AN ABSTRACT OF THE DISSERTATION OF

Medagama Liyanage Amila Udayanga Liyanage for the degree of Doctor of Philosophy in Chemistry presented on June 9, 2015.

Title: Synthesis of Intercalation Compounds and Nanocomposites of Inorganic Layered Hosts.

Abstract approved:

_____________________________________________________________________

Michael M. Lerner

Novel synthetic strategies are developed to prepare new intercalation compounds and nanocomposites with several layered hosts (NiPS₃, Na-montmorillonite, MoS₂ and MoO₃). In these products, alkali metals are ionic intercalates and linear polymers, dendrimers or amines act as co-intercalates. In addition to new synthetic approaches, new structures are identified and characterized.

A template synthesis method to prepare NiPS₃/polymer nanocomposites is reported for the first time. Polymers studied were polyethylene oxide (PEO), polyethylenimine (PEI), polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP). NiPS₃/PEO nanocomposites prepared by this template method contain polymer monolayers ($\Delta d = 0.42$ nm) between host layers, in contrast to the polymer bilayers reported in previous reports using a topotactic method. Packing fraction calculations reveals that the interlayer space is denser for template synthesized NiPS₃/PEO than for the topotactically-derived MPS₃/PEO nanocomposites ($M = \text{Ni, Fe, Cd, and Mn}$).
NiPS$_3$/PEI, NiPS$_3$/PVA and NiPS$_3$/PVP nanocomposites were prepared for the first time and also have polymer monolayers between host layers ($\Delta d = 0.41$, 0.42 and 1.56 nm, respectively). The monomer unit / NiPS$_3$ formula ratio is ~ 1 for PEO, PEI and PVA nanocomposites and ~ 0.5 for PVP nanocomposites. More dilute conditions, more polar solvents, and longer aging times increase the crystallite size of the obtained products. Reaction progress studies indicate that the P$_2$S$_6^{4-}$ and Ni$^{2+}$ concentrations in the reaction mixture govern nanocomposite nucleation and growth.

Intercalated nanocomposites with lower generation (G0.0–2.0) polyamidoamine (PAMAM) dendrimers and Na-montmorillonite (Na-MMT) are synthesized using an exfoliation–adsorption method. This is the first report of the G0.0 and G1.0 PAMAM/Na-MMT nanocomposites and of a structurally-ordered G2.0 PAMAM/Na-MMT nanocomposite. The structures obtained depend on the PAMAM generation and the starting reactant ratio. The spherical PAMAM in aqueous medium transforms to a highly flattened conformation after incorporation between the host layers. G0.0 PAMAM forms only monolayer galleries ($\Delta d = 0.42$ nm), while G2.0 PAMAM forms monolayers, bilayers ($\Delta d = 0.84$ nm), and mixed phase structures at lower, higher, and intermediate, organic content, respectively, and exhibits an interesting monolayer to bilayer transition. G1.0 PAMAM shows intermediate behavior, with a monolayer to mixed-phase transition observed at the reactant ratios studied. This is the first report of a monolayer arrangement for PAMAM/clay nanocomposites. The maximum organic contents of G0.0 PAMAM monolayer and G2.0 PAMAM bilayer nanocomposites are ~7% and ~14% respectively, and these materials have ~2 times lower packing fractions (0.31–0.32)
than for linear polymer intercalate nanocomposites of Na-MMT. Under acidic conditions all these nanocomposites form only monolayer galleries, which is ascribed to the stronger electrostatic attraction between negatively charged MMT layers and protonated PAMAM. Acidic conditions also slow the rate of formation of the nanocomposites and generate more ordered products. The Na\(^+\) ions in the Na-MMT structure play a significant role in PAMAM/Na-MMT nanocomposite formation. Both Na-MMT and PAMAM structural units are preserved in the nanocomposites obtained.

Electride solutions obtained by dissolution of Na(m) in ethylenediamine (en) are used for the first time to generate MoS\(_2\) intercalation compounds with Na and en as intercalate and cointercalate, respectively. Two new phases, labeled \(\alpha\) and \(\beta\), have \(\Delta d = 0.35\) and 0.57 nm, respectively; the different gallery dimensions are ascribed to parallel vs. perpendicular orientations of en in the galleries. The \(\beta\) phase structure has not been reported previously in any MS\(_2\) intercalation compounds. The intercalation reaction proceeds via the formation of a metastable kinetic product, the \(\beta\) phase, and the subsequent generation of the thermodynamically stable \(\alpha\) phase. Lower electride concentrations, lower reaction temperatures and shorter reaction times favor production of the \(\beta\) phase. The products obtained have compositions of Na\(_{0.2–0.3}\)MoS\(_2\)·0.3–0.4en with a larger packing fraction than the structurally analogous A-en-GICs (A = alkali metal, GIC = Graphite intercalation compound). The electrochemical reduction of MoS\(_2\) in en/NaPF\(_6\) does not result in these intercalation reactions.
The incorporation of dendrimers into MoO$_3$ is reported for the first time. PAMAM/MoO$_3$ nanocomposites are synthesized using an exfoliation - adsorption method. G0.0 PAMAM only forms monolayers ($\Delta d = \sim 0.5$ nm) between MoO$_3$ layers and G2.0 PAMAM forms both monolayer and bilayers ($\Delta d = \sim 0.7$-$0.8$ nm). In addition to these two structures, a third unknown phase is observed with a much larger gallery expansion ($\Delta d = \sim 1.4$ nm). These nanocomposites have a comparable structures, compositions (12-14% organic component for G0.0 monolayer and 22-25% for G2.0 bilayer) and packing fractions (0.5-0.7 for monolayer and 0.7-0.9 for bilayer) to those in the previously reported linear polymer/MoO$_3$ nanocomposites.

In the above studies, analyses by powder X-ray diffraction (PXRD) are supported by compositional data from thermogravimetric analyses (TGA) and structural optimization (Gaussian). Additionally, the product morphologies, surface properties and constituents are evaluated using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier transform infrared (FTIR) and Raman spectroscopies. UV-visible spectroscopy (UV-vis) is used to monitor reaction progress. Capillary zone electrophoresis (CZE) is used to study compositions and reaction progress.
©Copyright by Medagama Liyanage Amila Udayanga Liyanage
June 9, 2015
All Rights Reserved
Synthesis of Intercalation Compounds and Nanocomposites of Inorganic Layered Hosts

by
Medagama Liyanage Amila Udayanga Liyanage

A DISSERTATION

submitted to
Oregon State University

in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Presented June 9, 2015
Commencement June 2016
Doctor of Philosophy dissertation of Medagama Liyanage Amila Udayanga Liyanage presented on June 9, 2015

APPROVED:

__________________________________________________________________________
Major Professor, representing Chemistry

__________________________________________________________________________
Chair of the Department of Chemistry

__________________________________________________________________________
Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

__________________________________________________________________________
Medagama Liyanage Amila Udayanga Liyanage, Author
ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to my advisor, Prof. Michael M. Lerner for the guidance, encouragement and resources provided throughout my studies at Oregon State University.

I am grateful to Profs. Douglas A. Keszler, MAS Subramanian, Vincent T. Remcho, and Chih-hung (Alex) Chang for serving on my graduate committee and for allowing me to use their laboratory facilities and instruments whenever needed.

I would also like to acknowledge the nice company and discussions of Dr. Bahar Özmen-Monkul, Dr. Tosapol Maluangnont, Dr. Esther Ikhuoria, Dr. Weekit Sirisaksoontorn, Hanyang Zhang, and Xiaochao Liu who are the past and present members of Lerner group.

I take this opportunity to thank Dr. Christine Pastorek for assisting and allowing me to use instruments in teaching labs. My gratitude goes to Dr. Adeniyi Adenuga, Dr. Sean Muir and Changqing Pan (OSU Chemical Engineering) for their assistance in various experiments.

Thank goes to the members of Subramanian and Remcho research groups, Cindy, Paula, Luanne, Talley, Kristi, Todd, Greg, Jenna, Dan, Mark, Teresa (OSU Electron Microscopy Facility) and Nick (OSU Chemical Engineering) for being helpful at various research, administrative, and teaching environments. Also, I would like to thank all the instructors and lab coordinators of General Chemistry Sequence and Integrated Lab program.

I thank OSU Chemistry for the financial support provided throughout my graduate studies and especially for Whiteley Fellowship in Materials Sciences for Summer 2014, Travel awards in Summer 2011 and Summer 2014, and TA award for Winter 2015. Also, I would like to thank College of Science for the Travel award (COSSTA) in Summer 2014.

I thank all my teachers who enlightened me with their wisdom.
Special thanks to my friends and fellow graduate students; Weekit, Adeniyi, and Mohamad Nazari, and the small Sri Lankan community in Corvallis for making the life in Corvallis eventful and joyful.

Finally, and most importantly, I would like to thank my family. I thank my loving parents, father Karunarathne Liyanage and mother Sunila Vithanage for raising me up to who I am today. Your endless love, guidance and dedication made me come this far. I wish to thank my little sister Achala Liyanage, my grandmother Alice Ranathunga and my lovely wife Sulochana Wasala for the love and support given throughout this journey.
CONTRIBUTION OF AUTHORS

Prof. Michael M. Lerner has contributed to the design and writing of each manuscript. Dr. Esther U. Ikhuoria assisted in sample preparation in Chapter 3. Dr. Adeniyi A. Adenuga, and Prof. Vincent T. Remcho assisted in capillary zone electrophoresis experiments in Chapter 3. Dr. Esther U. Ikhuoria contributed in sample preparation and analysis in Appendix A.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Introduction</td>
<td>108</td>
</tr>
<tr>
<td>1.1 Intercalation chemistry</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Metal phosphorous trisulfides (MPS₃)</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Sodium montmorillonite</td>
<td>14</td>
</tr>
<tr>
<td>1.4 Transition metal dichalcogenides (MX₂)</td>
<td>20</td>
</tr>
<tr>
<td>1.5 Molybdenum(VI) oxide (MoO₃)</td>
<td>24</td>
</tr>
<tr>
<td>1.6 Summary</td>
<td>27</td>
</tr>
<tr>
<td>1.7 References</td>
<td>27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Template preparation of NiPS₃ polymer nanocomposites</td>
<td>33</td>
</tr>
<tr>
<td>2.1 Abstract</td>
<td>34</td>
</tr>
<tr>
<td>2.2 Introduction</td>
<td>35</td>
</tr>
<tr>
<td>2.3 Experimental</td>
<td>37</td>
</tr>
<tr>
<td>2.3.1 Reagents and Analytical Methods</td>
<td>37</td>
</tr>
<tr>
<td>2.3.2 Syntheses</td>
<td>38</td>
</tr>
<tr>
<td>2.4 Results and discussion</td>
<td>40</td>
</tr>
<tr>
<td>2.5 Conclusions</td>
<td>50</td>
</tr>
<tr>
<td>2.6 References</td>
<td>51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 Synthesis and characterization of low-generation polyamidoamine (PAMAM) dendrimer – sodium montmorillonite (Na-MMT) clay nanocomposites</td>
<td>54</td>
</tr>
<tr>
<td>3.1 Abstract</td>
<td>55</td>
</tr>
<tr>
<td>3.2 Introduction</td>
<td>57</td>
</tr>
<tr>
<td>3.3 Experimental</td>
<td>59</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1 Reagents</td>
<td>59</td>
</tr>
<tr>
<td>3.3.2 Syntheses</td>
<td>59</td>
</tr>
<tr>
<td>3.3.3 Analytical methods</td>
<td>60</td>
</tr>
<tr>
<td>3.4 Results and discussion</td>
<td>63</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
<td>81</td>
</tr>
<tr>
<td>3.6 Associated content</td>
<td>82</td>
</tr>
<tr>
<td>3.7 References</td>
<td>82</td>
</tr>
<tr>
<td>4 Use of amine electride chemistry to prepare molybdenum disulfide intercalation compounds</td>
<td>87</td>
</tr>
<tr>
<td>4.1 Abstract</td>
<td>88</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>89</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>95</td>
</tr>
<tr>
<td>4.3.1 Reagents</td>
<td>95</td>
</tr>
<tr>
<td>4.3.2 Chemical Syntheses</td>
<td>95</td>
</tr>
<tr>
<td>4.3.3 Electrochemical syntheses</td>
<td>96</td>
</tr>
<tr>
<td>4.3.4 Analyses</td>
<td>96</td>
</tr>
<tr>
<td>4.4 Results and Discussion</td>
<td>97</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>110</td>
</tr>
<tr>
<td>4.6 Acknowledgements</td>
<td>111</td>
</tr>
<tr>
<td>4.7 References</td>
<td>111</td>
</tr>
<tr>
<td>5 Conclusion</td>
<td>115</td>
</tr>
<tr>
<td>5.1 Conclusion</td>
<td>115</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bibliography</td>
<td>120</td>
</tr>
<tr>
<td>Appendices</td>
<td>129</td>
</tr>
<tr>
<td>A. Preparation and characterization of nanocomposites of polyamidoamine (PAMAM) dendrimers with molybdenum (VI) oxide (MoO$_3$)</td>
<td>129</td>
</tr>
<tr>
<td>A.1 Abstract</td>
<td>130</td>
</tr>
<tr>
<td>A.2 Introduction</td>
<td>131</td>
</tr>
<tr>
<td>A.3 Experimental</td>
<td>133</td>
</tr>
<tr>
<td>A.3.1 Materials</td>
<td>133</td>
</tr>
<tr>
<td>A.3.2 Syntheses</td>
<td>134</td>
</tr>
<tr>
<td>A.3.3 Characterization</td>
<td>135</td>
</tr>
<tr>
<td>A.4 Results and Discussion</td>
<td>135</td>
</tr>
<tr>
<td>A.5 Conclusion</td>
<td>146</td>
</tr>
<tr>
<td>A.6 References</td>
<td>146</td>
</tr>
<tr>
<td>B. Supplementary Data</td>
<td>150</td>
</tr>
<tr>
<td>B.1 Supplementary Data</td>
<td>151</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Structure of a typical layered host and intercalation compound</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Daumas-Herold models for staging in graphite intercalation chemistry</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Some intercalate arrangements within galleries</td>
<td>6</td>
</tr>
<tr>
<td>1.4 The FePS$_3$ structure</td>
<td>8</td>
</tr>
<tr>
<td>1.5 Topotactic, exfoliation-adsorption vs template preparation method</td>
<td>13</td>
</tr>
<tr>
<td>1.6 Structure of anhydrous Na-montmorillonite</td>
<td>15</td>
</tr>
<tr>
<td>1.7 The layered structure of 2H-MoS$_2$</td>
<td>20</td>
</tr>
<tr>
<td>1.8 Structure of MoO$_3$</td>
<td>24</td>
</tr>
<tr>
<td>2.1 PXRD patterns for PEO/NiPS$_3$ nanocomposites obtained by the template method. a-NiPS$_3$ obtained by the same approach without PEO is shown for comparison</td>
<td>40</td>
</tr>
<tr>
<td>2.2 SEM image for a PEO/NiPS$_3$ nanocomposite (Sample R0.5V10)</td>
<td>41</td>
</tr>
<tr>
<td>2.3 TGA of nanocomposites with different PEO compositions (* loss shoulder ascribed to surface PEO) DTG indicates the first derivative of TGA curves</td>
<td>42</td>
</tr>
<tr>
<td>2.4 Calculated C$_2$H$_4$O unit volumes from VABC</td>
<td>43</td>
</tr>
<tr>
<td>2.5 UV-visible spectra of some reactants and products of the template reactions. The absorbance at 330 nm (*) is used to monitor nanocomposite formation</td>
<td>48</td>
</tr>
<tr>
<td>2.6 Effect of Ni$^{2+}$ and PEO concentrations on the rate of nanocomposite formation. Curves are obtained using the indicated Ni$^{2+}$ concentrations</td>
<td>49</td>
</tr>
<tr>
<td>2.7 Effect of P$_4$S$_6$$^{4-}$ concentration on the rate of nanocomposite formation. Curves are obtained using the indicated P$_4$S$_6$$^{4-}$ concentrations</td>
<td>50</td>
</tr>
<tr>
<td>3.1 PXRD patterns for (a) G(0.0), (b) G(1.0), and (c) G(2.0) PAMAM/Na-MMT nanocomposites. The reactant ratios (g/g PAMAM/Na-MMT) are indicated</td>
<td>63</td>
</tr>
<tr>
<td>3.2 Mass loss and differential plots for 0.6G(1.0)-2 PAMAM/Na-MMT nanocomposite</td>
<td>65</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>3.3 Interlayer expansion variation with reactant ratios, PAMAM/Na-MMT g/g, at room temperature and pH 10-11</td>
<td>68</td>
</tr>
<tr>
<td>3.4 Dendrimer mass % variation with reactant ratios, PAMAM/Na-MMT g/g, at room temperature and pH 10-11</td>
<td>69</td>
</tr>
<tr>
<td>3.5 A structural model for the G0.0 monolayer nanocomposites. (H - white, O - black, C - light grey, N - dark grey)</td>
<td>71</td>
</tr>
<tr>
<td>3.6 PXRD patterns of (a) G(0.0), (b) G(1.0), and (c) G(2.0)/Na-MMT nanocomposites synthesized in acidic (pH=2-3) and basic (pH=10-11) conditions. Reactant ratios for all the nanocomposites were 0.6 g/g PAMAM/Na-MMT</td>
<td>72</td>
</tr>
<tr>
<td>3.7 Packing fraction vs dendrimer mass % of nanocomposites synthesized at room temperature and pH 10-11. Labels show reactant ratios (g/g PAMAM/Na-MMT). Packing fractions were not calculated for mixed phases</td>
<td>74</td>
</tr>
<tr>
<td>3.8 Capillary electrograms for different PAMAM generations at pH 2.7 (a) and 10.9 (b)</td>
<td>76</td>
</tr>
<tr>
<td>3.9 FTIR spectra of (a) NaMMT, (b) PAMAM G(0.0) and (c) 0.4 PAMAM G(0.0)/Na-MMT nanocomposite. The 2850-3500 cm⁻¹ region of (c) is intensified x10 for clarity.</td>
<td>79</td>
</tr>
<tr>
<td>4.1 Schematic representations of MoS₂ and NaₓMoS₂∙δH₂O, where H₂O is a cointercalate.</td>
<td>90</td>
</tr>
<tr>
<td>4.2 Powder XRD of MoS₂ and the intercalation compounds obtained after 48 h reaction at 60 °C (S-60C-48h) and after 24 h reaction at 60 °C using decreased Na mass (M½-60C-24h).</td>
<td>98</td>
</tr>
<tr>
<td>4.3 Powder XRD of MoS₂ and the intercalation compounds obtained after 24 h at reaction temperatures ambient to 100 °C.</td>
<td>99</td>
</tr>
<tr>
<td>4.4 Powder XRD data obtained for reaction of MoS₂ with Na/en electride solution at 60 °C. Reaction times are indicated at the right.</td>
<td>101</td>
</tr>
<tr>
<td>4.5 Ln(A/A₀) vs. reaction time at 60 °C.</td>
<td>102</td>
</tr>
<tr>
<td>4.6 Proposed reaction mechanism; MoS₂ forms a metastable β phase, which converts to the more stable α phase.</td>
<td>103</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7 Gaussian-optimized molecular dimensions of ethylenediamine.</td>
<td>104</td>
</tr>
<tr>
<td>4.8 Thermograms of MoS₂, en, (a) the α phase Na-en-MoS₂ intercalation compound (S-60C-48h) and (b) a β phase predominant product (S-60C-3h) under Ar flow, and (c) β phase predominant product (S-60C-3h) analyzed under air flow.</td>
<td>105</td>
</tr>
<tr>
<td>4.9 SEM images of (a) MoS₂ and (b) α phase intercalation compound Na₀.3MoS₂·0.4en.</td>
<td>107</td>
</tr>
<tr>
<td>4.10 Raman spectra of MoS₂ and Na-en-MoS₂ intercalation compound (S-60C-3h) indicates the structural change upon intercalation.</td>
<td>108</td>
</tr>
<tr>
<td>4.11 Powder XRD profiles for MoS₂ and products of electrochemical reduction in en/NaPF₆ with applied charges indicated.</td>
<td>109</td>
</tr>
<tr>
<td>4.12 Relative peak areas and widths for MoS₂ and reduction products at different applied charges.</td>
<td>109</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Representative host lattices for intercalation</td>
<td>2</td>
</tr>
<tr>
<td>2.1 Compositional data from thermal analyses and calculated packing fractions for PEO/NiPS₃ nanocomposites</td>
<td>44</td>
</tr>
<tr>
<td>2.2 Effect of synthetic conditions on crystallite size</td>
<td>45</td>
</tr>
<tr>
<td>2.3 Structural and compositional data for new polymer/NiPS₃ nanocomposites</td>
<td>46</td>
</tr>
<tr>
<td>2.4 Comparison of packing fractions of known PEO/MPS₃ nanocomposites. The packing fractions were derived from compositional and structural data in the references indicated</td>
<td>47</td>
</tr>
<tr>
<td>3.1 Structural and compositional data for PAMAM/Na-MMT nanocomposite products obtained using PXRD (d and Δd) and TGA (organic mass %), and derived packing fractions and crystallite sizes (L)</td>
<td>66</td>
</tr>
<tr>
<td>3.2 Compositional and packing data for polymer/A-MMT nanocomposites</td>
<td>70</td>
</tr>
<tr>
<td>3.3 Migration data from CZE and calculated charge data for PAMAM dendrimers</td>
<td>76</td>
</tr>
<tr>
<td>3.4 Comparison of IR bond vibrations in reactants and nanocomposites</td>
<td>80</td>
</tr>
<tr>
<td>4.1 Compositional data for en containing intercalation compounds</td>
<td>106</td>
</tr>
<tr>
<td>5.1 Summary of template synthesized NiPS₃/polymer nanocomposites reported in this dissertation</td>
<td>116</td>
</tr>
<tr>
<td>5.2 Summary of exfoliation-adsorption synthesized selected PAMAM/Na-MMT nanocomposites reported in this dissertation</td>
<td>117</td>
</tr>
<tr>
<td>5.3 Summary of synthesized MoS₂ intercalation compounds using electride chemistry in this dissertation</td>
<td>118</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>A1.</td>
<td>PXRD patterns of $\text{[Na(H}_2\text{O)}<em>2\text{]}</em>{0.25}\text{MoO}_3$ and PAMAM/MoO$_3$ nanocomposites with G0 (a) or G2 (b) PAMAM at different reactant ratios</td>
</tr>
<tr>
<td>A2.</td>
<td>Proposed schematic structure of obtained nanocomposites. (a) G0/MoO$_3$ monolayer and (b) G2/MoO$_3$ bilayer</td>
</tr>
<tr>
<td>A3.</td>
<td>Interlayer expansions ($\Delta d$) obtained at different reactant ratios for PAMAM/MoO$_3$ nanocomposites using PAMAM G0 (Δ) and G2 ( ■)</td>
</tr>
<tr>
<td>A4.</td>
<td>Thermographs of $\text{[Na(H}_2\text{O)}<em>2\text{]}</em>{0.25}\text{MoO}_3$ (a), and the nanocomposites G0-0.5 (b) and G2-0.5 (c)</td>
</tr>
<tr>
<td>A5.</td>
<td>PXRD patterns showing the effect of temperature on G2 PAMAM/MoO$_3$ nanocomposites</td>
</tr>
<tr>
<td>A6.</td>
<td>SEM micrographs of (a) MoO$_3$, (b) Na$_x$MoO$_3$ and (c) the nanocomposite G2-0.8</td>
</tr>
<tr>
<td>A7.</td>
<td>IR spectra of G2 PAMAM (a), nanocomposite G2-0.7 (b) and MoO$_3$ (c)</td>
</tr>
<tr>
<td>B1.</td>
<td>PXRD data for (a) G(0.0), (b) G(1.0), and (c) G(2.0)/Na-MMT nanocomposites synthesized at room temperature and 60 °C. Reactant ratios were 0.3 g/g PAMAM/Na-MMT</td>
</tr>
<tr>
<td>B2.</td>
<td>FTIR spectrum of dehydrated Na-MMT</td>
</tr>
<tr>
<td>B3.</td>
<td>FTIR spectrum of a 0.4 PAMAM G(2.0)/Na-MMT nanocomposite. The 2850-3500 cm$^{-1}$ region is intensified x10 for clarity</td>
</tr>
</tbody>
</table>
LIST OF APPENDIX TABLES

