It should be noted that the PE expands preferentially in the ‘c’ direction as
compared to ‘a’ or ‘b’ direction. This phase diagram differs significantly from that of Barrio et al. published in 1992\textsuperscript{1}.

6.2 PE-PG-NPG Ternary Phase Diagram

In the area of polyalcohols for heat storage applications, to the best of our knowledge, this work is the first ever to develop a ternary experimental phase diagram for PE-PG-NPG system. X-ray diffraction, differential scanning calorimetry and Nuclear Magnetic Resonance techniques were used to characterize and analyze the ternary samples. Appropriate in-situ x-ray diffraction (XRD) and differential scanning calorimetry (DSC) data was used and the PE-PG-NPG ternary slices at many temperatures were determined. Tie triangles were extrapolated from the two phase region surrounding them.

From practical stand point, one can obtain lower phase transition temperature than can be achieved with just pure PE, PG, or NPG polyalcohols, or their binaries. In some cases in the NPG rich areas, phase transition were observed blew room temperature. These lower temperature transitions are useful for the cooling applications of these thermal energy storage materials studied in this program.

Ternary isothermal sections of the PE-PG-NPG phase diagram based on the experimental data in this study, and using established phase diagrams of PE-PG, PG-NPG binary phase diagram from the literature, and our newly re-determined PE-NPG phase diagram in this study to make projection to the ternary bases of PE-PG, PE-NPG, and PG-NPG legs of the Gibbs triangle. The ternary PE-PG-NPG phase diagrams determined experimentally,
obeyed the phase rules. There were approximations made for the determining the phase boundaries particularly in the NPG rich phase region. The salient features of the various phases at different temperatures are mentioned below.

The isothermal section of PE-PG-NPG at 30°C shows two large regions; $\alpha$ phase and $\alpha + \beta$ region, and smaller regions of $\gamma_i, \alpha + \gamma_i, \beta + \gamma_i$, and tie triangle with $\alpha + \beta + \gamma_i$ phases that are, in general, NPG rich. The $\beta$ phase transforms to $\gamma$ at $\sim$40°C; isothermal sections at 45°C and 60°C shows a large region of $\alpha + \gamma$ phase that is PE-NPG rich, a smaller $\alpha$ phase region that is PE-PG rich, and $\gamma_i, \alpha + \gamma_i, \gamma + \gamma_i$, and tie triangle with $\alpha + \gamma + \gamma_i$ phases. Then there is a change in the 80°C isothermal section in which PE-PG rich $\alpha$ phase region is small, and the $\alpha + \gamma_i$ is very large (as compared to the 60°C one), and smaller regions of $\gamma_i, \gamma, \alpha + \gamma, \gamma + \gamma_i$, and a ternary $\alpha + \gamma + \gamma_i$ are found.

The phase fields change quite aburptly when the temperature is increased to 140°C and liquid phase begins to appear. On the PE-NPG side, single $\alpha$ and $\gamma$ phases encompass the two phase region of $\alpha + \gamma$, and on the PE-PG rich side of the ternary slice, $\alpha, \gamma_i, L + \gamma_i$, and $\alpha + \gamma_i$ phases. On the NPG rich side $L, L + \gamma, L + \gamma_i$ phases are stable, these encompass the ternary regions of the tie triangle. The isothermal ternary sections at 160°C and 190°C are similar to that of 140°C section, except the $\gamma_i$ region is very large, and liquid phase region expands. At 205°C and 220°C there is large region of the liquid (L) phase, a smaller $\gamma_i$ region surrounding the L+$\gamma_i$ region, and at 240°C the liquid phase regions cover nearly all the phase field. Finally at 280°C there is complete liquid phase region.