A1. Physical properties of amine surface functional PAMAM dendrimers ...............134

A2. PXRD repeat distances (d) and derived interlayer expansions (Δd) of PAMAM/MoO₃ nanocomposites at different reactant ratios ..........................................137

A3. Comparison of PAMAM/MoO₃ with other polymer/MoO₃ nanocomposites .....137

A4. Compositional data for different reactant ratios using PAMAM G0 and G2 .....141

A5. Effect of temperature on the structure of G2-0.3 nanocomposites ..................143
CHAPTER 1

INTRODUCTION

1.1 INTERCALATION CHEMISTRY

The term intercalation is derived from the Latin verb “intercalate”, which refers to the insertion of an additional day in special years to synchronize the calendar with the solar year. In 1959, Rüdorff applied this term to all chemical derivatives of graphite, indicating that atoms or ions have been inserted, or intercalated, with a lattice expansion perpendicular to the nearly unchanged graphite layers. The terms “inclusion”, “interstitial”, and “intercalation” compounds were used interchangeably in the early days of this chemistry. Lerf has more recently distinguished clearly the differences among these terms and redefined intercalation compounds as described below.

Solids that form intercalation compounds contain stable structural elements like chains, layered sheets or three dimensional frameworks (with a network of channels or unidirectional channels) (Table 1.1). If the 1D or 2D structural elements are electrically neutral, such as in graphite or MoS$_2$, they are bound by weak van der Waals forces. Neutral framework structures, such as aluminophosphates, contain empty 1D channels or interconnected cavities. If these structural elements carry an electrical charge, these are compensated by small counter ions contained between them or occupying their channels and cavities. Most such compounds have many empty lattice sites, or can be expanded to generate sites, that can be occupied by
additional atoms or molecules. Therefore the mobility of the interstitial atoms can be very high if their interaction with the host structure is not too strong. This allows many intercalation reactions to be carried out at or near ambient temperature, which permits the preparation of metastable products that cannot be obtained by traditional high temperature solid state reactions. In summary, intercalation is the reversible uptake of atoms, ions, molecular cations, or molecules, generally at moderate temperatures, and with conservation of structural elements in the host lattice. However, the term intercalation refers to topology, and does not describe the nature of the chemical reaction underlying this process.\(^1\)

Table 1.1 Representative host lattices for intercalation\(^{1,4,5}\)

<table>
<thead>
<tr>
<th>Three-dimensional structures</th>
<th>Zeolites</th>
<th>Aluminophosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M\textsuperscript{+}(Al\textsubscript{x}Si\textsubscript{2-x}O\textsubscript{2})\cdot nH\textsubscript{2}O</td>
<td>Al\textsubscript{2}O\textsubscript{3}\cdot P\textsubscript{2}O\textsubscript{5}\cdot nH\textsubscript{2}O</td>
</tr>
<tr>
<td>Two-dimensional structures</td>
<td>Clays and layered silicates</td>
<td>Montmorillonite Na\textsubscript{x}(Al\textsubscript{2−x}Mg\textsubscript{x})Si\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{2}\cdot mH\textsubscript{2}O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Graphite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal dichalcogenides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MX\textsubscript{2} (M = Sn, Ti, Zr, Hf, V, Nb, Ta, Mo, W; X = S, Se, Te)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal phosphorus trichalcogenides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MPX\textsubscript{3} (M = Mg, V, Mn, Fe, Co, Ni, Zn, Cd, In; X = S, Se)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal oxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molybdenum trioxide MoO\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vanadium pentoxide V\textsubscript{2}O\textsubscript{5}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Transition metal dioxides M\textsuperscript{i}M\textsuperscript{iii}O\textsubscript{2} (M\textsuperscript{i}=alkali metal; M\textsuperscript{iii}=Ti, V, Cr, Mn, Fe, Co, Ni)</td>
</tr>
</tbody>
</table>
One-dimensional structures | Carbon nanotubes | \( \text{MX}_3 \) (M = Ti, Zr, Hf, Nb, Ta; X = S, Se)

Framework structures can intercalate species (molecules or ions) that can be accommodated within their channels or cavities. On the other hand, 1D and 2D lattices can expand in two or one dimensions, and are therefore relatively unrestricted by intercalate size. This expansion potential allows the intercalation of a large variety of intercalate species including atoms, ions, small molecules, organic cations, metal complexes and polymers. From here onwards, this dissertation will focus only on the intercalation compounds with layered host materials.

Figure 1.1 Structure of a typical layered host and intercalation compound

The repeat distance in the stacking direction for layered structures is defined as the interlayer distance \( (d_h) \); in many cases this is the same as the layer thickness (Figure 1.1). As an example sodium montmorillonite sheet thickness and \( d_h \) are the same which is 0.96 nm. In the case of graphite which has an AB stacking arrangement, the repeat distance is 2 × sheet thickness (0.335 nm for graphite). The incorporation/uptake of intercalate species to form galleries expands the lattice along this direction; the new repeat distance is defined as \( d_{IC} \). The difference between the
interlayer repeat distance of the intercalation compound and the host, \( d_{IC} - d_h \), can be called the interlayer expansion (\( \Delta d \)), or gallery height, and reflects the steric requirements of the intercalate. Powder X-ray diffraction technique can be used to determine \( d_h \) and \( d_{IC} \) for both the layered host and intercalation compounds that are produced. On the molecular scale, interlayer expansions can be very small (\(< 0.1 \text{ nm} \) for some Li\(^+\) intercalation compounds) to very large (\(> 5 \text{ nm} \)),\(^8\) depending on the nature of the intercalate species, their arrangement in the galleries, and in some cases on the synthetic methods and post-reaction processing employed.

When the intercalate species are oligomers, polymers, or dendrimers, the resulting intercalation compounds are often called nanocomposites, as both organic and inorganic components co-exist alternatively with domains (in at least one dimension) in the nanometer scale.\(^1\) These nanocomposites have properties markedly differ from those of their components or micro- or macro-scaled composites with similar compositions. As an example, nylon-6-based montmorillonite nanocomposites have been shown to achieve a \(~2\) times higher Young’s modulus with respect to the commercial nylon-6.\(^9\) In another study, a poly(ethylene oxide)/Li-montmorillonite nanocomposite was shown to enhance the stability of the ionic conductivity when compared to a PEO/LiBF\(_4\) polymer-salt complex.\(^{10}\)

In most intercalation compounds, intercalate species are present between all the host layers. In some cases, especially in graphite intercalation chemistry, some of the layers do not separate to admit intercalate, and ordered sequences can form comprising intercalate galleries and more than one host layer. This phenomenon is referred to as staging. Stage 1, 2, and 3 intercalation compounds indicates that one,
two and three host layers, respectively, are separated by the expanded galleries in an ordered sequence. Daumas and Herold introduced a more realistic model to describe this staging phenomenon in terms of intercalate domains (Figure 1.2). There are also examples where disordered or random sequences of intercalate and host layers can arise, this is termed interstratification and is common in clay chemistry.\textsuperscript{1,3}

![Figure 1.2 Daumas-Herold models for staging in graphite intercalation chemistry](image)

Intercalate species are observed with a variety of arrangements within the expanded galleries (Figure 1.3). Most common are monolayers or bilayers, although trilayers and other organizations are also known. If the intercalate is anisotropic, it may be oriented with longer axis “parallel” to the host layers, i.e. in a manner leading to a minimal gallery height. Often the intercalates are charged and contain more and less polar surfaces - the charged or polar ends will typically orient towards opposite charges on the host, with nonpolar ends directed towards the gallery center. The paraffinic structure arises when two intercalate layers are present to compensate the charges of the host layers. These bilayers can be arranged with the intercalates
oriented at an angle to the host surfaces, where $90^\circ$ is defined as the orientation perpendicular to the host layer.$^{11,12}$

![Diagram showing intercalate arrangements in galleries](image)

Figure 1.3 Some intercalate arrangements within galleries

One characteristic property of the expanded galleries is a packing density or packing fraction, which can be defined as the ratio of the volume occupied by intercalates to the total expanded volume. The expanded volume in intercalation compounds can be obtained from the known host layer structure and the interlayer expansion ($\Delta d$). The packing density can then be calculated if the product composition and molecular dimensions are known or can be estimated. The size, shape and degree of free rotational motion of the intercalate species can all play a role in the intercalate orientation, arrangement, and packing density. The host sheet charge density and charge distribution is often a dominant factor, as this determines the
required surface density of the intercalate counter charges in the galleries. This latter property varies widely in different hosts, and may depend on synthetic conditions. If the intercalate species are small and have a higher charge density, they tend to form monolayers. On the other hand, larger intercalate species may form bilayers because the ratio of charge to available host surface (or footprint) is too small to allow charge compensation for the host in a monolayer arrangement. Therefore, bilayer, pseudo-trilayers, or paraffinic structures may be observed.¹

In clays such as Na-montmorillonite, the host is electronically insulating and the sheet charge density and distribution are less dependent on chemical potential. This is in marked contrast to graphite or many metal dichalcogenides, which are electronically conductive and redox active, with variable sheet charge densities and distributions.¹ Next, we will focus on a selected set of host materials, and the reported syntheses and structures of their intercalation compounds and nanocomposites.

1.2 METAL PHOSPHOROUS TRISULFIDES (MPS₃)

Metal phosphorous trisulfides (MPS₃) form a broad and varied class of compounds that exhibit several related structure types. FePS₃ is often used as a representative structure. FePS₃ is monoclinic and deviates slightly from hexagonal symmetry (Figure 1.4). The structure can be described by analogy to the layered CdCl₂ structure. In FePS₃, the S atoms form an essentially cubic close packed array. Alternate layers of octahedral sites within this array are vacant, the remaining octahedral sites are filled by metal (M) and phosphorous atom pairs (P₂). The formula can be rewritten as M₂/³(P₂)¹/³S₂, to highlight the analogy to transition metal
disulfides (MS\textsubscript{2}). In one direction, the MPS\textsubscript{3} layers (d\textsubscript{h} = 0.65 nm) are held together by van der Waals forces, which can separate to admit intercalate guests. These compounds can also be visualized as salts of divalent metal cations with hexathiohypodiphosphate anions (P\textsubscript{2}S\textsubscript{6}\textsuperscript{4-}). X-ray data indicated that MPS\textsubscript{3} compounds with M = Mg, V, Mn, Co, Ni, Pd, Zn and Cd have structures very similar to FePS\textsubscript{3}.\textsuperscript{13-15}

![Figure 1.4 The FePS\textsubscript{3} structure (octahedral units - FeS\textsubscript{6}, connected small spheres - P\textsubscript{2})](image)

MPS\textsubscript{3} compounds can be prepared by several methods, including the direct heating of stoichiometric quantities of the elements (or metal sulfides) in an evacuated silica tube,\textsuperscript{13-15} or the reaction of aqueous solutions of the divalent cations with aqueous P\textsubscript{2}S\textsubscript{6}\textsuperscript{4-} anions.\textsuperscript{16-18}
Several MPS₃ hosts directly react with n-alkylamines to form intercalation compounds. This chemistry has been studied extensively with MgPS₃, MnPS₃ and ZnPS₃. The interlayer distances obtained are invariant to the carbon number of the n-alkylamine, with d_{IC} = 1.05 and Δd = 0.40 nm. The observed expansion can be attributed to the van der Waals radius of a methyl group. From these observations it is evident that the amine carbon chains are arranged parallel to the host layers. Based on the interlayer expansions reported for n-alkylamine intercalates of MgPS₃ and ZnPS₃, bilayer of amines are obtained arranged perpendicular to the host layers.¹³,¹⁵,¹⁹

Alkali metal cations can intercalate into MPS₃ hosts by either chemical or electrochemical reduction. The chemical approach uses a reactive organoalkali metal compound like n-butyllithium, or sodium or potassium naphthalenide, at mild temperatures (20-70 °C). However, not all MPS₃ hosts react similarly with n-butyllithium. Complete occupancy of the vacant octahedral sites would lead to Li₁.₅MPS₃. When the lithium content exceeds Li₁.₂NiPS₃, X-ray diffraction data indicate that the NiPS₃ host lattice is degraded irreversibly with the formation of Li₂S. FePS₃ and some other MPSe₃ compounds react with lower degrees of lithiation, and CdPS₃, ZnPS₃ and MnPS₃ do not react at all under these conditions. Another interesting observation is that no interlayer expansion occurs upon Li⁺ intercalation. For this same reason, the reaction can be difficult to monitor using powder X-ray diffraction alone.¹³,¹⁵

LiₓNiPS₃ is hygroscopic and reacts with atmospheric moisture, resulting in a new intercalation phase with an interlayer expansion of 0.58 nm. This increased expansion is attributed to the uptake of a bilayer of water molecules that solvate the
intercalate Li\(^+\) ions. Other alkali metal intercalation compounds with MPS\(_3\) show a similar water uptake.\(^{13}\)

Lithium intercalation into MPS\(_3\) has also been achieved electrochemically, for example with NiPS\(_3\) as the cathode and Li(m) as the anode of an electrochemical cell containing a Li salt electrolyte dissolved in an aprotic solvent. When the cell is connected, Li(m) is spontaneously oxidized and NiPS\(_3\) reduced. Two different Li\(_x\)NiPS\(_3\) phases (with x = 0-0.5 or x = 0.5-1.5) were obtained with this approach. For x < 1.5, the intercalation reaction is electrochemically reversible, whereas lithiation to x > 1.5 results in irreversible decomposition of the host lattice. The reaction rates depend in part on the electrolyte employed. LeMehaute\(^{20}\) reported different discharge curves obtained in dimethoxyethane-based electrolytes due to the co-intercalation of solvent molecules along with Li\(^+\). Although many MPS\(_3\) hosts have been tested, only NiPS\(_3\) and FePS\(_3\) have been found to undergo substantial electrochemical intercalation. CdPS\(_3\), MnPS\(_3\) and ZnPS\(_3\) are less reactive or unreactive under similar conditions. This has been explained in terms of the electronic band structure. ZnPS\(_3\) and CdPS\(_3\) contain d\(^{10}\) ions; because the 4s and 4p molecular orbitals levels are too high in energy (~12eV) with respect to e\(_g\) sub band, these compounds do not undergo reductive intercalation.\(^{13,15}\)

MnPS\(_3\) also reacts with aqueous salt solutions to form intercalation compounds of general composition Mn\(_{1-x}\)PS\(_3\)A\(_{2x}\)(H\(_2\)O)\(_y\). These compositions result from the abstraction of Mn\(^{2+}\) from the host structure, generating new cation vacancies and a negative layer charge, rather than by the reduction of the transition metal cations. To compensate this host layer charge, guest cations must intercalate between
host layers. A wide range of cations, including $K^+$ and alkylammonium ions, have been intercalated in this manner. Other relatively ionic hosts such as $\text{ZnPS}_3$ and $\text{CdPS}_3$, with $M^{2+}$ ions less stabilized by ligand field, show similar behavior. The more covalent hosts $\text{NiPS}_3$ have greater ligand field stabilization and do not show this layer metal abstraction behavior; $\text{FePS}_3$ is in this class and rarely show this chemistry.\textsuperscript{13,15}

These reactions and the intercalation compounds produced have been explored for applications in ion exchange and as precursors to new materials. For example, the intercalate cations and/or solvent co-intercalates can be exchanged; $\text{Mn}_{1-x}\text{PS}_3\text{A}_{2x}(\text{H}_2\text{O})_y$ ($\text{A} = \text{Na, K}$) reacts in a solution of polyethylene oxide (PEO) to generate new polymer nanocomposites.\textsuperscript{21}

$\text{MPS}_3$ compounds are mostly broad band semiconductors with bandgaps from 1.5-3.5 eV. The electrochemically active $\text{NiPS}_3$ (1.6 eV) and $\text{FePS}_3$ (1.5 eV) have smaller band gaps. The optical properties and dc conductivities of these hosts can change markedly upon intercalation. As an example, Brec et al. found that the electronic resistivities of $\text{FePS}_3$ and $\text{NiPS}_3$ decreased gradually or rapidly, respectively, when reacted with n-butyllithium. They suggested that reduction inserts electrons to delocalized conduction bands resulting in enhanced conductivity, also leading to free carrier absorption and increased reflectivity. The increased conductivities also allow these materials to function efficiently as cathodes in electrochemical cells. Chemical intercalation has little effect on the magnetic properties of $\text{FePS}_3$, but decreases the overall susceptibility with increasing Li content in $\text{NiPS}_3$. It was proposed that the populated band was not associated with either metal 3d orbitals or P orbitals, but derives instead from S or metal 4s orbitals.\textsuperscript{13}
Lagadic et al. first reported the synthesis of nanocomposites containing PEO and MPS$_3$ (M = Mn, Cd) via the reaction of an aqueous polymer solution with M$_{1-x}$PS$_3$A$_{2x}$(H$_2$O)$_y$ (A = Na, K). The products obtained showed $\Delta d \sim 0.8$–0.9 nm, attributed to the intercalation of bilayers of zig-zag-like PEO chains which also coordinate alkali metal ions.$^{21}$ Jeevanandam et al. prepared PEO/A$_x$CdPS$_3$ nanocomposites in a methanolic solution at 55 °C.$^{22}$ Manriquez et al. reported PEO/Li$_x$MPS$_3$ (M = Ni, Fe) using a similar method, and proposed a polymer helical conformation.$^{23}$ Manova et al. reported the intercalation of polyethylene glycol into Na$_x$NiPS$_3$ by reaction in a methanolic aqueous solution, with $\Delta d \sim$0.8 nm.$^{24}$ Other polymers that have been reported to form nanocomposites with MPS$_3$ include linear polyethylenimine (LPEI) and polyvinylpyrrolidone (PVP). LPEI was reported by Oriakhi et al. to form nanocomposites with polymer monolayers ($\Delta d = 0.4$ nm) via the reaction of K$_x$(H$_2$O)$_y$M$_{1-x/2}$PS$_3$ (M = Mn, Cd) and polymers in aqueous solution.$^{25}$ The PVP-containing nanocomposite was reported by Yang et al. via reaction of a potassium-intercalated MPS$_3$ (M = Mn, Cd) and an aqueous PVP solution. The reported $\Delta d \sim 2.3$ nm was much greater than that observed for the PEO nanocomposites.$^{26}$

A solvent-free, melt intercalation approach to obtain PEO/MPS$_3$ nanocomposites (M = Mn, Cd) was first reported by Sukpirom et al. With this method, K$_x$M$_{1-x/2}$PS$_3$$\delta$H$_2$O was shown to directly intercalate PEO at 125 °C. The nanocomposite basal repeat distances were increased by $\sim 0.8$ nm, attributed to the presence of PEO bilayers within the intercalate galleries.$^{27}$
These synthetic approaches involve either topotactic reactions or an exfoliation/reassembly processes. Some potential limitations of these approaches can include the need for higher temperatures (i.e. melt intercalation) or the use of highly-reactive organoalkali reductants (such as butyllithium). A new low-temperature approach utilizing templated synthesis to obtain polymer NiPS\(_3\) nanocomposites (Figure 1.5) will be discussed in Chapter 2.

![Diagram of synthesis methods](image)

Figure 1.5 Topotactic, exfoliation-adsorption vs template preparation method
1.3 SODIUM MONTMORILLONITE

Montmorillonites belong to the structural family known as the 2 : 1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is encased by silica tetrahedra, with oxygen ions of the octahedral sheet shared with SiO$_4$ units (Figure 1.6). The layer thickness/interlayer distance is ~ 1 nm. Substitution within the layers (for example, Al$^{3+}$ replaced by Mg$^{2+}$) generates negative charges that are counterbalanced by alkali or alkaline earth cations, situated in the interlayer volume. Sodium montmorillonite (Na-MMT), has the formula Na$_x$(Al$_{4-x}$Mg$_x$)Si$_8$O$_{20}$(OH)$_4$ with a stacking repeat distance of 0.96 nm for the anhydrous structure. The layer charge is not constant - it varies from layer to layer, and derived values must be considered as an average value over the whole crystal. The cation exchange capacity (CEC) is usually a good qualitative or quantitative measure of the average sheet surface charge densities. Smectite clays such as montmorillonite have a moderately negative surface charge, and a CEC of 60-120 mEq/100 g.$^{12,13,28}$
Figure 1.6 Structure of anhydrous Na-montmorillonite (octahedral sheets – SiO$_6$ and some AlO$_6$, tetrahedral sheets – AlO$_4$, large white spheres – Na, small white spheres – H)

The exchange of Na$^+$ cations with other metal cations, or with organic cations, usually results in larger interlayer distances (1.2 - 2.3 nm). Alternately, the co-intercalation of solvent can also cause considerable gallery expansion. For example, Na-montmorillonite in the hydrated form Na$_{0.5}$(Al$_{3.5}$Mg$_{0.5}$)Si$_8$O$_{20}$(OH)$_4$·3.5H$_2$O has a $\Delta d = 1.24$ nm. Ion exchange or co-intercalation of molecules, surfactants, or polymers between the layers, can result in an ordered expansion of the layers, or in delamination of the sheets to form a colloidal suspension.
In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium. These modified organoclays have lower surface energies and are more compatible with non-polar organic intercalates.\textsuperscript{11}

Intercalation of larger molecules like polyethylene glycol (PEG) and polymers such as polyethylene oxide (PEO) can be achieved for both hydrophilic and organophillic montmorillonites. Polymer-clay nanocomposites combine constituents in at least one nanoscale dimension, typically on the order of 1 to 10 nm. Because of this nanostructure, polymer-clay nanocomposites can possess unique properties. As reported in the literature, polymer-clay nanocomposites can show enhanced mechanical and thermal properties, gas permeability resistance, and fire retardancy.\textsuperscript{11}

Nanocomposites can be produced by an in-situ polymerization, by solid phase melt blending, or by reaction in solution phase (exfoliation/reassembly). The synthetic method employed, as well as other material processing such as annealing time, can have a significant impact on the product structure and properties. The dimensions and microstructures of the dispersed phase significantly influence the properties of polymer composites. When registry between the host layers is maintained, the material is described as an intercalation compound. When this registry is lost, and the clay layers are more randomly distributed throughout the polymer matrix, the system is described as an exfoliated or delaminated nanocomposite. If the clay is not dispersed, it is simply a microfiller. Polymer composite materials are used widely as structural materials in diverse applications.
such as transport (vehicles), construction, electronics and consumer products such as packaging and sporting goods.\textsuperscript{11}

The melt intercalation process was first reported relatively recently, in 1993, by Vaia \textit{et al.}\textsuperscript{29} A thermoplastic polymer is mechanically mixed with an organophilic clay at elevated temperatures. The polymer chains intercalate between the individual silicate layers of the clay. The proposed driving force is the enthalpic contribution from polymer/organoclay interactions.\textsuperscript{11}

In solution phase syntheses, both the clay (hydrophilic or organophilic), and the polymer, are dissolved in water or a polar organic solvent. The entropy gain due to solvent desorption drives the polymer chains to diffuse between the clay layers, compensating for any decrease in chain conformational entropy. Solvent evaporation leads to the desired nanocomposites product.\textsuperscript{11}

\textit{In situ} polymerization is an earlier strategy used to synthesize polymer-clay nanocomposites. This is similar to the solution method indicated above, with the solvent replaced by a polar monomer solution. Once the organoclay is swollen by the monomer, a curing agent is added and, in favorable cases, complete exfoliation occurs. According to previous studies, polymerization is believed to be the indirect driving force of the exfoliation. The clay, due to its high surface energy, attracts polar monomer molecules into the clay galleries until equilibrium is reached. The polymerization reaction lowers the intercalate polarity and therefore displaces the equilibrium. This allows new polar species to diffuse between the layers, and this
process progressively exfoliates the clay. Therefore, the nature of the curing agent as well as the curing conditions can each play a role in the exfoliation process.\textsuperscript{11}

Nanocomposites comprising polyethylene oxide and Na-montmorillonite can form polymer monolayer or bilayer galleries, with $\Delta d = 0.41$ or $0.81$ nm, respectively.\textsuperscript{6} Polyethylene imine nanocomposites are only reported to form intercalate monolayers with $\Delta d = 0.42$ nm.\textsuperscript{25} Ca-montmorillonite forms nanocomposites with polyvinyl alcohol and the interlayer expansion ranged 0.59-0.74 nm, depending on processing conditions.\textsuperscript{30} There are a limited number of reports related to the intercalation and formation of nanocomposites of montmorillonite with dendrimers. Those structures include hyperbranched polymers,\textsuperscript{31,32} higher-generation polyamidoamines,\textsuperscript{33} dendrons,\textsuperscript{34} or dendritic quaternary ammoniums\textsuperscript{26}. Intercalation of these species was found to result in very large gallery expansions ($\sim 3$ nm),\textsuperscript{26,31,34} or pure and mixed phase nanocomposites,\textsuperscript{26,31,33,34} and or in some cases result in exfoliated nanocomposites.\textsuperscript{31} Ratanarat \textit{et al.} reported that generation 2.0 (G2.0) polyamidoamine (PAMAM) forms an exfoliated nanocomposite with Na-montmorillonite.\textsuperscript{35} Alongi \textit{et al.} reported the synthesis of nanomposites containing higher generation (G4.0–7.0) PAMAM with Na-montmorillonite ($\Delta d = 0.78–0.97$ nm).\textsuperscript{33}

Nanocomposites can show dramatic property changes with respect to their native constituents, or even to micro/macromeso-composites of similar composition. The thermal stability of a polymer-layered-silicate nanocomposite of poly(methylmethacrylate) (PMMA) and montmorillonite clay increases by 40-50 $^\circ$C.\textsuperscript{36} The nanocomposited forms of both linear and cross-linked PMMA in
Montmorillonite are more stable by 40–50 °C than the native polymers. This increased stability is ascribed to both the structure change and to the restricted thermal motion of the PMMA intercalates in the nanocomposite galleries. Aside from thermal stability, reduced gas & liquid permeability, increased flame retardancy and increased optical clarity have all been reported for polymer montmorillonite nanocomposites.

Adding to previous reports on the formation of some dendrimer-montmorillonite nanocomposites, in Chapter 3 this dissertation will report the formation and characterization of new lower generation polyamidoamine dendrimer Na-montmorillonite nanocomposites. The materials contain a flattened PAMAM monolayer or bilayer arrangement within galleries, and a monolayer to bilayer transition with increasing dendrimer content.
1.4 TRANSITION METAL DICHALCOGENIDES (MX₂)

Many transition metal dichalcogenides (MX₂) are layered structures consisting of metal cations bound between hexagonal planes of chalcogenide anions. The transition metal cations may have either trigonal prismatic or octahedral coordination. The large number of relative dispositions of chalcogenide planes leads to a wide variety of MX₂ structures and polytypes. Some commonly observed arrangements are represented by 1T-TiS₂ with an (AbC)n stacking repeat, 2H-TaS₂ with an (AbACbC)n stacking repeat, and 2H-MoS₂ with an (AbABcB)n stacking repeat. 1T-TiS₂ has octahedral coordination, whereas 2H-TaS₂ and 2H-MoS₂ have trigonal prismatic coordination around transition metal cations. Typically the sheet thickness for MS₂ hosts is ~ 0.6 nm (Figure 1.7).¹³,³⁷,³⁸

![Figure 1.7](image_url)  
Figure 1.7 The layered structure of 2H-MoS₂ (containing trigonal prismatic MoS₆ sheets)
These layered materials have been investigated intensively as intercalation hosts. Known intercalates include the alkali metal cations, alkylammonium cations, ammonia, amines, water and other solvents. Alkali metal intercalation compounds can be obtained directly by high temperature solid state synthesis, either by the reaction of an MX₂ host with an alkali metal, or by the direct reaction of the A, M and X constituent elements.¹³, ³⁷ Another widely-used technique is the intercalation of the MX₂ host using a liquid-phase reductant like butyllithium or sodium naphthalide dissolved in suitable organic solvents, or with alkali metals dissolved in liquid ammonia.²,¹³, ³⁹⁻⁴¹ Another common synthetic approach involves the electrochemical reduction of the MX₂ host in a suitable electrolyte.⁴²,⁴³

For the MX₂ host structures with more readily reduced transition metal cations, reductive intercalation can be accomplished using ammonia, amines or aqueous solutions. This redox process need not involve any other reductant. In many cases, additional neutral solvent co-intercalates along with cations.¹³

Alkali metal intercalation of MS₂ was first observed in 1959, when Rudorff reported a wide range of A₃MX₂ intercalation compounds prepared from MoS₂, MoSe₂, WS₂, WSe₂, ReS₂, TiS₂, and TiSe₂.², ³⁹ Rouxel and coworkers also extensively studied the intercalation of the group 4 transition metal MX₂ compounds.³⁷ Whittingham et al. studied the lithium intercalation of MX₂, and Schollhorn et al. reported several different syntheses and exchange reactions for MX₂ intercalation compounds.¹³, ⁴⁴
Rudorff reported the formation of Li$_{0.8}$MoS$_2$·0.8NH$_3$, Na$_{0.6}$MoS$_2$, K$_{0.6}$MoS$_2$ and Cs$_{0.5}$MoS$_2$ compounds with interlayer expansions of 0.335, 0.135, 0.195 and 0.274 nm, respectively.\textsuperscript{39} The much larger expansion seen in Li$_{0.8}$MoS$_2$·0.8NH$_3$ arises from the presence of NH$_3$ co-intercalate. Schollhorn and Weiss reported that these intercalation compounds absorb water with a further increase in $\Delta d$ of 0.29–0.70 nm, depending on the reaction conditions.\textsuperscript{44}

A series of alkali metal and alkaline earth intercalation compounds of MoS$_2$ were synthesized in anhydrous NH$_3$(l), with the observed $\Delta d$ values ranging from 0.14 to 0.37 nm.\textsuperscript{40,41} The same method was utilized to prepare intercalation compounds for TaS$_2$, with the resulting products Na$_x$TaS$_2$ and K$_x$TaS$_2$ giving $\Delta d$ of 0.11 and 0.21 nm, respectively.\textsuperscript{45}

Some organic and inorganic bases react to form intercalation compounds with groups 4 and 5 MX$_2$ hosts, with $\Delta d$ ranging from 0.30 nm (for smaller molecules like NH$_3$) to 5.23 nm (for octadecylamine), with compositions reflecting the uptake of 0.1 to 1.0 guests per MX$_2$ unit.\textsuperscript{37} Schollhorn and Zagefka have suggested that in these reactions the metals are reduced and amine molecules are protonated and intercalate as ammonium cations; the interaction between the host and guest has been ascribed to either charge transfer or a redox reaction.\textsuperscript{46} The correlation of reactivities to redox potentials supports the latter interpretation. For example, the Group 6 chalcogenides hosts are less easily reduced and do not react to form intercalation compounds with organic bases.\textsuperscript{13,37}
Some MX₂ hosts react in strong aqueous base to intercalate hydrated alkali metal cations, e.g. Na₀.₃TaS₂·δH₂O. These complex intercalates undergo facile exchange in aqueous salt solutions. The water co-intercalate can be displaced in polar inorganic or organic solvents (i.e. alcohols, ethers, amines, sulfoxides, etc). The product compositions, including both the contents of intercalate cations and of cointercalates, depend on the degree of reduction, conditions of exposure to the exchange solutions, and post-reaction processing.

Ethylenediamine (en) and trimethylenediamine (tn) react directly with TiS₂, NbS₂, and TaS₂ to form intercalation compounds with Δd = 0.34–0.41 nm. These gallery dimensions indicate that the amine intercalates form monolayers with long molecular axes oriented parallel to the host layers. These products show a compositional range that depends on the host and the sample processing conditions, with intercalate to MX₂ ratios of 0.17–0.39 for en and 0.15–0.33 for tn. Secondary amines, such as diethylamine, dibutylamine, and dipentylamine react with exfoliated MoS₂, generating Li₀.₁MoS₂·δdialkylamine, with ranges of δ = 0.11–0.42 and Δd = 0.37–0.45 nm, depending on the dialkylamine cointercalate.

Recently, electride solutions in liquid amines have been used to synthesize graphite intercalation compounds. In Chapter 4, the use of amine electride chemistry to synthesize intercalation compounds of MoS₂ will be described in detail.
1.5 MOLYBDENUM(VI) OXIDE (MoO$_3$)

The binary molybdenum(VI) oxide (MoO$_3$), has a layer structure consisting of distorted MoO$_6$ octahedra that share edges and vertices to form sheets (Figure 1.8). The sheet thickness for MoO$_3$ is 0.69 nm, and the material is a well-known host for intercalation chemistry.$^{13}$

![Structure of MoO$_3$, showing the sheets containing edge-sharing MoO$_6$ octahedra.](image)

Various techniques have been employed to synthesize intercalation compounds of MoO$_3$. Reaction with an n-butyllithium/hexane solution gives Li$_2$MoO$_3$. Product homogeneity is facilitated by subsequent equilibration of the product in a non-aqueous electrolyte containing lithium ions.$^{13}$
Li(s)|Li⁺(nonaqueous solvent)|MoO₃ electrochemical cells with non-aqueous electrolytes have an open-circuit voltage of ~ 2.8 V and have been utilized to intercalate lithium into MoO₃. Typical electrolytes are LiClO₄ or LiI dissolved in organic solvents like dimethylsulfoxide (DMSO) or propylene carbonate (PC). The extent of these reactions can often be monitored coulometrically, and the products obtained have the general formula of LiₓMoO₃ and Δd ~ 0.1 nm. The charge/discharge reaction is reversible up to x = 1.5.

The intercalation of MoO₃ by hydrogen is perhaps the most extensively investigated. Chemical reduction of MoO₃ in aqueous acid was first shown by Glemser et al. to form a series of compounds that could be formulated as HₓMoO₃. The vigorous reduction of MoO₃ by Zn/HCl produces H₂MoO₃. Intermediate phases in the 0 < x < 2 range are obtained by the reaction of H₂MoO₃ with MoO₃ in sealed tubes at < 100 °C. Four distinct and highly colored hydrogen bronze phases are observed: blue orthorhombic (0.23 < x < 0.40), blue monoclinic (0.85 < x < 1.04), red monoclinic (1.55 < x < 1.72), and green monoclinic (x = 1.99). These hydrogen intercalation compounds are acidic and will react with Lewis bases (L) to form intercalation compounds of general composition LₓHₓMoO₃.

Stoichiometric MoO₃ is a white insulator; reductive intercalation, even at low levels, results in both a large increase in electronic conductivity and a dramatic color change to metallic blue-black. The intercalation compounds are often rapidly re-oxidized when exposed to air.
The cathodic reduction of MoO$_3$ in aqueous solutions (typically mineral acids) results in protonation to form H$_x$MoO$_3$; whereas the use of aqueous electrolytes containing alkali metal or transition metal ions leads to metallic blue hydrated phases A$_x^+(\text{H}_2\text{O})_y[\text{MoO}_3]^{-}.\text{ For example, MoO}_3 \text{ is reduced in Na}_2\text{S}_2\text{O}_4(\text{aq}) to form Na$_4(\text{H}_2\text{O})_2\text{MoO}_3$. Both intercalate ions and co-intercalate solvent are often readily exchanged by reaction with aqueous or polar organic solutions (e.g. DMSO). Observed interlayer expansions are ~ 0.28 nm with large monovalent cations (Rb$^+$, Cs$^+$), ~ 0.46 nm with small monovalent cations (Li$^+$, Na$^+$, K$^+$, NH$_4^+$) and ~ 0.71 nm for divalent cations.$^{13,55}$

The reaction of Li$_x(\text{H}_2\text{O})_y\text{MoO}_3$ with aqueous polymer solutions can result in exchange of water for a polymer co-intercalate.$^{25}$ Previous studies have reported the intercalation of polyethylene oxide (PEO),$^{27,60}$ linear polyethylenimine (LPEI),$^{25}$ polyaniline (PANI),$^{61}$ polyvinylpyrrolidone (PVP) and polyacrylamide (PAM),$^{62}$ using this method or melt intercalation method.$^{27}$ The interlayer expansions vary from 0.47 - 0.83 nm, depending on the polymer and how it is arranged in the galleries (for example, to form mono or bilayers).$^{25,61,63}$

Dendrimers are branched polymers which can similarly exchange into the galleries. There have been no previous reports on the intercalation of dendrimers into MoO$_3$. The synthesis and characterization of dendrimer-MoO$_3$ nanocomposites are discussed in Appendix A.
1.6 SUMMARY

The further development of intercalation chemistry holds numerous possibilities and potential impacts. The discovery of new synthetic routes, new compounds, and new nanocomposites, may all solve important technological problems. The next three chapters and Appendix A of this dissertation will describe some novel experimental techniques to synthesize intercalation compounds and the characterization of the new materials thereby obtained.

1.7 REFERENCES


CHAPTER 2

TEMPLATE PREPARATION OF NiPS₃ POLYMER NANOCOMPOSITES

Amila Udayanga Liyanage, and Michael M. Lerner

Department of Chemistry
Oregon State University
Corvallis, OR 97331-4003, USA

2.1 ABSTRACT

A template synthesis method can be used to prepare NiPS$_3$ nanocomposites with polyethylene oxide (PEO), polyethylenimine (PEI), polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP). Nanocomposites of NiPS$_3$/PEI, NiPS$_3$/PVA and NiPS$_3$/PVP have not been previously reported. The resulting materials are characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). Reaction progress was monitored using UV-visible spectroscopy. Template synthesized NiPS$_3$/PEO nanocomposites show only polymer zig-zag monolayers, in contrast to the bilayers obtained using the topotactic method, and can generate denser interlayers than those obtained by topotactic methods. The crystallite sizes increase for more dilute conditions, a more polar solvent, and longer aging time. P$_2$S$_6^{4-}$ and Ni$^{2+}$ concentrations govern nanocomposite nucleation and growth, respectively.
2.2 INTRODUCTION

MPS\textsubscript{3} and materials containing MPS\textsubscript{3} layers show interesting properties for nonlinear optics\textsuperscript{1,2}, magnetic\textsuperscript{3,4} or photomagnetic devices\textsuperscript{5}, catalysis\textsuperscript{6}, and energy storage in secondary batteries\textsuperscript{7}. For the latter example, NiPS\textsubscript{3} shows an electrochemical reduction that proceeds in several stages at potentials from 2.7 to 1.8 V up to a Li/Ni ratio of ~7.5. The reduction occurs quasi-reversibly over the range 0 ≤ Li/Ni ≤ 3 range, providing a high theoretical capacity as a secondary cathode\textsuperscript{7}.

Xiao et al. reported that MoS\textsubscript{2} shows a significantly higher reversible capacity after an exfoliation process. Furthermore, the formation of a nanocomposite with polyethylene oxide (PEO) allows both higher capacities and improved charge/discharge cycling\textsuperscript{8}. Since MS\textsubscript{2} and MPS\textsubscript{3} are both layered materials with intercalation chemistries, the preparation and electrochemical characterization of PEO/NiPS\textsubscript{3} nanocomposites are therefore of interest.

The synthesis and structures of MPS\textsubscript{3} nanocomposites with different polymers have been studied by several groups. In all cases, a topotactic method has been employed, starting with a compound containing alkali metal cations between MPS\textsubscript{3} layers. This intercalation compound may be obtained directly at high temperature\textsuperscript{9}, or by introduction of alkali metal cations into the MPS\textsubscript{3} host via ion exchange\textsuperscript{10} or reduction of the M(II) cations in the host layers\textsuperscript{6}. The alkali metal cations likely enable nanocomposite formation by coordinating to polymer functional groups, as has been observed with many other layered hosts\textsuperscript{11}.
Lagadic *et al.* first reported the synthesis of nanocomposites of PEO and MPS$_3$ ($M = \text{Mn}, \text{Cd}$) by reacting an aqueous polymer solution with $M_{1-x}\text{PS}_3\text{A}_2\text{(H}_2\text{O})_y$ ($A = \text{Na}, \text{K}$). The products obtained showed gallery expansions of $\approx 0.8$-$0.9$ nm, consistent with the intercalation of bilayers of zig-zag-like PEO chains that coordinate to alkali metal ions. Jeevanandam *et al.* subsequently prepared PEO/CdPS$_3$ nanocomposites in a methanolic solution at 55 °C. Manriquez *et al.* reported the preparation of PEO nanocomposites from Li$_x\text{MPS}_3$ ($M = \text{Ni}, \text{Fe}$) using a similar approach. However, in this case the authors proposed a polymer helical conformation.

Manova *et al.* reported the intercalation of polyethylene glycol into a Na$_x\text{NiPS}_3$ by reaction in a methanolic aqueous solution, with a gallery expansion of $\approx 0.8$ nm.

Other polymers that are known to form nanocomposites with MPS$_3$ layers include linear polyethylenimine, LPEI, and polyvinylpyrrolidone, PVP. The former was reported by Oriakhi *et al.* to form nanocomposites with polymer monolayers (expansion of 0.4 nm) via the reaction of $K_x\text{(H}_2\text{O})_yM_{1-x/2}\text{PS}_3$ ($M = \text{Mn}, \text{Cd}$) and polymer in aqueous solution; the latter was reported by Yang *et al.* via reaction of a potassium intercalated intermediate MPS$_3$ ($M = \text{Mn}, \text{Cd}$) and an aqueous PVP solution. The interlayer expansion in that case was $\approx 2.3$ nm, much greater than that for PEO.

A solvent-free, melt intercalation approach to obtain PEO/MPS$_3$ nanocomposites ($M = \text{Mn}, \text{Cd}$) was reported by Sukpirom *et al.* With this method,
KₓM₁₋ₓ₂PS₃·δH₂O was shown to directly intercalate PEO at 125 °C. The nanocomposite basal repeat distances were increased by ≈ 0.8 nm, again ascribed to the presence of PEO bilayers.¹⁵

MPS₃ compounds are normally prepared by combining the elements or simple precursors at elevated temperature.¹⁶,¹⁷ However, the synthesis of highly disordered or amorphous NiPS₃ at ambient temperature has been reported by reaction of Ni²⁺ salts with alkali metal hexathiohypodiphosphate (Na₄P₂S₆·6H₂O or Li₄P₂S₆·6H₂O) in aqueous solution.¹⁸⁻²⁰ In the following study, we describe the first template approach to MPS₃ compounds, where layered nanocomposites are obtained directly using a one-pot reaction with solution-phase precursors at ambient temperature.

2.3 EXPERIMENTAL

2.3.1 REAGENTS AND ANALYTICAL METHODS

Li₂S (99.9%, Cerac), P (99%, Johnson Matthey), S (99.9%, Mallinckrodt), Ni(NO₃)₂·6H₂O (Aldrich), PEO (Aldrich, Mₙ=100,000), linear polyethylenimine (Alfa Aeser, Mₙ=25,000), polyvinyl alcohol, 80% hydrolyzed (Aldrich, Mₙ=9⁻⁻⁻10,000) and polyvinylpyrrolidone (Alfa Aeser, Mₙ=8,000) were purchased and used without further purification.

Powder XRD (PXRD) patterns from 3⁻⁻⁻60° 2θ were obtained on a Rigaku Miniflex II diffractometer, using Ni-filtered Cu-Kα radiation at a scan rate of 3° min⁻¹ and step size of 0.020° 2θ. A modified Scherrer equation²¹ was used to determine crystallite size (L) for the prepared nanocomposites:
where $\lambda = 0.15406$ nm, $\Delta(2\theta_{hkl})$ = full width at half maximum (in radians) and $\theta_{hkl} =$ diffraction angle. A Si(m) powder standard was employed for these measurements. Thermogravimetric (TGA) analyses were performed under Ar flow (20 mL min$^{-1}$) using a Shimadzu TGA-50 analyzer, from ambient to 500 °C at 5 °C min$^{-1}$. An Agilent 8453 UV-visible spectrophotometer was used for UV analyses. Background subtractions were carried out for all the UV-visible measurements. Scanning electron micrographs (SEMs) were obtained using an FEI Quanta 600F FEG SEM. Energy-dispersive X-ray spectroscopy (EDS) was used as a semi-quantitative elemental analysis method.

Van der Waals volumes of C$_2$H$_4$O oligomers (C = 2–40) were calculated based on Bondi radii using a method termed Atomic and Bond Contributions of van der Waals volume (VABC). \(^{22}\)

2.3.2 SYNTHESSES

Li$_4$P$_2$S$_6$ was synthesized as a white powder according to a published procedure. \(^{23}\) Li$_2$S, P and S were combined in 1 : 1 : 2 mole ratio and sealed in a quartz tube under an inert atmosphere. The mixture was heated to 900 °C at 100 °C h$^{-1}$, maintained at 900 °C for 0.5 h, rapidly cooled to 450 °C and held at 450 °C for 24 h. Highly disordered or amorphous NiPS$_3$ was synthesized via a process previously reported by Prouzet \textit{et al.} \(^ {19}\) An aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O (0.31 g, 5.00 mL) was added dropwise to an aqueous solution of Li$_4$P$_2$S$_6$ (0.10 g, 5.00 mL) and stirred
vigorously for 24 h. The reddish precipitate was centrifuged for 15 min, triple washed with deionized (DI), and then dried under vacuum at room temperature.

To prepare the nanocomposites, Ni(NO$_3$)$_2$·6H$_2$O (0.31 g) and PEO (0.01-0.05 g) were dissolved in 5-500 mL of DI water and then slowly added to a solution Li$_4$P$_2$S$_6$ (0.1 g) dissolved in DI water (5.00-500.0 mL) and stirred vigorously for 24 h. Depending on the solvent volume, the precipitation time varied from few minutes to 12 days. After aging (1-7 days) the resulting brown precipitate was centrifuged for 15 min and washed three times with a copious amount of DI water. The solid product was dried under vacuum at 60 °C for 18 h. Where noted, some reactions substituted water with 10% ethanol as the solvent.

Samples are identified below based on starting g/g PEO/Li$_4$P$_2$S$_6$ ratio (R) and total solvent volume (V). For example, the product of Ni(NO$_3$)$_2$·6H$_2$O (0.31 g) and PEO (0.05 g) dissolved in 5 mL of DI water with 5 mL of aqueous Li$_4$P$_2$S$_6$ (0.1 g) solution is labeled R0.5V10.

The same procedures were used to synthesize other polymer/NiPS$_3$ nanocomposites with linear polyethylenimine (LPEI), polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP).
2.4 RESULTS AND DISCUSSION

PXRD patterns (Figure 2.1) show that polymer nanocomposite structures are obtained by the template method. The basal repeat distance increases from 0.64 nm in a-NiPS$_3$ to 1.06 nm for all the PEO nanocomposites. This expansion of 0.42 nm along the stacking direction indicates the presence of PEO monolayers incorporated between NiPS$_3$ layers.

Figure 2.1 PXRD patterns for PEO/NiPS$_3$ nanocomposites obtained by the template method. a-NiPS$_3$ obtained by the same approach without PEO is shown for comparison. (*Al holder)
Figure 2.2 shows a typical microstructure of the prepared PEO/NiPS$_3$ nanocomposites, in this case for sample R0.5V10. The nanocomposites show an expanded layered morphology with most particle dimensions above 10 μm. For samples with $R = 0.5$, i.e. with a high polymer content, SEM images also reveal the presence of surface adsorbed polymer and show charging effects during imaging, indicating the presence of non-conducting polymer on surfaces. TGA data (see below) support the presence of surface-adsorbed PEO.

![Figure 2.2 SEM image for a PEO/NiPS$_3$ nanocomposite (sample R0.5V10).](image)

EDS data indicates the presence of Ni, P, S, C and O in the nanocomposite samples with an Ni : P : S ratio of 1 : 1 : 2.7. This supports the formation of host NiPS$_3$ structure from the precursors. Some sample degradation during analysis may account for the less than nominal sulfur content.

Figure 2.3 shows thermal analysis data of the obtained products. The DTG loss peak at 100–150 °C is ascribed to volatilization of intercalated water, and the loss peak around 250 °C to PEO decomposition and volatilization. From the mass losses, the relative contents of these components can be determined. For the R0.5V10
sample, some new features are observed. The water loss region occurs over a broad range starting at lower temperature, a shoulder appears on the low temperature side of the main PEO loss peak, and a high temperature loss is observed at 350 °C. The low temperature shoulder on the main PEO loss peak, and the high temperature loss, are ascribed to the presence of surface-adsorbed or bulk PEO. The separation of thermal loss events allows quantification of PEO intercalate vs. surface PEO. Water content was close to 1 mol/formula unit of NiPS$_3$, but this composition was highly dependent on sample history and environmental conditions (humidity and temperature).

Figure 2.3 TGA of nanocomposites with different PEO compositions (* loss shoulder ascribed to surface PEO) DTG indicates the first derivative of TGA curves.
The packing fractions, i.e. fraction of volume in the expanded galleries occupied by intercalates, were derived from the known host MPS₃ cell dimensions, the gallery expansion determined by PXRD, the product stoichiometries and intercalate volumes. The PEO monomer unit volume was estimated by calculating the \( \text{C}_2\text{H}_4\text{O} \) monomer unit volume for increasing oligomer sizes until a stable volume of 0.050 nm\(^3\) was observed. (Figure 2.4) As an example, for sample R0.1V10, the packing fraction, was calculated as:

\[
Packing\ fraction = \frac{[(Z \times 0.34 \times 0.050 \text{ nm}^3)/(a \times b \times \Delta d)]}{0.28} \tag{2}
\]

where \( a = 0.5812 \text{ nm} \) and \( b = 1.0070 \text{ nm} \) are NiPS₃ unit cell parameters, \( \Delta d = \) gallery expansion = 0.42 nm, and \( Z = \) NiPS₃ units per unit cell = 4. Water content was highly variable, as noted above, and may be on particle surfaces or intercalated, and thus was not considered in these packing fractions. The calculated PEO packing fractions are shown in Table 2.1. Intercalate PEO content and packing fractions

Figure 2.4 Calculated C\(_2\)H\(_4\)O unit volumes from VABC.
increase with higher PEO/Li$_4$P$_2$S$_6$ up to $R = 0.3$. At higher ratios, the additional PEO does not intercalate, although some remains as surface-adsorbed polymer.

Table 2.1 Compositional data from thermal analyses and calculated packing fractions for PEO/NiPS$_3$ nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reacted (PEO)/NiPS$_3$ (mol/mol)</th>
<th>Product (PEO)/NiPS$_3$ (mol/mol)</th>
<th>H$_2$O/NiPS$_3$ (mol/mol)</th>
<th>Packing fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Intercalated</td>
<td>Surface</td>
<td></td>
</tr>
<tr>
<td>R0.1V10</td>
<td>0.34</td>
<td>0.34</td>
<td>-</td>
<td>1.29</td>
</tr>
<tr>
<td>R0.2V10</td>
<td>0.68</td>
<td>0.69</td>
<td>-</td>
<td>1.21</td>
</tr>
<tr>
<td>R0.3V10</td>
<td>1.01</td>
<td>1.02</td>
<td>-</td>
<td>1.01</td>
</tr>
<tr>
<td>R0.4V10</td>
<td>1.35</td>
<td>1.03</td>
<td>-</td>
<td>1.17</td>
</tr>
<tr>
<td>R0.5V10</td>
<td>1.69</td>
<td>1.30</td>
<td>0.29</td>
<td>1.34</td>
</tr>
</tbody>
</table>

As determined from diffraction peak widths, crystallite sizes for the nanocomposites, which are the products of 0.3 g/g PEO/Li$_4$P$_2$S$_6$ reaction mixtures, increases from 2.6 nm to 4.2 nm upon a 20-fold decrease in the reaction concentrations as shown in Table 2.2. A further dilution of 5 x results in a crystallite size increase to 4.5 nm. Aggregation times were also greatly increased in the more dilute solutions.
Table 2.2 Effect of synthetic conditions on crystallite size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aggregation time (days)</th>
<th>Solvent</th>
<th>Aging time (days)</th>
<th>L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0.3V10</td>
<td>0.004</td>
<td>DI water</td>
<td>1</td>
<td>2.6</td>
</tr>
<tr>
<td>R0.3V200</td>
<td>4-5</td>
<td>DI water</td>
<td>1</td>
<td>4.2</td>
</tr>
<tr>
<td>R0.3V1000</td>
<td>11-12</td>
<td>DI water</td>
<td>1</td>
<td>4.5</td>
</tr>
<tr>
<td>R0.3V1000</td>
<td>11-12</td>
<td>DI water</td>
<td>4</td>
<td>4.7</td>
</tr>
<tr>
<td>R0.3V1000</td>
<td>11-12</td>
<td>DI water</td>
<td>7</td>
<td>5.2</td>
</tr>
<tr>
<td>R0.3V1000</td>
<td>5-6</td>
<td>10% ethanol</td>
<td>1</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The use of an ethanolic solvent also decreases the aggregation time with respect to the aqueous reaction mixtures, and results a smaller crystallite size. For an R0.3V1000 sample prepared using 10% ethanol, the crystallite size decreased from 4.5 nm (in DI water) to 4.2 nm. Crystallite size increased from 4.5 to 5.2 when the aging time was increased from 1 to 7 days, suggesting that exchange between solution and precipitate continues after aggregate formation.

Nanocomposites of PEI/NiPS$_3$, PVA/NiPS$_3$ and PVP/NiPS$_3$ have not been previously reported, but can be prepared by this template method. Table 2.3 shows the structural and compositional data for these new nanocomposites, obtained as for PEO/NiPS$_3$. 
Table 2.3 Structural and compositional data for new polymer/NiPS$_3$ nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>d (nm)</th>
<th>Δd (nm)</th>
<th>Polymer/ NiPS$_3$ ratio (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/NiPS$_3$</td>
<td>1.06</td>
<td>0.42</td>
<td>1.0</td>
</tr>
<tr>
<td>PEI/NiPS$_3$</td>
<td>1.05</td>
<td>0.41</td>
<td>1.0</td>
</tr>
<tr>
<td>PVA/NiPS$_3$</td>
<td>1.06</td>
<td>0.42</td>
<td>0.9</td>
</tr>
<tr>
<td>PVP/NiPS$_3$</td>
<td>2.20</td>
<td>1.56</td>
<td>0.5</td>
</tr>
</tbody>
</table>

In previous reports, PEO/MPS$_3$ (M = Mn, Cd) nanocomposites have shown interlayer expansions of 0.8-0.9 nm, corresponding to the presence of PEO bilayers between host sheets. For these nanocomposites the polymer/MPS$_3$ ratio is 1.9-2.1 which supports the zig-zag bilayer arrangement.$^{10}$ Alternately, Manriquez et al. describe a single helical PEO arrangement in MPS$_3$ nanocomposites (M = Ni, Fe) with an interlayer expansion of ≈ 0.8 nm.$^9$ All these compounds were synthesized using a topotactic method. The current template method results in only single PEO zig-zag polymer layers. However, these layers are more densely packed, as is indicated by the derived packing fractions shown in Table 2.4. Topotactic methods are kinetically limited by the slow diffusion of polymers,$^{24}$ which may impede development of densely packed intercalate layers. With a template method, denser polymer layers can form before the host layer structure fully develops.
Table 2.4 Comparison of packing fractions of known PEO/MPS₃ nanocomposites. The packing fractions were derived from compositional and structural data in the references indicated.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Method of synthesis</th>
<th>Alkali ion</th>
<th>Packing fraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/NiPS₃</td>
<td>Topotactic</td>
<td>Li⁺</td>
<td>0.27</td>
<td>9</td>
</tr>
<tr>
<td>PEO/FePS₃</td>
<td>Topotactic</td>
<td>Li⁺</td>
<td>0.40</td>
<td>9</td>
</tr>
<tr>
<td>PEO/CdPS₃</td>
<td>Topotactic</td>
<td>Li⁺, Na⁺</td>
<td>0.58, 0.72</td>
<td>12</td>
</tr>
<tr>
<td>PEO/CdPS₃</td>
<td>Topotactic</td>
<td>Cs⁺, K⁺</td>
<td>0.62, 0.69</td>
<td>12</td>
</tr>
<tr>
<td>PEO/CdPS₃</td>
<td>Topotactic</td>
<td>K⁺</td>
<td>0.61</td>
<td>10</td>
</tr>
<tr>
<td>PEO/MnPS₃</td>
<td>Topotactic</td>
<td>Na⁺, K⁺</td>
<td>0.73, 0.77</td>
<td>10</td>
</tr>
<tr>
<td>PEO/NiPS₃</td>
<td>Template</td>
<td>Li⁺</td>
<td>0.84</td>
<td>this work</td>
</tr>
</tbody>
</table>

The PEI/NiPS₃ nanocomposites obtained show a similar interlayer expansion to that from the topotactic preparation (0.41 nm vs. 0.4 nm for PEI/MPS₃ (M = Mn, Cd) reported by Oriakhi et al.¹³) corresponding to a PEI monolayer. PVA/NiPS₃ shows a similar interlayer expansion of 0.42 nm. The template synthesis of NiPS₃/PVP gives a much smaller expansion of 1.46 nm than for the topotactic method.¹⁴

In order to evaluate the growth mechanism for these template reactions, the evolution of UV-visible absorption spectra were recorded under different reaction conditions. As shown in Figure 2.5, a new absorbance at 330 nm indicates the formation of the nanocomposite. This absorbance can be ascribed to Ni coordination...
by sulfide in $\text{P}_2\text{S}_6^{4-}$ (Ni-dithiolene complexes show a prominent absorbance in this region).  

![Absorbance spectrum](image)

Figure 2.5 UV-visible spectra of some reactants and products of the template reactions. The absorbance at 330 nm (*) is used to monitor nanocomposite formation.

In the first set of experiments, the concentrations of Ni$^{2+}$ and PEO were varied while maintaining a constant $\text{P}_2\text{S}_6^{4-}$ concentration and a constant Ni$^{2+}$/PEO ratio of 1 : 1. The initial absorbances at 330 nm under these conditions remain unchanged (Figure 2.6, compare the y-intercept of the three plots), indicating that nanocomposite nucleation is independent of PEO and Ni$^{2+}$ concentration. These initial values are all obtained within 15 s of solution mixing.

The growth in the absorbance peak (from about 1.75 to 2.25 (Figure 2.6, curve for 2 mM)), indicates that the rate of nucleation (as indicated by the initial values) are significantly greater than the rate of nanocomposite growth. The growth rate, however, is strongly dependent on Ni$^{2+}$ concentration.
Figure 2.6 Effect of Ni$^{2+}$ and PEO concentrations on the rate of nanocomposite formation. Curves are obtained using the indicated Ni$^{2+}$ concentrations.

In contrast, the initial absorbances vary significantly for reactions using three different concentrations of P$_2$S$_6$$^4-$ with a constant Ni$^{2+}$ and PEO concentrations and Ni$^{2+}$/PEO = 1. (Figure 2.7) This confirms the role of P$_2$S$_6$$^4-$ in nucleation. The growth curves are parallel under these conditions, indicating that nanocomposite growth is not significantly affected by P$_2$S$_6$$^4-$ concentration in this range.
Figure 2.7 Effect of P₄S₆⁴⁻ concentration on the rate of nanocomposite formation. Curves are obtained using the indicated P₄S₆⁴⁻ concentrations.

2.5 CONCLUSIONS

A template synthesis method can be used to synthesize NiPS₃ nanocomposites. The obtained NiPS₃/PEO nanocomposites show polymer zig-zag monolayers at all combination ratios, in contrast to PEO nanocomposites derived from a topotactic method, and the packing fractions are greater. The product crystallite size increases with higher solvent volume, use of polar solvent and higher aging time. P₂S₆⁴⁻ and Ni²⁺ concentrations govern nanocomposite nucleation and growth, respectively. Nanocomposites of NiPS₃/PEI, NiPS₃/PVA and NiPS₃/PVP are reported for the first time using this template method.
2.6 REFERENCES


CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF LOW-GENERATION POLYAMIDOAMINE (PAMAM) DENDRIMER – SODIUM MONTMORILLONITE (Na-MMT) CLAY NANOCOMPOSITES

Amila U. Liyanage, Esther U. Ikuoria, Adeniyi A. Adenuga, Vincent T. Remcho, and Michael M. Lerner

Department of Chemistry
Oregon State University
Corvallis, OR 97331-4003, USA

a Fulbright visiting scholar, Oregon State University, 2011/2012. Permanent address: Department of Chemistry, University of Benin, Benin City, Nigeria.

3.1 ABSTRACT

Polymer-inorganic nanocomposites are a recently developed class of materials which have altered physical or chemical properties with respect to the pure polymer, inorganic host, or their micro- and macro composites. Lower generation (G0.0-2.0) polyamidoamine (PAMAM) dendrimer/Sodium montmorillonite (Na-MMT) nanocomposites were synthesized in a solution-phase exfoliation adsorption reaction. These are the first reports of the G0.0/ and G1.0/Na-MMT nanocomposites, and of a structurally-ordered G2.0/Na-MMT. The materials were characterized using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). PAMAM characteristics at acidic and basic aqueous media were studied using capillary zone electrophoresis (CZE). Pseudospherical PAMAM dendrimers in aqueous medium attain a highly flattened conformation within the confined space between MMT sheets upon nanocomposite formation. The nanocomposite structure depends on the PAMAM generation and the starting dendrimer/organic composition. G0.0 always forms monolayer structures ($\Delta d = 0.42$ nm), while G2.0 forms monolayer structure, mixed phase and bilayer structures ($\Delta d = 0.84$ nm) at lower, intermediate, and higher organic content respectively, showing an interesting monolayer to bilayer transition. G1.0 showed an intermediate behavior, with monolayer to mixed-phase transition at the reactant ratios studied. This monolayer arrangement of PAMAM/clay nanocomposites is reported for the first time. Maximum organic contents of G0.0 monolayer and G2.0 bilayer nanocomposites were ~7% and ~14%, respectively. Gallery expansions were similar to those observed with linear polymer intercalates, but the packing fractions (0.31-
0.32) were 2-3 times lower. At acidic pH, the nanocomposites forming only monolayer structures are obtained, indicating a stronger electrostatic attraction between MMT and protonated PAMAM, and these nanocomposites formed more slowly and were more ordered. Na⁺ ions play a significant role in nanocomposite formation. At high pH, PAMAMs show high mobility, zeta potential, and surface charge densities due to Na⁺ complexation in solution. FTIR data indicates that both Na-MMT and PAMAM structural units are preserved in the nanocomposites obtained.
3.2 INTRODUCTION

Polymer-inorganic nanocomposites are a recently developed class of materials with at least one dimension of the phase combination in the nanometer range. Depending on the overall dimensionality, there are several types of nanocomposites; a prominent example is where two-dimensional (layered) inorganic structures incorporate or are dispersed into polymers. In these polymer-containing layered nanocomposites, some polymers studied include poly(ethylene oxide) (PEO), linear polyethylenimine (LPEI), polyvinyl alcohol (PVOH), poly(vinyl pyrrolidone) (PVPyr), and polyaniline (PANI) polymers; the inorganic structures include clays, transition metal oxides, sulfides, selenides or phosphorous trisulfides and layered double hydroxides. Depending on the nature and relative composition of these constituents and also on the preparative method employed, the nanocomposites may form as intercalation compounds (ordered) or as exfoliated (amorphous) structures. Some preparative methods include exfoliation-adsorption, in situ intercalative polymerization, melt intercalation, and template synthesis. A major reason for the growing interest in these nanocomposite materials is their remarkably changed mechanical, thermal, optical or physicochemical properties with respect to the constituent phases or conventional microcomposites. Specific improvement for applied materials include increased moduli, tensile stress, thermal stability and flame retardancy, decreased gas permeability, and enhanced thermal stability of the ionic conductivity.

Sodium montmorillonite, \( \text{Na}_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4 \) (Na-MMT), is a smectite belonging to the structural family known as 2:1 phyllosilicates, which has layers with
central alumina or magnesia octahedra bound and covered by silica surfaces.\textsuperscript{1,13} These anionic sheets are stacked with monovalent cation (Na\textsuperscript{+}) residing in between them. The stacking repeat for the anhydrous structure is 0.96 nm; ion exchange or co-intercalation of molecules, surfactants, or polymers between the layers can result in expansion of the layer repeat or delamination of the sheets into solution.\textsuperscript{5,14,15}

Dendrimers are monodisperse macromolecules with a regular and highly branched three-dimensional architecture, which consists of three basic components; an initiator core, interior zones comprising cascading tiers of branches with radial connectivity to the initiator core, and an exterior surface with terminal groups.\textsuperscript{16,17} Higher generation dendrimers add to the interior zone tiers. Polyamidoamines (PAMAMs) are the first synthetic dendrimers, with potential applications in drug or gene delivery, sensors, and nanoparticle synthesis.\textsuperscript{18-21} Although dendrimers can have functional groups similar to those in linear polymers, the net connectivity contrasts with that of linear polymers and provides an opportunity to evaluate the effect of organic component on nanocomposite structure and the gallery composition of intercalated nanocomposites.

Previous studies have reported nanocomposites combining hyperbranched polymers,\textsuperscript{22,23} higher-generation PAMAMs,\textsuperscript{24} dendrons,\textsuperscript{25} or dendritic quaternary ammoniums\textsuperscript{26} with smectite clays including montmorillonite,\textsuperscript{22-26} or kaolinite.\textsuperscript{27} Those reports indicated very large gallery expansions,\textsuperscript{22,25,26} both pure and mixed-phase intercalated nanocomposites,\textsuperscript{22,24-26} and exfoliated nanocomposites.\textsuperscript{22}
Ratanarat *et al.*  have reported the only lower generation PAMAM/Na-MMT nanocomposite, an exfoliated nanocomposite of generation 2.0 (G2.0) PAMAM and Na-MMT. Alongi *et al.*  have reported the synthesis of higher generation (G4.0-7.0) PAMAM/Na-MMT nanocomposites. Here we report the first systematic compositional study on the synthesis and characterization of lower generation PAMAM/Na-MMT nanocomposites and clarify the adsorbed monolayer/bilayer arrangements that occur in dendrimer nanocomposite galleries.

### 3.3 EXPERIMENTAL

#### 3.3.1 REAGENTS

Polyamidoamine (PAMAM) aqueous solutions (~16% w/w, Dendritech), sodium montmorillonite (Na-MMT) (SWy-2, Clay Minerals Society), HCl (36.5-38.0%, EMD), H₃PO₄ (85%, Mallinckrodt), Na₂HPO₄ (ACS grade, Mallinckrodt Baker), NaOH (ACS grade, Mallinckrodt), NaCl (ACS grade, Mallinckrodt), Montmorillonite K 10 (Sigma-Aldrich), and AgNO₃ (ACS grade, Alfa Aesar) were purchased and used without further purification.

#### 3.3.2 SYNTHESSES

Aqueous solutions of PAMAM (0.01-0.08 g, 10.00 mL, pH 11-12) were added dropwise to aqueous suspensions of Na-MMT (0.1000 g, 10.00 mL, pH 5-6). Cloudy or powder-like white particles were visible within a few seconds to several minutes of combining the reactants. The suspensions had a pH = 10-11 and were stirred vigorously overnight at room temperature. The white precipitate was collected after centrifugation for 10 minutes, washed twice with deionized (DI) water, and then
dried under vacuum at 60 °C for 18 h. Some reactions were performed at ambient temperature, some at 60 °C.

In another set of nanocomposite syntheses, the PAMAM aqueous solutions were adjusted to pH = 2-3 using 1M HCl prior to addition of the Na-MMT suspension. Higher temperatures (50, 80 °C) were also utilized for some of these syntheses. These obtained products were washed repeatedly until no precipitate formed on reaction with dilute AgNO₃ (aq).

Samples are labeled below based on the reacted g/g PAMAM/Na-MMT ratios and PAMAM generation. For example, the sample obtained by reaction of 0.010 g of generation 0.0 PAMAM with 0.1000 g of suspended Na-MMT is labeled “0.1G(0.0)”. For reactions carried out at temperatures other than ambient temperature and pHs other than pH=10-11, the temperature (in °C) and pH are also indicated, for example “0.6G(2.0)-50-2”.

3.3.3 ANALYTICAL METHODS

Powder XRD (PXRD) patterns from 2° to 15° 2θ were obtained on a Rigaku Miniflex II diffractometer, using Ni-filtered Cu Kα radiation at a scan rate of 1° min⁻¹ and step size of 0.020° 2θ. A modified Scherrer equation⁴ was used to determine crystallite size (L) for the prepared nanocomposites:

\[
L_{hkl} = \frac{0.9\lambda}{\cos\theta_{hkl} \left[ \Delta^2(2\theta_{hkl}) - \Delta^2(2\theta_{hkl})_{std} \right]^{1/2}}
\]  

(1)

where \( \lambda = 0.15418 \) nm, \( \Delta(2\theta_{hkl}) \) = full width at half-maximum (in radians), and \( \theta_{hkl} \) = diffraction angle. A Si(m) powder standard was employed for these measurements.
Thermogravimetric (TGA) analyses were performed under Ar flow (20 mL/min) using a Shimadzu TGA-50 analyzer. Approximately 10-15 mg of sample was placed into an open platinum pan and heated from ambient to 600 °C at 5 °C/min.

Capillary zone electrophoresis was performed to determine migration times using an HP 3DCE instrument equipped with a UV detector, using a 75 μm inner diameter, 58.5 cm long fused silica capillary (50.0 cm to the detection window). New capillaries were sequentially conditioned by flushing with methanol (30 min), water (Milli-Q) (5 min), 1.0 M NaOH (30 min), water (5 min), and finally the background electrolyte (BGE) for 30 min. As preconditioning, the capillary was flushed with 0.1 M NaOH (3 min), water (1 min), and BGE (4 min). As postconditioning, the capillary was flushed with water (1 min). Background electrolytes used were 100 mM H$_3$PO$_4$, pH adjusted to 2.7, and 50 mM Na$_2$HPO$_4$, pH adjusted to 10.9 with NaOH. Ionic strengths of BGEs were adjusted to ~0.16 mol L$^{-1}$ using NaCl. Samples were prepared by freshly dissolving in H$_3$PO$_4$ or Na$_2$HPO$_4$, and the sample was adjusted to the pH and the ionic strength of BGE, using NaOH and NaCl, respectively. Migrations were accomplished at applied voltages of +15 kV (pH 2.7) and +18 kV (pH 10.9). The capillary was thermostatted at 25 °C (pH 2.7) or 30 °C (pH 10.9). Solutions were injected hydrodynamically at 50 mbar for 5 s. Direct detection was employed at a wavelength of 210 nm.

The dimensionless mobility ($\mu_0'$) of the dendrimers was calculated using

$$\mu_0' = \frac{\mu_0 v e}{2 \zeta_0 kT} = \frac{IL}{Vt_m} \frac{3 e}{2 kT}$$

(2)
where \( l \) is the effective length, \( L \) is the total length, \( V \) is the voltage, \( t_m \) is the migration time, \( \mu_0 \) is the electrophoretic mobility, \( \xi \) is the dielectric constant of water (80.5), \( \varepsilon_0 \) is the dielectric permittivity of the vacuum, \( k \) is the Boltzmann constant, \( T \) is the temperature in kelvin, \( \eta \) is the viscosity and \( e \) is charge of the electron.

Dimensionless zeta potentials and charge distribution functions (\( I_0 \)) were obtained using numerical solutions published by Wiersema et al.\textsuperscript{28} and Loeb et al.\textsuperscript{29} Zeta potential (\( \zeta \)) and surface charge densities (\( \sigma \)) were calculated according to the following empirical formulas:\textsuperscript{30}

\[
\zeta = \zeta' \frac{kT}{e}
\]

\[
\sigma = 5.8718 \times 10^{-2} \times I_0^{\frac{1}{2}} \text{C/m}^2
\]

IR spectra were taken using a Nicolet iS10 FT-IR spectrometer with an ATR sample cell, using background corrections for air and collection geometry. Aqueous PAMAM solutions were preconcentrated at 80 °C before collecting spectra. Diamond and Ge ATR cells were used for liquid and solid samples, respectively.

Van der Waals volumes of PAMAM dendrimers (G 0.0, 1.0, and 2.0) were calculated based on Bondi radii using a method termed “Atomic and Bond Contributions of van der Waals volume” (VABC).\textsuperscript{31} Packing fractions were calculated\textsuperscript{4} using

\[
\text{Packing fraction} = \frac{[Z n V_{vdw}]}{(a b \Delta d)}
\]
where \( a = 0.517 \) and \( b = 0.894 \) nm are Na-MMT unit cell parameters, \( \Delta d = \) interlayer expansion = \( d_i - 0.96 \) nm, where \( d_i \) and 0.96 nm are interlayer repeat distances of the nanocomposite and anhydrous Na-MMT, respectively, \( Z = \) the number of Na-MMT formula units per cell = 1, \( n = \) the number of PAMAM molecules per Na-MMT formula unit, and \( V_{vdw} = \) van der Waals volume of the PAMAM molecule.

Energy optimization of the gas-phase highly flattened and pseudospherical G0.0 PAMAM molecules was performed using DFT B3LYP method with 6-31G(d) basis set using Gaussian 09W software.

### 3.4 RESULTS AND DISCUSSION

![Figure 3.1 PXRD patterns for (a) G(0.0), (b) G(1.0), and (c) G(2.0) PAMAM/Na-MMT nanocomposites. The reactant ratios (g/g PAMAM/Na-MMT) are indicated.](image-url)
As shown in Figure 3.1, G0.0 nanocomposites show interlayer repeat spacings (d) of 1.37-1.38 nm. Since the interlayer repeat distance of anhydrous Na-MMT is 0.96 nm, these spacings correspond to an interlayer expansion (Δd) of 0.41-0.42 nm. For G2.0 PAMAM, the nanocomposites obtained show a compositional effect with a more expanded phase, with Δd = 0.83-0.84 nm appearing only at compositions richer in dendrimer content. Except for 0.1G(1.0), which shows only the Δd = 0.42 nm phase, G(1.0) PAMAM nanocomposites show both these expanded phases, with the more expanded phase increasing in relative intensity at higher starting dendrimer compositions. These observations differ from Ratanarat et al.\textsuperscript{15} report on exfoliated G2.0 PAMAM/Na-MMT nanocomposite. But the observed d values and the corresponding Δd calculated are comparable to those obtained by Alongi et al. with higher generation (G4.0-7.0) PAMAM and Na-MMT (d = 1.74-1.93 nm; Δd = 0.78-0.97 nm)\textsuperscript{24} and Amin et al. with a hyperbranched polymer and Na-MMT (d = 1.397, 1.705 nm, Δd = 0.437, 0.745 nm).\textsuperscript{33}

As will be discussed below, the two expanded phases obtained in our compositional studies contain galleries comprising ~0.4 nm thick PAMAM mono- or bilayers. The dendrimers are strongly adsorbed onto the clay surface and do not structurally resemble their solution-phase conformations.
Figure 3.2 Mass loss and differential plots for 0.6G(1.0)-2 PAMAM/Na-MMT nanocomposite.

TGA data for these nanocomposites show four mass loss regions, also indicated by four peaks in the derivative (DTG) curves at <100, 210, 350 and >590 °C (Figure 3.2). These are attributed, respectively, to loss of intercalate water, a two-step degradation of PAMAM, and finally the degradation of the MMT sheet structure to liberate H₂O. Alongi et al.²⁴ observed a decomposition step around 200 °C that was ascribed to nonintcalated PAMAM. Since native PAMAM degrades in a single step around 300 °C, the lower temperature loss was attributed to a previously reported catalytic effect for organic decomposition on clays, for example, with quaternary ammonium/MMT intercalated composites.³⁴ Because the PAMAM content in our
products does not change significantly upon extended washing, and many different starting compositions resulted in similar mass losses, the presence of a significant fraction of nonintercalated PAMAM residue appears unlikely, and both mass loss steps at 210 and 350 °C are ascribed to the decomposition of intercalated PAMAM.

Table 3.1 compares interlayer distance (d), interlayer expansion (Δd), composition, packing fraction and crystallite size (L) of different nanocomposites obtained in this study.

Table 3.1 Structural and compositional data for PAMAM/Na-MMT nanocomposite products obtained using PXRD (d and Δd) and TGA (organic mass %), and derived packing fractions and crystallite sizes (L).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reactant ratio (g/g PAMAM/Na-MMT)</th>
<th>Condition Temp./pH</th>
<th>Phase</th>
<th>d (nm)</th>
<th>Δd (nm)</th>
<th>Organic mass %</th>
<th>Packing fraction</th>
<th>L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1G(0.0)</td>
<td>0.1</td>
<td>RT/10-11</td>
<td>monolayer</td>
<td>1.38</td>
<td>0.42</td>
<td>5.6</td>
<td>0.23</td>
<td>129</td>
</tr>
<tr>
<td>0.2G(0.0)</td>
<td>0.2</td>
<td>mixed</td>
<td>1.39, 1.74</td>
<td>0.43, 0.78</td>
<td>8.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>0.3G(0.0)</td>
<td>0.3</td>
<td>mixed</td>
<td>1.38</td>
<td>0.42</td>
<td>6.6</td>
<td>0.28</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>0.4G(0.0)</td>
<td>0.4</td>
<td>mixed</td>
<td>1.37</td>
<td>0.41</td>
<td>6.6</td>
<td>0.28</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>0.5G(0.0)</td>
<td>0.5</td>
<td>mixed</td>
<td>1.38</td>
<td>0.42</td>
<td>7.2</td>
<td>0.30</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>0.6G(0.0)</td>
<td>0.6</td>
<td>mixed</td>
<td>1.37</td>
<td>0.41</td>
<td>7.4</td>
<td>0.31</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>0.7G(0.0)</td>
<td>0.7</td>
<td>mixed</td>
<td>1.38</td>
<td>0.42</td>
<td>7.3</td>
<td>0.31</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>0.8G(0.0)</td>
<td>0.8</td>
<td>mixed</td>
<td>1.38</td>
<td>0.42</td>
<td>7.5</td>
<td>0.31</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>0.1G(1.0)</td>
<td>0.1</td>
<td>monolayer</td>
<td>1.38</td>
<td>0.42</td>
<td>5.6</td>
<td>0.23</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>0.2G(1.0)</td>
<td>0.2</td>
<td>mixed</td>
<td>1.39, 1.74</td>
<td>0.43, 0.78</td>
<td>8.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Layer</td>
<td>Layer Type</td>
<td>RT/°C</td>
<td>Monolayer</td>
<td>Bilayer</td>
<td>Mixed</td>
<td>60 °C/10-11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>------------</td>
<td>--------</td>
<td>-----------</td>
<td>---------</td>
<td>-------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3G(1.0)</td>
<td>0.3</td>
<td></td>
<td>1.42, 1.74</td>
<td>0.46, 0.78</td>
<td>9.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4G(1.0)</td>
<td>0.4</td>
<td></td>
<td>1.39, 1.78</td>
<td>0.43, 0.82</td>
<td>9.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5G(1.0)</td>
<td>0.5</td>
<td></td>
<td>1.40, 1.76</td>
<td>0.44, 0.80</td>
<td>10.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(1.0)</td>
<td>0.6</td>
<td></td>
<td>1.41, 1.75</td>
<td>0.45, 0.79</td>
<td>10.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7G(1.0)</td>
<td>0.7</td>
<td></td>
<td>1.72, 1.42</td>
<td>0.76, 0.46</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8G(1.0)</td>
<td>0.8</td>
<td></td>
<td>1.77, 1.41</td>
<td>0.81, 0.45</td>
<td>11.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1G(2.0)</td>
<td>0.1</td>
<td>monolayer</td>
<td>1.39, 0.43</td>
<td>5.3, 0.21</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2G(2.0)</td>
<td>0.2</td>
<td>mixed</td>
<td>1.77, 1.42</td>
<td>0.81, 0.46</td>
<td>10.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3G(2.0)</td>
<td>0.3</td>
<td></td>
<td>1.80, 1.42</td>
<td>0.84, 0.46</td>
<td>11.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4G(2.0)</td>
<td>0.4</td>
<td>RT/10-11</td>
<td>1.79, 1.42</td>
<td>0.83, 0.46</td>
<td>13.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5G(2.0)</td>
<td>0.5</td>
<td></td>
<td>1.79, 1.42</td>
<td>0.83, 0.46</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(2.0)</td>
<td>0.6</td>
<td>bilayer</td>
<td>1.80, 0.84</td>
<td>14.1, 0.32</td>
<td>116</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7G(2.0)</td>
<td>0.7</td>
<td></td>
<td>1.80, 0.84</td>
<td>13.9, 0.31</td>
<td>108</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8G(2.0)</td>
<td>0.8</td>
<td></td>
<td>1.80, 0.84</td>
<td>14.5, 0.33</td>
<td>103</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(0.0)-2</td>
<td>0.6</td>
<td>RT/2-3</td>
<td>1.36, 0.40</td>
<td>6.6, 0.29</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(1.0)-2</td>
<td>0.6</td>
<td>monolayer</td>
<td>1.36, 0.40</td>
<td>6.6, 0.29</td>
<td>145</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(2.0)-50-2</td>
<td>0.6</td>
<td>50 °C/2-3</td>
<td>1.36, 0.40</td>
<td>7.9, 0.35</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6G(2.0)-80-2</td>
<td>0.6</td>
<td>80 °C/2-3</td>
<td>1.36, 0.40</td>
<td>7.1, 0.31</td>
<td>144</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3G(0.0)-60</td>
<td>0.3</td>
<td>monolayer</td>
<td>1.37, 0.41</td>
<td>6.2, 0.26</td>
<td>133</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3G(1.0)-60</td>
<td>0.3</td>
<td>mixed</td>
<td>1.40, 1.80</td>
<td>0.44, 0.84</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3G(2.0)-60</td>
<td>0.3</td>
<td></td>
<td>1.81, 1.41</td>
<td>0.85, 0.45</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RT = ambient temperature, n.a. = not applicable
Depending on the relative charge densities of the clay host and guest, different intercalate arrangements can arise, including monolayers, lateral bilayers, pseudotrilayers, or an inclined paraffin-like structure.\textsuperscript{1,35} Linear polymer/Na-MMT and linear alkyl ammonium/Na-MMT nanocomposites have shown monolayer intercalate structures that transition to bilayers with increasing intercalate content.\textsuperscript{2,14} For all the obtained materials, only two interlayer expansions were observed, ~0.42 and ~0.84 nm, as shown in Figure 3.3 and Table 3.1. A plot of organic mass content for the G0.0 nanocomposites reaches a plateau at ~7\% and that for G2.0 at ~14\% (Table 3.1, Figure 3.4). Where two intercalated phases have both gallery dimensions and organic compositions in a 2:1 ratio, a monolayer/bilayer structure model is strongly indicated. Because only mixed phases and no intermediate values for interlayer expansion are observed, a monolayer to bilayer transition is observed with increasing PAMAM content for G1.0 and G2.0.

![Figure 3.3 Interlayer expansion variation with reactant ratios, PAMAM/Na-MMT g/g, at room temperature and pH 10-11.](image)
Figure 3.4 Dendrimer mass % variation with reactant ratios, PAMAM/Na-MMT g/g, at room temperature and pH 10-11.

The interlayer distances and interlayer expansion values for PAMAM/Na-MMT nanocomposites were also comparable with previously reported polymer/Na-MMT nanocomposites (Table 3.2), supporting the proposed monolayer and bilayer models. Although PVOH/Ca-MMT nanocomposites showed higher interlayer expansion values than with typical polymer monolayers, Carrodo et al.\textsuperscript{6} note that extensive drying \textit{in vacuo} at 65 °C also results in $\Delta d \approx 0.4$ nm.
Table 3.2 Compositional and packing data for polymer/A-MMT nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Phase</th>
<th>$d_{001}$ (nm)</th>
<th>$\Delta d$ (nm)</th>
<th>Organic mass %</th>
<th>Packing fraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/Na-MMT</td>
<td>Monolayer</td>
<td>1.37</td>
<td>0.41</td>
<td>13</td>
<td>0.67</td>
<td>2</td>
</tr>
<tr>
<td>PEO/Na-MMT</td>
<td>Bilayer</td>
<td>1.77</td>
<td>0.81</td>
<td>23</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>PEI/Na-MMT</td>
<td>Monolayer</td>
<td>1.38</td>
<td>0.42</td>
<td>18</td>
<td>0.93</td>
<td>5</td>
</tr>
<tr>
<td>PVOH/Ca-MMT (heated)</td>
<td>-</td>
<td>1.70</td>
<td>0.74</td>
<td>10.3</td>
<td>0.24</td>
<td>6</td>
</tr>
<tr>
<td>PVOH/Ca-MMT</td>
<td>-</td>
<td>1.55</td>
<td>0.59</td>
<td>8</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from the compositional and structural data provided in the references indicated.

These small dimensions require a highly flattened dendrimer conformation within the galleries. Compared with a solution diameter of >1.5 nm, the maximum thickness for the dendrimers in the mono- and bilayers is ~0.4 nm for the nanocomposites we report. The strong adsorption of the dendrimers on the clay surfaces, coupled with the favorable lattice enthalpy for smaller expansions, result in minimum gallery expansions. The larger dendrimers show more favorability for the bilayer structure, most likely because their greater footprint in adsorbed form requires a larger intercalate volume for charge compensation of the anionic host.

Previous studies have shown altered PAMAM conformations due to interfacial or host-guest interactions. Lower generation (G0.0–G3.0) PAMAM dendrimers with an ethylenediamine core have an ellipsoidal shape, whereas the higher generation dendrimers (G4.0–G10.0) have a roughly spherical shape. A significant flattening of dendrimers has been observed on mica, Au, Ag, and Pt.
substrates; Hierlemann et al. provided evidence for 0.5-0.8 nm thick G4.0 dendrimers on a Au surface.\textsuperscript{41} Even the highly branched net PAMAM, at least for the lower generations, can compress into a highly flattened conformation with minimum dimension comparable to those observed in the mono- and bilayers obtained.

To further explore the feasibility for such highly flattened structures, a PAMAM G0.0 dendrimer was structurally optimized with flattened conformation of only 0.38 nm using Gaussian 09W (see Figure 3.5). While the flattened model may not correspond to the precise conformation of the dendrimer intercalates, the result does support the feasibility of such PAMAM conformations in the obtained nanocomposites. We calculate the flattened conformation energy of PAMAM G0.0 to be \(~100\text{-}200\) kcal/mol than the pseudospherical conformation. However, these are gas-phase calculations and do not account for the real synthetic conditions, where both solvation and clay surface interactions are important.

![Figure 3.5](image)

**Figure 3.5** A structural model for the G0.0 monolayer nanocomposites. (H, white; O, black; C, light grey; N, dark grey).
Under acidic synthetic conditions (pH = 2-3), all the obtained nanocomposites show only intercalate monolayers. Figure 3.6 compares PXRD patterns obtained under acidic and basic conditions for the different PAMAM generations. As shown in Table 3.1, the interlayer expansion for acidic syntheses decreases slightly, by ~0.02 nm, while the crystallite domain size increases by ~10-15 nm. Under these acidic conditions, the terminal primary amines on PAMAM (pKₐ ≈ 9-10),⁴³-⁴⁵ are protonated, and the cationic dendrimers must ion exchange with Na⁺ ions in Na-MMT. The slightly smaller interlayer expansion suggests that the protonated PAMAM bonds strongly via electrostatic interaction with the anionic MMT sheets. A similar observation was reported by Alongi et al.²⁴ using protonated G4.0 PAMAM, where a smaller interlayer expansion occurs than for materials prepared at higher pH.

![Figure 3.6 PXRD patterns](image)

Figure 3.6 PXRD patterns of (a) G(0.0), (b) G(1.0), and (c) G(2.0)/Na-MMT nanocomposites synthesized in acidic (pH = 2-3) and basic (pH = 10-11) conditions. Reactant ratios for all the nanocomposites were 0.6 g/g PAMAM/Na-MMT.
The increase in crystallite size at lower pH can be attributed to the observed slower reaction rates. For example, under acidic conditions, a flocculate does not appear at ambient temperature with G2.0 PAMAM. At 50 °C, particles appear after reaction for 30 minutes, and at 80 °C they appear after 10 minutes. Elevated temperature also increases the nanocomposite yield, although the yield remains lower than that under basic conditions. The slower reaction kinetics may again be associated with an ion exchange process required for a positively charged dendrimer.

When reactions are performed where a protonated montmorillonite, K10 (H-MMT) is substituted for Na-MMT, no dendrimer intercalation is observed. This difference implicates Na⁺ in the intercalation reaction, either via ion exchange or dendrimer complexation.

To study the effect of synthesis temperature, 0.3 g/g PAMAM/Na-MMT nanocomposites with all G0.0, G1.0, and G2.0 PAMAM were prepared at ambient temperature and at 60 °C. The obtained gallery dimensions (Table 3.1, Δd) and relative phase contents for mixed phases as indicated by PXRD reflection intensities (Figure B1, Appendix B) did not change significantly at higher temperature. However, the organic mass contents were lower at higher temperature (Table 3.1), which suggests that the higher rate of nanocomposite formation prevents efficient packing of the expanded galleries with PAMAM.
Figure 3.7 Packing fraction vs dendrimer mass % of nanocomposites synthesized at room temperature and pH 10-11. Labels show reactant ratios (g/g PAMAM/Na-MMT). Packing fractions were not calculated for mixed phases.

For G0.0 nanocomposites, an increase of PAMAM packing fraction was also observed at higher initial dendrimers ratios (Figure 3.7, left). G2.0 nanocomposites which formed with higher organic loading are more tightly clustered (Figure 3.7, right) indicating less effect of starting composition on product composition. It is very clear that there are two structures having similar packing fractions at full loading (0.31 for the monolayer, and 0.33 for the bilayer). H$_2$O may partially fill the available volume in the galleries; water content was not considered in the packing fraction calculation because the water contents are highly variable and depend in part on sample history. For comparison, packing fractions of ~0.67-0.68 can be deduced from reported data for PEO/Na-MMT mono- and bilayer intercalate structures$^2$ and of 0.93 for PEI/Na-MMT,$^5$ although a much lower value can be deduced from data reported for PVOH/Ca-MMT.$^6$ Linear polymers can yield packing fractions 2-3 times higher
than those observed for the PAMAM/Na-MMT nanocomposites. This difference may be due to inefficiencies in packing the flattened dendrimers but may also be an electrostatic effect related to the higher charge density of the dendrimers.

To help understand the mechanism of nanocomposite formation, capillary zone electrophoresis (CZE) was used to evaluate the nature of solvated PAMAM at pH conditions employed in these syntheses. Figure 3.8 shows electropherograms of PAMAM at pH 2.7 and 10.9, with results summarized in Table 3.3. The positively charged PAMAM dendrimers migrate toward the cathode under a positive applied voltage. Migration times increase with increasing PAMAM generation, reflecting a decreased charge density for the higher generation dendrimers. Surface charge densities at pH 2.7 were estimated 0.10–0.19 C/m². Shi et al.30 and Ebber et al.46 also observed clear separation of PAMAM generations 2.0–5.0 at pH 2.5 and generations 1.0–5.0 at pH 2.7. Although these PAMAM generations have similar theoretical charge/mass ratios, Shi et al.30 proposed a shielding model that retards migration for larger dendrimers.
Figure 3.8 Capillary electrograms for different PAMAM generations at pH 2.7 (a) and 10.9 (b).

Table 3.3 Migration data from CZE and calculated charge data for PAMAM dendrimers.

<table>
<thead>
<tr>
<th></th>
<th>pH 2.7</th>
<th>pH 10.9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G(0.0)</td>
<td>G(1.0)</td>
</tr>
<tr>
<td><strong>Hydrodynamic radius (nm)</strong></td>
<td>0.75</td>
<td>1.10</td>
</tr>
<tr>
<td><strong>Ionic strength (mol L(^{-1}))</strong></td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Average migration time (min)</strong></td>
<td>8.41</td>
<td>9.22</td>
</tr>
<tr>
<td><strong>Electrophoretic mobility (m(^2)/V.s)</strong></td>
<td>3.87E-08</td>
<td>3.52E-08</td>
</tr>
<tr>
<td><strong>Dimensionless mobility</strong></td>
<td>2.82</td>
<td>2.57</td>
</tr>
<tr>
<td><strong>Dimensionless zeta potential</strong></td>
<td>3.45</td>
<td>2.94</td>
</tr>
<tr>
<td><strong>Zeta potential (V)</strong></td>
<td>0.089</td>
<td>0.076</td>
</tr>
<tr>
<td><strong>Charge distribution function (I(_0))</strong></td>
<td>8.18</td>
<td>5.59</td>
</tr>
<tr>
<td><strong>Surface charge density (C/m(^2))</strong></td>
<td>0.192</td>
<td>0.131</td>
</tr>
</tbody>
</table>
At pH 10.9, the PAMAM dendrimers (terminal primary amine pK\(_a\) ≈ 9-10)\(^{43-45}\) are not protonated. However, they may readily coordinate to Na\(^+\) ions in the aqueous solution, forming positively charged complexes. The much faster migration shows that these complexes have higher charge densities than the protonated dendrimers, with calculated surface charges of 0.49-4.5 C/m\(^2\). As in acidic solution, the dendrimers generations show differential shielding and can be separated by migration time.

The differential shielding effects observed for PAMAM generations involve CZE buffer anions, and this mechanism is not necessarily operative under reaction conditions. However, the much higher dendrimer surface charge densities observed in basic aqueous conditions correlates with the faster, higher-yield nanocomposite reactions observed above. On the other hand, more highly charged dendrimers should favor monolayer structures over bilayers, whereas the opposite case was observed. The explanation for this difference may be either that dendrimer complexation within clay galleries is not the same as in aqueous solution (due to the dramatic conformation change) or related to the reduced MMT surface charge under acidic conditions. The reported zeta potentials and surface charge densities vs pH indicate less negative zeta potential and surface charge density at lower pHs for Na-MMT,\(^ {47}\) bolstering the latter explanation.

Figure 3.9 and Table 3.4 compare the FTIR spectra and bond vibrations observed for Na-MMT, PAMAM G(0.0) and a 0.4 PAMAM G(0.0)/Na-MMT nanocomposite. Characteristic bands observed for pristine Na-MMT at 1120 cm\(^{-1}\) (Si-O bend), 1048 (Si–O stretch), and 920 (Al–OH stretch) were also present in the
nanocomposites without significant shifts, confirming that the aluminosilicate sheets do not change.\textsuperscript{48,49} A sharp peak near 3600 cm\textsuperscript{-1} and a broad band at 3400 cm\textsuperscript{-1}, corresponding to O-H stretches, were each present in both Na-MMT and the nanocomposites. The former arises from intrasheet O-H\textsuperscript{5,49} the latter from H\textsubscript{2}O adsorbate or intercalate.\textsuperscript{49} The latter band, along with the associated O-H bend at 1636 cm\textsuperscript{-1}, are reduced or absent after Na-MMT is heated at 80 °C for 24 h (Figure B2, Appendix B). Both O-H absorption intensities are significantly reduced in the nanocomposite, indicating that less water is present in the nanocomposite than in Na-MMT. The terminal amine groups of dehydrated PAMAM G0.0 produce strong N-H stretches at 3284 cm\textsuperscript{-1} (asymmetric) and 3068 (symmetric).\textsuperscript{50,51} These absorption intensities increase for higher PAMAM generations, reflecting the larger number of terminal amine groups.\textsuperscript{51} The nanocomposites present a band at 3290 cm\textsuperscript{-1} (Figure 3.9c). The G2.0/Na-MMT nanocomposite (Figure B3, Appendix B) shows this band at higher intensity. Characteristic PAMAM absorptions at 2930, 1645, and 1554 cm\textsuperscript{-1}, corresponding to a C-H stretch, amide I (primarily C=O) stretch, and amide II (a combination of N-H in-plane bend and C-N stretch), respectively, are also seen in both dehydrated PAMAM and the obtained nanocomposites.\textsuperscript{50}
Figure 3.9 FTIR spectra of (a) NaMMT, (b) PAMAM G(0.0) and (c) 0.4 PAMAM G(0.0)/Na-MMT nanocomposite. The 2850-3500 cm$^{-1}$ region of (c) is intensified x10 for clarity.
Table 3.4 Comparison of IR bond vibrations in reactants and nanocomposites.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>PAMAM</th>
<th>Na-MMT</th>
<th>Nanocomposites</th>
<th>Bond Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600</td>
<td>X</td>
<td>X</td>
<td></td>
<td>O-H str.</td>
</tr>
<tr>
<td>3300-3400 (b)</td>
<td>X</td>
<td>X</td>
<td></td>
<td>O-H str.</td>
</tr>
<tr>
<td>3300</td>
<td>X</td>
<td></td>
<td>X</td>
<td>N-H asymmetric str.</td>
</tr>
<tr>
<td>3000</td>
<td>X</td>
<td></td>
<td>X</td>
<td>N-H symmetric str.</td>
</tr>
<tr>
<td>2900</td>
<td>X</td>
<td></td>
<td>X</td>
<td>C-H str.</td>
</tr>
<tr>
<td>1640</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Amide I (C=O str.)</td>
</tr>
<tr>
<td>1635</td>
<td></td>
<td>X</td>
<td></td>
<td>O-H bend.</td>
</tr>
<tr>
<td>1550</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Amide II (N-H bend. + C-N str.)</td>
</tr>
<tr>
<td>1120</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Si-O bend.</td>
</tr>
<tr>
<td>1045</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Si-O str.</td>
</tr>
<tr>
<td>920</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Al-OH str.</td>
</tr>
</tbody>
</table>
3.5 CONCLUSIONS

Lower generation (G0.0-2.0) PAMAM dendrimers form intercalated nanocomposites with Na-MMT. These are the first reports of the G0.0 and G1.0/Na-MMT nanocomposites and of a structurally ordered G2.0/Na-MMT. Compositional studies show clearly that the structures obtained depend on the generation of PAMAM and the starting organic composition. G0.0 always forms monolayer structures (\(\Delta d = 0.42 \text{ nm}\)), while G2.0 also forms bilayer structures (\(\Delta d = 0.84 \text{ nm}\)) at higher organic content, showing a marked monolayer to bilayer transition. G1.0 showed an intermediate behavior, with mixed-phase products obtained at the reactant ratios studied. This monolayer arrangement of PAMAM/clay nanocomposites is reported for the first time. Maximum organic contents of G0.0 monolayer and G2.0 bilayer nanocomposites were ~7% and ~14% respectively. Although gallery expansions were similar to those observed with linear polymer intercalates, packing fractions of 0.31-0.32 were 2-3 times lower. At acidic pH, the nanocomposites forming only monolayer structures are obtained, indicating a stronger electrostatic attraction between MMT and protonated PAMAM, and these nanocomposites formed more slowly and were more ordered. Na\(^+\) ions play a significant role in nanocomposite formation. At high pH, PAMAMs show high mobility, zeta potential, and surface charge densities due to Na\(^+\) complexation in solution. FTIR data indicates that both Na-MMT and PAMAM structural units are preserved in the nanocomposites obtained.
3.6 ASSOCIATED CONTENT

Supporting information available in the Appendix B. Comparison of PXRDs for room temperature and 60 °C syntheses, and FTIR spectra of dehydrated Na-MMT and 0.4G(2.0)/Na-MMT nanocomposite.

3.7 REFERENCES


CHAPTER 4

USE OF AMINE ELECTRIDE CHEMISTRY TO PREPARE MOLYBDENUM DISULFIDE INTERCALATION COMPOUNDS

Amila Udayanga Liyanage, and Michael M. Lerner

Department of Chemistry
Oregon State University
Corvallis, OR 97331-4003, USA

4.1 ABSTRACT

Electride solutions, formed by dissolution of Na(m) in ethylenediamine (en), are used to generate MoS$_2$ intercalation compounds. Two new intercalation compounds were obtained, labeled $\alpha$ and $\beta$ phases, containing both Na and en as intercalate and cointercalate respectively. The intercalation reaction proceeds via formation of a kinetic product, the $\beta$ phase, and subsequent generation of a stable thermodynamic product, the $\alpha$ phase. The $\beta$ and $\alpha$ phases have interlayer distances, $d_{IC}$, of 1.19 and 0.97 nm, respectively, which are ascribed to a perpendicular or parallel orientation of en within the intercalate galleries. Product compositions, morphologies and spectrochemical features are obtained from thermogravimetry, SEM and Raman measurement. Electrochemical reduction of MoS$_2$ in an en-based electrolyte is investigated, but does not show the same intercalation reactions. The chemistry observed is compared with that previously reported for this and other MS$_2$ hosts, and with graphite intercalation.
4.2 INTRODUCTION

Many transition metal dichalcogenides (MX$_2$) are layered structures consisting of metal cations bound between hexagonal planes of chalcogenide anions.$^{1-3}$ The MX$_2$ layers can often be chemically$^{4-8}$ or electrochemically$^{9-11}$ reduced with concomitant intercalation of cationic guests, including the alkali metals,$^{4-6,8}$ alkaline earths,$^7$ or other molecular or complex cations.$^{1,10}$ The electrostatic attraction between the positive intercalates and the negative MX$_2$ layers stabilize these intercalation compounds.$^1$ In order to accommodate the cation guests, the MX$_2$ sheets separate, with the interlayer expansion, $\Delta d$, defined as:

$$\Delta d = d_{IC} - d_h$$

where $d_{IC}$ and $d_h$ are the interlayer repeat distances observed for the intercalation compound and the MX$_2$ host, respectively (Figure 4.1). The many possible relative dispositions of chalcogenide planes leads to a rich variety of identified MX$_2$ structures and polytypes. The transition metal cations may have either trigonal prismatic or octahedral chalcogenide coordination. Some commonly observed arrangements are represented by 1T-TiS$_2$ with an (AbC)$_n$ stacking repeat, 2H-TaS$_2$ with an (AbACbC)$_n$ stacking repeat, and 2H-MoS$_2$ with an (AbABcB)$_n$ stacking repeat. 1T-TiS$_2$ has octahedral coordination, whereas 2H-TaS$_2$ and 2H-MoS$_2$ have trigonal prismatic coordination around transition metal cations.$^{1-3}$
MoS$_2$ is a rather chemically inert semiconductor, and is highly anisotropic, with an electrical resistivity 1000× greater in the direction perpendicular to the sheets. Important applications include use as a solid lubricant in both terrestrial and space environments (where graphite shows poor performance), as a catalyst in hydrodesulfurization and hydrogen evolution reactions, and as a photochemical catalyst in the oxidation of organics. MoS$_2$ holds promise for more efficient solar cells due to its resistance to photodegradation in water and photochemical activity over a wide frequency range.$^3$

Intercalation by alkali metal cations and co-intercalates can change MoS$_2$ from a semiconductor to a metal.$^3$ For example, the band gap decreases and the electrical conductivity increases by formation of Li$_{0.1}$MoS$_2$·δ(PEO)$^{12}$ and Li$_{0.1}$MoS$_2$·δdialkylamine,$^{13}$ which both act as mixed electronic-ionic conductors. Intercalation chemistry may thereby enable tailored conductivities for specific materials applications. Some alkali metal or alkali earth metal intercalation
compounds with MoS$_2$ are superconducting, with transition temperatures typically ~7° K.$^{7,8}$

Intercalation of promoter elements like Co or Ni has improved the catalytic activity of $\gamma$-Al$_2$O$_3$-supported MoS$_2$ in hydrodesulfurization.$^3$ Enhanced hydrogen evolution catalysis has been reported by use of metallic 1T-MoS$_2$ nanosheets obtained \textit{via} chemical exfoliation of 2H-MoS$_2$ nanostructures grown directly on graphite.$^{14}$

MoS$_2$ and its intercalation compounds may also be useful as electrodes in energy storage. Lemmon \textit{et al.} have reported improved Li cycling stability and a significant increase in reversible capacity for the PEO/MoS$_2$ and PEO/MoS$_2$/graphene composites.$^{15,16}$ MoS$_2$, MoS$_2$/graphene composites and MoS$_2$ nanosheets have recently been explored for use in Na-ion batteries where cycling performance is highly correlated to the nanostructure.$^{17-19}$

Several synthetic routes have been used to produce A$_x$MX$_2$ intercalation compounds where A is an alkali metal, including; (1) direct high temperature solid state synthesis by combining either the MX$_2$ host and an alkali metal or combining the A, M and X constituent elements,$^{1,2}$ (2) reaction of the MX$_2$ host with a reductant solution,$^{4-7}$ or (3) electrochemical reduction of the MX$_2$ host in a suitable electrolyte.$^{9,11}$ For some metal redox couples, such as Mo(IV)/Mo(III), the intercalation reaction requires powerful reductants such as an alkali metal dissolved in liquid ammonia.$^{4,5,8}$ This blue electride solution contains sodium ion complex cations and solvated electrons which are a powerful reductant.$^{20}$

$$\text{M(s)} \xrightarrow{\text{NH}_3} [\text{M(NH}_3)_6]^+ \text{(solv.)} + \text{e}^- \text{(solv.)} \quad (2)$$
Other strong reductants that have been used to form $A_xMX_2$ include butyllithium or sodium naphthalide dissolved in suitable organic solvents.\textsuperscript{1,6} For $MX_2$ hosts with more easily reduced metal cations, intercalation can be accomplished using ammonia,\textsuperscript{2,21,22} amines\textsuperscript{1,2,23-26} or aqueous solutions.\textsuperscript{27}

In some cases, solvent (Sol.) cointercalation is observed (Figure 4.1), to generate compounds represented as $A_xMX_2 \cdot \delta\text{Sol}$. The driving force for such cointercalation is the retention of some solvation of the alkali metal intercalate.

Alkali metal intercalation of $MS_2$ was first reported in 1959.\textsuperscript{4} Rüdorff has reported a wide range of $A_xMX_2$ intercalation compounds with the hosts including MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, ReS$_2$, TiS$_2$, and TiSe$_2$.\textsuperscript{4,5} Rouxel and coworkers have also extensively studied intercalation of the group 4 transition metal $MX_2$ compounds.\textsuperscript{2} Whittingham et al. studied the lithium intercalation of $MX_2$\textsuperscript{6} and Schöllhorn et al. reported several different syntheses and exchange reactions for $MX_2$ intercalation compounds.\textsuperscript{1,28}

Rüdorff reported formation of $Li_{0.8}MoS_2 \cdot 0.8\text{NH}_3$, $Na_{0.6}MoS_2$, $K_{0.6}MoS_2$ and $Cs_{0.5}MoS_2$ compounds with interlayer expansions ($\Delta d$, eqn (1)) of 0.335, 0.135, 0.195 and 0.274 nm, respectively.\textsuperscript{5} Since the ionic radius of $Li^+$ is $\approx 0.076$ nm,\textsuperscript{29} the much larger expansion of $Li_{0.8}MoS_2 \cdot 0.8\text{NH}_3$ indicates the presence of $\text{NH}_3$ cointercalate. Schöllhorn and Weiss reported that these intercalation compounds can also absorb water to form hydrated cation complexes with an increase in $\Delta d$ to 0.29–0.70 nm, depending on the reaction conditions.\textsuperscript{28}
A series of alkali metal and alkaline earth intercalation compounds of MoS$_2$ were synthesized in NH$_3$(l), with the observed $\Delta d$ values ranging from 0.14 to 0.37 nm.$^{7,8}$ The same method was utilized to synthesize intercalation compounds for TaS$_2$, with the resulting products Na$_x$TaS$_2$ and K$_x$TaS$_2$ giving $\Delta d$ of 0.11 and 0.21 nm, respectively.$^{30}$

Li$_x$TiS$_2$, Li$_x$MoS$_2$, and Li$_x$TaS$_2$ were obtained by reaction of the hosts with butyllithium in hexane, with $\Delta d$ from 0.025–0.05 nm.$^6$

Some organic and inorganic Lewis bases react to form intercalation compounds with groups 4 and 5 MX$_2$ hosts with $\Delta d$ ranging from 0.30 nm (for smaller molecules like NH$_3$) to 5.23 nm (for octadecylamine), with compositions reflecting the uptake of 0.1 to 1.0 guests per MX$_2$ unit.$^2$ This interaction between the host and guest has been ascribed either to charge transfer$^1$ or to a redox reaction where the host is reduced and the cationic form of base, solvated by the neutral base, intercalate (i.e. NH$_4^+$ and NH$_3$ respectively). Group 6 chalcogenides hosts do not react to form intercalation compounds with organic bases in this manner.$^{1,2}$

Some MX$_2$ hosts react in strong aqueous base to intercalate hydrated alkali metal cations, e.g. Na$_{0.3}$TaS$_2$·$\delta$H$_2$O.$^{2,27}$ These complex intercalates undergo facile displacement by subsequent reaction with aqueous salt solutions.$^{28}$ Alternately, the water cointercalate can be displaced by reaction in polar inorganic or organic solvents.$^{28}$ The product compositions, including both the contents of intercalate cations and of cointercalates, depend on the degree of reduction, exposure to exchange solutions, and post-reaction processing.
Ethylenediamine (en) and trimethylenediamine (tn) react directly with TiS$_2$, NbS$_2$, and TaS$_2$ to form intercalation compounds with $\Delta d = 0.34–0.41$ nm. From the known intercalate dimensions, these gallery dimensions indicate that the amine intercalates must form monolayers with long molecular axes oriented parallel to the host layers.$^{24-26}$ These products show a range of compositions depending on the host and sample processing conditions, with intercalate to MX$_2$ ratios of 0.17–0.39 for en and 0.15–0.33 for tn. Secondary amines, such as diethyamine, dibutylamine, and dipentylamine react with exfoliated MoS$_2$, generating Li$_{0.1}$MoS$_2$·$\delta$dialkylamine, where $\delta = 0.11$–0.42 and $\Delta d = 0.374$–0.445 nm, depending on the dialkylamine cointercalate.$^{13}$

Our group has previously explored the use of electride solutions to prepare graphite intercalation compounds containing amines or diamine intercalates.$^{31-34}$ Stage 1 and 2 graphite intercalation compounds (GICs) were reported for syntheses using Li(m) or Na(m) dissolved in liquid en. When the intercalate is the Li(en)$^+$ complex, the intercalate guests show an orientation transition of perpendicular to parallel upon evacuation. With Na(en)$^+$, the complexes show only a parallel orientation.$^{33}$

Since the reduction of graphite generally occurs at a lower potential than that for MoS$_2$, it is worthwhile to explore electride reactions for the intercalation of dichalcogenide hosts, especially since alkali metal-amine electride systems (other than with ammonia) have not previously been reported. In this work, we describe the first use of electride solutions to form MoS$_2$ intercalation compounds with amines, along with the product structures and compositions obtained. A novel intermediate
phase is found, and we propose a mechanism for the reaction. The results obtained are also analyzed in light of recent reports on electrochemical reduction of MoS$_2$.

4.3 EXPERIMENTAL

4.3.1 REAGENTS

Sodium metal (3-12 mm pieces in oil, 99.95%, Alfa Aesar), ethylenediamine (en) (99%, Alfa Aesar), molybdenum disulfide (MoS$_2$) (powder <2 micron, 99%, Aldrich), poly(ethylene-co-propylene-co-5-methylene-2-norbornene) (EPDM) (Aldrich), acetylene black (99.5+%, Alfa Aesar), cyclohexane (ACS grade, Alfa Aesar), sodium hexafluorophosphate (NaPF$_6$) (98%, Aldrich) and acetonitrile (HPLC grade, Fisher Scientific) were used as received.

4.3.2 CHEMICAL SYNTHESSES

Synthesis and handling of the air-sensitive reagents were performed under an inert atmosphere (N$_2$) using either a drybox or septum-syringe techniques. In a typical reaction, Na metal (50 mg) was stirred overnight in ethylenediamine (3.0 mL) at 60 °C under an inert (N$_2$) atmosphere to form a blue-colored electride solution. MoS$_2$ (100 mg) was then added to the electride solution, and the reaction vigorously stirring at 60 °C for 48 h. Samples were centrifuged for 10 minutes and the solution phase was extracted by syringe. The solid products were placed under vacuum for 12 h at 60 °C.

As specified below, the above reaction conditions (time, temperature, reagent amounts and chemical addition sequence) were varied for some experiments.
Products obtained are labeled with reaction temperature and time. For example, the sample obtained by reaction at 60 °C for 24 h has been labeled “S-60C-24h”.

4.3.3 ELECTROCHEMICAL SYNTHESES

Galvanostatic reduction was performed in a 2-compartment cell with a fritted glass separator maintained under an inert (N₂) atmosphere at ambient temperature. Working electrodes were prepared by painting SS mesh (geometric area ~1 cm²) with a cyclohexane slurry containing MoS₂ powder (80 mass pct.), acetylene black (15 mass pct.), and EPDM binder (5 mass pct.). The dried electrode mass was 18-20 mg. Counter and reference electrodes were SS mesh and SS wire. The electrolyte solution was 0.1 M NaPF₆ in ethylenediamine. Working electrodes were reduced at a constant current of 0.10 mA for 16–48 h, then immediately removed from the cell, rinsed briefly with 3–4 mL of acetonitrile, and dried overnight under vacuum at ambient temperature.

4.3.4 ANALYSES

Powder X-ray diffraction (XRD) data from 3–20° 2θ were collected on a Rigaku MiniFlex II diffractometer, using Ni-filtered Cu Kα radiation, at a scan rate of 3° min⁻¹ and step size of 0.02°. Diffraction peak areas were obtained using MDI JADE 9.0 XRD analysis software. Thermogravimetric (TGA) analyses were performed using a Shimadzu TGA-50 analyzer under flowing Ar gas (20 mL min⁻¹) from ambient to 400 °C at a heating rate of 10 °C min⁻¹ and under air from ambient to 900 °C at a heating rate of 10 °C min⁻¹. Scanning electron micrographs (SEM) were obtained using an FEI Quanta 600F scanning electron microscope equipped with a field emission gun and operated at 10 kV. Raman spectra were obtained from 60–
4000 cm\(^{-1}\) using a Witec Alpha 300 confocal Raman microscope with 514 nm laser source.

The van der Waals volume of en, \(V_{en} = 0.0651 \text{ nm}^3\) was calculated based on Bondi radii using a method termed “Atomic and Bond Contributions of van der Waals volume” (VABC).\(^{35}\) Volume of Na\(^+\), \(V_{Na} = 0.00445 \text{ nm}^3\) was calculated using the ionic radius of Na\(^+\) (0.102 nm).\(^{29}\) Packing fractions for MoS\(_2\) intercalation compounds were calculated\(^{36,37}\) as:

\[
Packing\ fraction = 2 \left( nV_{Na} + mV_{en} \right) / \sqrt{3}a^2\Delta d \tag{3}
\]

where \(n\) and \(m\) are the molar ratios of Na : MoS\(_2\) and en : MoS\(_2\) respectively, and \(a = 0.3160 \text{ nm}\).\(^{1,2}\)

Energy optimization of the gas-phase en molecule was performed using the DFT B3LYP method with a 6-31G+(d,p) basis set and Gaussian 09W software.

4.4 RESULTS AND DISCUSSION

The powder XRD patterns obtained from reactions of MoS\(_2\) with a sodium electride solution (Figures 4.2, and 4.3) shows host expansion to form new intercalation compounds. In Figure 4.2 (S-60C-48h), a single new phase is evident with interlayer distance, \(d_{IC} = 0.97 \text{ nm}\). The expansion relative to the host MoS\(_2\) sheet thickness (\(d_{002} = 0.615 \text{ nm}\))\(^3\) is \(\Delta d = 0.35 \text{ nm}\). Hereafter this new phase is labeled the \(\alpha\) phase.
Figure 4.2 Powder XRD of MoS$_2$ and the intercalation compounds obtained after 48 h reaction at 60 °C (S-60C-48h) and after 24 h reaction at 60 °C using decreased Na mass (M$\frac{1}{2}$-60C-24h).
Figure 4.3 Powder XRD of MoS$_2$ and the intercalation compounds obtained after 24 h at reaction temperatures ambient to 100 °C.

Figure 4.3 shows XRD patterns obtained after 24 h reaction at ambient to 100 °C. Ambient temperature reaction produces a different new phase (with d = 1.19 nm, $\Delta d = 0.57$ nm), labelled the $\beta$ phase, along with the unreacted host. Reaction products at 40 and 60 °C contain both the $\alpha$ and $\beta$ phases along with unreacted MoS$_2$. 
Higher temperature reactions, at 80 °C and 100 °C, produce mainly the α phase, with a very small residual of unreacted MoS₂.

Lower temperature reactions show an additional diffraction peak (tagged with an *) near d = 0.69 nm, attributed to NaₓMoS₂, i.e. the intercalation product without the en cointercalate. This phase has previously been reported, with d = 0.75 nm (ref. 28) or d=0.71 nm.³⁸ The small interlayer expansion observed for this phase (Δd ≈ 0.1 nm) eliminates the possibility of en contained in that product.

Summarizing the changes observed with varied reaction temperature, (i) lower temperature reactions result in a relatively large amount of unreacted host (an incomplete reaction), and are relatively rich in the β phase, and (ii) higher temperatures generate nearly complete reactions to form mainly the α phase.

The incomplete reactions observed at lower temperature could arise from the slow kinetics of amine electride (reactant) formation, resulting in a low reductant concentration, or alternately they may be related to a slower rate of diffusion of the Na(en)ₓ⁺ complex intercalate into the intercalation compound galleries.

In other experiments aimed at decreasing the electride reactant concentration, reactions for 48 h reaction at 60 °C were run using ½ the mass of Na or 5× the standard volume of en. Both changes results in products containing both the α and β phases and unreacted MoS₂. The association of β phase and incomplete reactions again provides some evidence that the β phase is a kinetic product. In one experiment using the decreased Na mass, the product obtained after 24 h reaction at 60 °C contained only the β phase (Figure 4.2. M½-60C-24h).
Products obtained at 60 °C with varied reaction times are shown in Figure 4.4. Shorter reaction times produce the β phase along with unreacted MoS₂; the α phase is first evident after reaction for 1 h. At longer reaction times, the β phase and MoS₂ are no longer observed. These data confirm that the β phase is formed more rapidly as a kinetic product, but ultimately disappears as the more stable α phase forms.

Figure 4.4 Powder XRD data obtained for reaction of MoS₂ with Na/en electride solution at 60 °C. Reaction times are indicated at the right.
Relative PXRD peak areas ($A/A_t$) were obtained by dividing the raw area of individual peak ($A$) by the total area of all observed peaks ($A_t = \Sigma A$), to normalize relative peak areas and more closely represent the volume fraction of the associated phases. Analysis of relative PXRD peak areas ($A/A_t$), shown in Figure 4.5, shows clearly the intermittent appearance of the $\beta$ phase during the 60 °C reaction.

![Figure 4.5 Ln($A/A_t$) vs. reaction time at 60 °C.](image)

Although lower electrider concentrations, lower reaction temperatures and shorter reaction times are seen to favor formation of the $\beta$ phase, this phase was difficult to obtain as a single-phase product. This indicates that the rates of conversion of MoS$_2$ to $\beta$ phase, and $\beta$ to $\alpha$ phase, i.e. rates $k_1$ and $k_2$ in Figure 4.6, were comparable under the range of reaction conditions studied.
Figure 4.6 Proposed reaction mechanism; MoS$_2$ forms a metastable $\beta$ phase, which converts to the more stable $\alpha$ phase.

We propose that the $\beta$ phase appears due to the more rapid diffusion of the Na(en)$_x^+$ complex with a perpendicular orientation within intercalate galleries. Thermodynamic stabilities of these products depend on several factors, such as electrostatic and solvation enthalpies. Smaller galleries, as observed for the $\alpha$ phase, should generally have a more favorable lattice enthalpy, since $E \propto -1/d$.

The $\alpha$ and $\beta$ phases obtained are both ascribed to the cointercalation of en with Na$^+$ to form an intercalate monolayer. The $\alpha$ phase expansion ($\Delta d = 0.35$ nm) corresponds to an en orientation with long axis parallel to host sheets, and the $\beta$ phase expansion ($\Delta d = 0.57$ nm) to a perpendicular en orientation. Optimized molecular dimensions obtained by Gaussian (Figure 4.7) correlate well with the observed gallery dimensions. Amine intercalates have been previously reported with $\Delta d = 0.37$–0.40 nm for MS$_2$ hosts$^{13,26}$ but we are not aware of any reports on the observed $\beta$ phase for any MX$_2$ intercalation products. Graphite intercalation compounds (GICs) containing en show both types of expansion, with the perpendicular orientation of $\Delta d = \sim 0.5$ nm for LiC$_x$·δen and a reported transition to parallel orientation observed upon
evacuation of the product.\textsuperscript{33} That work also reported the formation of a GIC with composition NaC\textsubscript{15}\textperiodcentered{}1.0en with $\Delta d = 0.36$ nm, indicating a parallel en orientation.\textsuperscript{33}

![Image of ethylenediamine molecule with dimensions 0.51 nm and 0.37 nm]

Figure 4.7 Gaussian-optimized molecular dimensions of ethylenediamine.

An alternate explanation for the appearance of $\alpha$ and $\beta$ phases could be the formation of en monolayers and bilayers, respectively, as occurs in the hydration of A\textsubscript{x}MS\textsubscript{2}.\textsuperscript{39} However, thermogravimetric data (\textit{vide infra}) show that the obtained phases have similar en content, which does not support this model. Additionally, the observed $d_{IC}$ for the $\alpha$ phase is 1.19 nm, which is significantly less than the 1.32 nm calculated to accommodate two en layers.
Figure 4.8 Thermograms of MoS$_2$, en, (a) the $\alpha$ phase Na-en-MoS$_2$ intercalation compound (S-60C-48h) and (b) a $\beta$ phase predominant product (S-60C-3h) under Ar flow, and (c) $\beta$ phase predominant product (S-60C-3h) analyzed under air flow.

Thermograms for the Na-en-MoS$_2$ intercalation compounds under Ar flow (Figure 4.8a, and b) show two mass loss events at 100–200 °C and 225–275 °C, which are attributed to volatilization (b.p. of en = 116 °C) and decomposition of the en cointercalate. Under air flow, a mass increase above 275 °C can be attributed to the formation of Na$_2$O (Figure 4.8c). From the mass loss and uptake, the composition for S-60C-48h ($\alpha$-phase) and S-60C-3h ($\beta$-phase predominant) are found to be Na$_{0.3}$MoS$_2$·0.4en and Na$_{0.2}$MoS$_2$·0.3en, respectively. Other studies of MS$_2$ (M = Ti, Ta and Nb) also give maximum en : MS$_2$ ratios in the 0.3-0.4 range.$^{24-26}$
Where all graphene sheets are separated by intercalate galleries (i.e. in the stage 1 products), GIC have an en mass of 20–22%. In comparison, the structurally-analogous MoS$_2$ intercalation compounds show en contents of ~12%. Calculated packing fractions (Table 4.1) correcting for the different host sheet surface areas and formula masses, indicate much denser intercalate packing for both $\alpha$ and $\beta$ phases in MoS$_2$ than for the corresponding orientations in GICs. In part, this reflects a higher en : Na ratios in MoS$_2$ intercalation compounds (1.3-1.5 in MoS$_2$ compounds vs. 0.6-1.0 in stage 1 GICs). Also, the packing fraction of $\beta$ phases is lower due to the greater gallery expansion.

Table 4.1 Compositional data for en containing intercalation compounds

<table>
<thead>
<tr>
<th>Composition</th>
<th>Stage</th>
<th>Phase</th>
<th>Packing fraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiC$_{15}$$\cdot$0.8en</td>
<td>1</td>
<td>$\alpha$</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>LiC$_{26}$$\cdot$0.7en</td>
<td>2</td>
<td>$\beta$</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>NaC$_{15}$$\cdot$1.0en</td>
<td>1</td>
<td>$\alpha$</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>NaC$_{25}$$\cdot$0.6en</td>
<td>2</td>
<td>$\alpha$</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}_0.3\text{MoS}_2$$\cdot$0.4en</td>
<td>1</td>
<td>$\alpha$</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}_0.2\text{MoS}_2$$\cdot$0.3en</td>
<td>1</td>
<td>$\beta$</td>
<td>0.43</td>
<td>This work</td>
</tr>
</tbody>
</table>

Less dense packing in the $\beta$-phase may facilitate Na(en)$_x^+$ complex diffusion, allowing more rapid formation of this phase. It may also be that the very high packing density in the $\alpha$-phase MoS$_2$ compound prohibits reduction to the extent observed where no en cointercalate is present (such as in Na$_{0.6}$MoS$_2$).
The calculated sheet charge densities for NaC\(_{15}\cdot 1.0\text{en}\), Na\(_{0.3}\text{MoS}_2\cdot 0.4\text{en}\) and Na\(_{0.2}\text{MoS}_2\cdot 0.3\text{en}\) are 2.5, 3.5, and 2.3 e\(^-\) per nm\(^2\), respectively. Again, we can propose that lower charge densities may allow for more rapid diffusion, but result in a less thermodynamically stable product.

SEM images (Figure 4.9) show that a layered microstructure is retained in all samples, with the reaction products displaying a somewhat delaminated appearance as compared to the starting MoS\(_2\).

![SEM images of (a) MoS\(_2\) and (b) α phase intercalation compound Na\(_{0.3}\text{MoS}_2\cdot 0.4\text{en}\)](image)

Figure 4.9 SEM images of (a) MoS\(_2\) and (b) α phase intercalation compound Na\(_{0.3}\text{MoS}_2\cdot 0.4\text{en}\)

Raman spectra of MoS\(_2\) and a representative Na-en-MoS\(_2\) intercalation compound are shown in Figure 4.10. MoS\(_2\) displays prominent sharp absorbance peaks at 390 cm\(^{-1}\) (E\(_{2g}\)\(^1\) mode) and 418 cm\(^{-1}\) (A\(_{2g}\) mode) as has been reported previously.\(^{40,41}\) After intercalation, the spectrum background increases significantly,
the two sharp peaks broaden and shift slightly to lower frequency, and two new strong broad peaks appear at ≈ 1350 and ≈ 1600 cm$^{-1}$. Very similar changes were previously observed following Li intercalation into MoS$_2$, with the new high frequency peaks ascribed to a disordered state arising from intercalate arrangement.$^{41}$ In the present case, en has molecular absorbances in this region, however, these should be relatively sharp and the other strong en absorbances expected at 3300 ($\nu$(NH$_2$)), 2900 ($\nu$(CH$_2$)) and 2850 ($\nu$(CH$_2$)) cm$^{-1}$ were not detected.$^{42}$ Therefore the high frequency broad bands present in the intercalation compound samples more likely arise from a transition associated with disorder within the intercalate galleries.

![Raman spectra of MoS$_2$ and Na-en-MoS$_2$ intercalation compound (S-60C-3h) indicates the structural change upon intercalation.](image)

Figure 4.10 Raman spectra of MoS$_2$ and Na-en-MoS$_2$ intercalation compound (S-60C-3h) indicates the structural change upon intercalation.

In contrast to the chemical syntheses, galvanostatic reduction of MoS$_2$ in en/NaPF$_6$ did not generate predominant intercalation products. A very weak XRD
peak associated with the $\alpha$ phase is observed, but the principal change is a weakening and broadening of the MoS$_2$ host diffraction peaks (Figures 4.11 and 4.12).

Figure 4.11 Powder XRD profiles for MoS$_2$ and products of electrochemical reduction in en/NaPF$_6$ with applied charges indicated.

Figure 4.12 Relative peak areas and widths for MoS$_2$ and reduction products at different applied charges.
Lemmon et al. reported that reduction of MoS$_2$ in a 7 : 3 vv ethylene methyl carbonate : ethylene carbonate electrolyte with LiPF$_6$ resulted in formation of Li$_2$S and an amorphous form of Mo or Li$_x$Mo.$^{15,16}$ The analogous reduction for Na reaction is in eqn (4):

$$\text{MoS}_2 + (4+x)\text{Na}^+ + (4+x)e^- \rightarrow 2\text{Na}_2\text{S} + \text{Na}_x\text{Mo} \quad (4)$$

Theoretically the capacity required for the above reduction is $\approx 840 \text{ mA h g}^{-1}$ (if $x = 1$); each $\text{e}^-$ reduction translates to 167 mA h g$^{-1}$. After applying from half to twice the latter charge, almost no intercalation products were evident. As can be seen, the ordered layered structure is destroyed even at much lower applied charges, suggesting an entirely different and non-intercalative mechanism for this electrochemical reduction.

4.5 CONCLUSIONS

MoS$_2$ reacts with electride solutions with amine to form intercalation compounds of composition Na$_{0.2-0.3}$MoS$_2$$^{0.3-0.4}$en. A metastable product, identified as the $\beta$ phase, shows a perpendicular en orientation with interlayer expansion of 0.57 nm, and the thermodynamic product, or $\alpha$ phase, shows a parallel orientation and interlayer expansion of 0.35 nm. Shorter reaction time, dilution and lower temperatures favor formation of the $\beta$ phase. The intercalation products are not obtained by electrochemical reduction in en/NaPF$_6$. 
4.6 ACKNOWLEDGEMENTS

We thank Professor Chih-Hung Chang and Changqing Pan (OSU Chemical Engineering) for assistance with Raman measurements. A.U.L. thanks the Whiteley Fellowship in Material Sciences for financial support.

4.7 REFERENCES


CHAPTER 5

CONCLUSION

5.1 CONCLUSION

The development of novel synthetic methods, along with resulting new intercalation compounds and nanocomposites, and their structural and compositional analyses, are reported in this dissertation. Below are some conclusions and proposals for additional studies on new synthetic reactions.

A template synthesis method was developed to obtain NiPS$_3$/polymer nanocomposites. A summary of the resulting nanocomposites is shown in Table 5.1. The observed monolayer arrangement in intercalate galleries for NiPS$_3$/PEO is different from the previously-reported bilayers obtained by a topotactic route for MPS$_3$/PEO nanocomposites. Three other polymer/NiPS$_3$ nanocomposites (NiPS$_3$/PEI, NiPS$_3$/PVA and NiPS$_3$/PVP) are also reported for the first time using this new synthetic approach. The template method results in more densely packed galleries. More dilute conditions, a more polar solvent and longer aging times increases the crystallite size of the nanocomposites. The concentrations of P$_2$S$_6^{4-}$ and Ni$^{2+}$ in the reaction solution govern the nanocomposite nucleation and growth, respectively.
Table 5.1 Summary of template synthesized NiPS₃/polymer nanocomposites reported in this dissertation

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Composition</th>
<th>(\Delta d) (nm)</th>
<th>Polymer arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPS₃/PEO</td>
<td>NiPS₃(C₂H₄O)₁</td>
<td>0.42</td>
<td>Parallel monolayer</td>
</tr>
<tr>
<td>NiPS₃/PEI</td>
<td>NiPS₃(C₂H₅O)₁</td>
<td>0.41</td>
<td>Parallel monolayer</td>
</tr>
<tr>
<td>NiPS₃/PVA</td>
<td>NiPS₃(C₂H₄O)₀.₉</td>
<td>0.42</td>
<td>Parallel monolayer</td>
</tr>
<tr>
<td>NiPS₃/PVP</td>
<td>NiPS₃(C₆H₉NO)₀.₅</td>
<td>1.56</td>
<td>Parallel monolayer</td>
</tr>
</tbody>
</table>

An exfoliation–adsorption method is used to prepare lower generation (G0.0–2.0) PAMAM/Na-montmorillonite nanocomposites. These are the first reports of the G0.0 and G1.0 PAMAM/Na-MMT nanocomposites and of a structurally ordered G2.0 PAMAM/Na-MMT nanocomposite. A summary of selected PAMAM/Na-MMT nanocomposites is shown in Table 5.2. G0.0 PAMAM always forms monolayers within intercalate galleries while G1.0 and G2.0 indicates formation of both monolayer and bilayer arrangements. G2.0 PAMAM/Na-MMT nanocomposites show monolayer to bilayer transition with increasing organic content in the reaction mixture. This is the first report of monolayer PAMAM arrangement in clays. Lower packing fractions are obtained with respect to the linear polymer/Na-MMT nanocomposites. Acidic conditions favor monolayer formation for all three of the dendrimer generations studied. The presence of Na⁺ ions in the Na-MMT structure has a significant effect on nanocomposite formation. In basic conditions, PAMAMs show high mobility, \(\zeta\) potential, and surface charge densities due to Na⁺.
complexation in solution. Both Na-MMT and PAMAM structural units are preserved in the nanocomposites obtained.

Table 5.2 Summary of exfoliation-adsorption synthesized selected PAMAM/Na-MMT nanocomposites reported in this dissertation

<table>
<thead>
<tr>
<th>Sample $^a$</th>
<th>Reaction condition temp.$^b$/pH</th>
<th>Organic mass %</th>
<th>$\Delta d$ (nm)</th>
<th>Polymer arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6G(0.0)</td>
<td>RT/10-11</td>
<td>7.4</td>
<td>0.41</td>
<td>Monolayer</td>
</tr>
<tr>
<td>0.6G(1.0)</td>
<td>RT/10-11</td>
<td>10.2</td>
<td>0.45, 0.79</td>
<td>Mix of monolayer and bilayer</td>
</tr>
<tr>
<td>0.6G(2.0)</td>
<td>RT/10-11</td>
<td>14.1</td>
<td>0.84</td>
<td>Bilayer</td>
</tr>
<tr>
<td>0.6G(0.0)-2</td>
<td>RT/2-3</td>
<td>6.6</td>
<td>0.40</td>
<td>Monolayer</td>
</tr>
<tr>
<td>0.6G(1.0)-2</td>
<td>RT/2-3</td>
<td>6.6</td>
<td>0.40</td>
<td>Monolayer</td>
</tr>
<tr>
<td>0.6G(2.0)-80-2</td>
<td>80 °C/2-3</td>
<td>7.1</td>
<td>0.40</td>
<td>Monolayer</td>
</tr>
</tbody>
</table>

$^a$ For all the samples the reactant ratio (g/g PAMAM/Na-MMT) = 0.6, $^b$ RT = ambient temperature

An electride solution containing Na(m) and ethylenediamine (en) is used to synthesize intercalation compounds of MoS$_2$. Summary of obtained intercalation compounds is shown in Table 5.3. The $\beta$ phase (perpendicular en arrangement) is not reported previously for any MS$_2$ intercalation compounds. The intercalation reaction proceeds via formation of a metastable kinetic product, the $\beta$ phase, and subsequent generation of a stable thermodynamic product, the $\alpha$ phase. Lower electride concentrations, lower reaction temperatures and shorter reaction times favor formation of the $\beta$ phase. These products have a greater packing fractions compared
to the structural analogous alkali metal-en-graphite intercalation compounds. Electrochemical reduction of MoS$_2$ in an en based electrolyte does not show the same intercalation behavior.

Table 5.3 Summary of synthesized MoS$_2$ intercalation compounds using electride chemistry in this dissertation

<table>
<thead>
<tr>
<th>Intercalation compound</th>
<th>Composition</th>
<th>$\Delta d$ (nm)</th>
<th>en arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-phase Na-en-MoS$_2$</td>
<td>Na$_{0.3}$MoS$_2$0.4en</td>
<td>0.35</td>
<td>Parallel monolayer</td>
</tr>
<tr>
<td>$\beta$-phase Na-en-MoS$_2$</td>
<td>Na$_{0.2}$MoS$_2$0.3en</td>
<td>0.57</td>
<td>Perpendicular monolayer</td>
</tr>
</tbody>
</table>

Overall, this dissertation introduces several new synthesis intercalation strategies to expand both intercalation chemistry and nanocomposite chemistry. During the process novel structures and reaction mechanisms were obtained.

The synthetic reactions discussed in this dissertation can be extended to other host structures. Template synthesis method could be utilized whenever the solution phase precursors are available to form the host. Sol-gel synthesis could be coupled with this method to form nanocomposites. As another example, the electride chemistry can be extended to synthesize possible intercalation compounds of other structurally similar MX$_2$ hosts. Other alkali metal, and amine combinations can be utilized to obtain electride solutions with complexes other than [Na(en)$_x$$^+$]. Since the redox chemistries of transition metal, chemistries of alkali metal and coordination and structures of amine are different; such exploration is likely to lead to new structures.
and compositions, along with different materials properties. The application of electride chemistry in NiPS₃ is another possibility. Since electride solution can apply a greater reduction potential, this may allow new intercalation or nanocomposite chemistry.

Intercalation compounds may also act as precursors in the synthesis of other intercalation compounds and nanocomposites. For an example Na-en-MoS₂ could reacted with surfactants to obtain larger galleries, ultimately forming stable exfoliated nanosheets of MoS₂δ-, or can react with polymers or dendrimers to form Na-polymer-MoS₂ nanocomposites.

Previously there were reports on stabilization and/or higher capacity effected by PEO incorporation into LiₓMoS₂. Since Na-ion batteries are of interest currently, new path to obtain analogous nanocomposites are of interest. Since dendrimers have the capability to encapsulate other molecules, those are a very important topic in drug delivery. Future attempts can be directed to form nanocomposites with a dendrimer encapsulated compound. Nanocomposites containing dendrimers could act as a reservoir for the slow release of encapsulating drug or molecules.


APPENDIX A

PREPARATION AND CHARACTERIZATION OF NANOCOMPOSITES OF POLYAMIDOAMINE (PAMAM) DENDRIMERS WITH MOLYBDENUM(VI) OXIDE (MoO₃)

Esther U. Ikuhuria,¹ Amila U. Liyanage, and Michael M. Lerner

Department of Chemistry
Oregon State University
Corvallis, OR 97331-4003, USA

¹ Fulbright visiting scholar, Oregon State University, 2011/2012.
Department of Chemistry, University of Benin, Benin City, Nigeria.

A.1 ABSTRACT

The preparation and characterization of polymer nanocomposites is an important research area because of the significant changes in materials properties relative to the component phases or to conventional microscale or macroscale composites. Polyamidoamine (PAMAM)/molybdenum(VI) oxide (MoO₃) nanocomposites were synthesized using an exfoliation/adsorption method and characterized by powder X-ray diffraction, thermogravimetric analyses, scanning electron microscopy and infrared spectroscopy. Generation 0 (G0) and generation 2 (G2) PAMAM forms nanocomposites with MoO₃ with either intercalate monolayers or bilayers, with resulting gallery expansions (Δd) of ~ 0.5 and ~ 0.7-0.8 nm, respectively. G0 only forms monolayers whereas G2 forms mono and bilayers. The spherical PAMAM conformation in aqueous medium changes dramatically to a highly-flattened conformation within the intercalate galleries. Reaction temperature also affects the structure of the obtained G2 PAMAM nanocomposites. Bilayer nanocomposites obtained at 40 and 120 °C show Δd = 1.4 nm and 0.7 nm, respectively. Mixed phases were obtained at 60 °C. The obtained nanocomposite compositions and structures are compared with previously-reported polymer/MoO₃ nanocomposites.
A.2 INTRODUCTION

Nanocomposites are materials derived from two or more phases where at least one dimension of the combination is in the nanometer scale. Polymer nanocomposites are a new class of advanced polymer composites that often display enhanced physical properties such as strength, hardness, thermal and viscoelasticity. Nanocomposite properties depend not only on those of their parent phases, but also on the structural complexity, morphology and interfacial interactions of these constituents. With an eye towards new and improved devices, nanocomposites often display dramatically improved performance relative to those currently available.\(^1\) For example, a material’s stiffness can be improved without sacrificing mechanical toughness, or its barrier properties enhanced without sacrifice of desirable properties such as transparency, flame retardancy and biodegradability.\(^2\) The ability to avoid the trade-off in functional materials which is typical of conventional composites illustrates the potential importance of nanocomposites.

Two dimensional (2D) layered structures have been investigated intensively as host lattices for preparing nanocomposites. These host lattices may exfoliate into a polymer matrix or incorporate polymer guests within well-defined interlayer galleries.\(^3\) Many two dimensional compounds which involve intercalation of molecules or ions between inorganic layered sheets have been reported.\(^4,5\) Again, the preparation and detailed characterization of polymer nanocomposites is an active area of research because of the possibility of a remarkable improvement in materials properties when compared with purely organic or inorganic phases or conventional micro and macro composites.
Dendrimers are synthetic, mono-disperse macromolecules with a regular and highly-branched three-dimensional architecture. In contrast to traditional polymers, dendrimers have core-shell structures consisting of three basic architectural components: a core, interior shells (generations) with repeating branch-cell units, and terminal functional groups. They are produced by an interactive sequence of reaction steps, in which each added step leads to a higher-generation material. This approach provides unprecedented control over composition and architecture, as well as the ability to add numerous different terminal groups that affect their surface chemistry. Polyamidoamine (PAMAM) dendrimers are one of the most well investigated families and have been evaluated for diverse applications ranging from drug delivery to molecular encapsulation and gene therapy, as well as for building blocks for nanostructures.

Molybdenum trioxide (MoO$_3$) is an example of 2D layered structure that has been examined as a potentially useful electrode because of its rich redox chemistry. It exhibits a unique layered structure in which Mo atom is surrounded by distorted octahedron of oxygen atoms with two layers of corner-sharing MoO$_6$ units. As an electrode material for rechargeable battery application, MoO$_3$ is limited by slow kinetics for Li-ion transport, an electronically-insulating state upon full oxidation, and poor cycling behavior when compared to other metal oxides/chalcogenides. One approach to modify the properties of the layered MoO$_3$ has been intercalation of electronically-conducting guests. Previous studies have also reported on the intercalation of polyethylene oxide (PEO), linear polyethylenimine (LPEI), polyaniline (PANI), polyvinylpyrrolidone (PVP) and
polyacrylamide (PAM). Polymer/MoO₃ nanocomposites have also been studied as a cathode for secondary lithium ion batteries, where monolayer and bilayer nanocomposites of PEO/MoO₃ have indicated significant differences from each other in both lithium ion transport and cell capacity in cycling. Unlike polymers, dendrimers have a confined shape and a size which is possibly useful for a controlled intercalation and electrode behavior. However, there has been no report on the intercalation of dendrimers into MoO₃. Here we report on the synthesis and characterization of layered nanocomposites derived from PAMAM dendrimers and MoO₃.

A.3 EXPERIMENTAL

A.3.1 MATERIALS

MoO₃ (99.5%, Sigma-Aldrich), Na₂MoO₄·2H₂O (99%, Strem Chemicals) and Na₂S₂O₄ (Laboratory grade, Fisher) were used as received. [Na(H₂O)₂]₀.₂₅MoO₃ was prepared by reacting MoO₃ with an aqueous solution of Na₂S₂O₄ according to a literature method. Distilled water (DI) was used in all experiments. Aqueous suspensions of amine terminated polyamidoamine (PAMAM) dendrimers of different generations (G0, G1, G2) were obtained from Dendritech (Midland, M.I) and used as supplied. Some of the physical properties of the generations of PAMAM dendrimer used are presented in Table A1.
Table A1. Physical properties of amine surface functional PAMAM dendrimers.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Surface groups</th>
<th>Molar mass</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>517</td>
<td>1.4</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>1430</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>3256</td>
<td>2.6</td>
</tr>
</tbody>
</table>

A.3.2 SYNTHESES

[Na(H₂O)₉]₀.₂₅MoO₃ was reacted with PAMAM to form PAMAM/MoO₃ nanocomposites using the exfoliation/adsorption method described previously¹⁸ for polymer/MoO₃ nanocomposites with slight modifications indicated below. The ratio of reactants PAMAM to [Na(H₂O)₉]₀.₂₅MoO₃ was varied from 0.10/1.0 to 0.80/1.0 (g/g). In a typical experiment, [Na(H₂O)₉]₀.₂₅MoO₃ (80 mg) was exfoliated by ultrasonication (GE 600W) at ambient temperature in 20 mL of DI. An aqueous solution of PAMAM (8-64 mg in 20 mL) was slowly added to the resulting suspension and stirred for 6 h on a hotplate with surface temperature 60 °C. The suspension temperatures were 0-15° less than the heating surface but were not directly measured. The flocculate was separated by centrifugation, washed with a copious amount of DI, and dried under vacuum at 80 °C for 24 h. Experimental variables evaluated included the PAMAM generation selected, the reactant ratios employed, and the temperature of the aqueous suspension during the 6 h reaction. The nanocomposites obtained are designated by the PAMAM generation and reactant ratio, thus G2-0.1 indicates the product obtained by reacting generation 2 PAMAM with [Na(H₂O)₉]₀.₂₅MoO₃ in a 0.10/1.0 g/g ratio. For reactions carried out on a heating
surface other than at 60 °C, the heating surface temperature (in °C) is also indicated in the label, for example G2-0.1-80.

A.3.3 CHARACTERIZATION

Products were characterized by powder X-ray diffraction (PXRD) using a Rigaku Miniflex II X-Ray diffractometer with Ni-filtered Cu Kα radiation (λ = 0.15418 nm) at a scan rate of 1° min⁻¹ between 3° and 30° 2θ. Thermogravimetric analyses were collected on a Shimadzu TGA-50 at 5 °C min⁻¹ under flowing Ar. Scanning electron micrographs (SEMs) were obtained using an FEI Quanta 600F FEG instrument. IR spectra were recorded using a Nicolet iS10 FT-IR spectrometer with Smart iTR ATR sampling accessory and Ge crystal from 4000-700 cm⁻¹.

A.4 RESULTS AND DISCUSSION

When PAMAM/MoO₃ nanocomposites were synthesized at room temperature, only multiple phase products were obtained. However, after reactions on the 60 °C heating surface, PXRD single phase products could also be obtained. Figure A1 shows the PXRD patterns of the nanocomposites prepared at 60 °C from different reactant ratios of G0 or G2 PAMAM and [Na(H₂O)₂]₀.₂₅MoO₃. The MoO₃ sheet thickness is 0.69 nm, and the repeat distance (d) increases to 0.97 nm in [Na(H₂O)₂]₀.₂₅MoO₃, so that the interlayer expansion (Δd) is 0.28 nm. This expansion is consistent with a Na⁺ plus water monolayer intercalate.¹⁴,²¹ The repeat distance, d, further increases to approximately 1.2 nm for all nanocomposites derived from G0 PAMAM and [Na(H₂O)₂]₀.₂₅MoO₃. This interlayer expansion (Δd) of ~ 0.5 nm relative to MoO₃ is much less than the diameter of solution-phase G0 PAMAM
(Table A1), and therefore indicates the formation of an intercalate gallery containing PAMAM in a highly flattened conformation. In the case of G2 PAMAM, G2-0.1 shows unreacted $[\text{Na(H}_2\text{O)}_2]_{0.25}\text{MoO}_3$ along with a phase similar to that described above ($\Delta d = 0.51$ nm). For other compositions, one or more of three phases with interlayer expansions of $\approx 0.5$, 0.7-0.8, or 1.4-1.5 nm are obtained. Table A2 shows the observed PXRD repeat distance and derived interlayer expansions at different reactant ratios of the nanocomposites. Samples G2-0.2, G2-0.3, and G2-0.4 show two of the expanded phases; at higher reactant ratios only a single phase with $\Delta d \approx 0.8$ nm is observed. The (010) reflection is observed in all PXRD patterns, along with higher-order reflections in some patterns, indicating that the MoO$_3$ sheets themselves remain intact and largely unchanged from the host structure. The phases with $\Delta d = 0.5$ and 0.7-0.8 nm are ascribed to PAMAM monolayers and bilayers between MoO$_3$ galleries, respectively (Figure A2), and these assignments are consistent with compositional data presented below and with previous reports (Table A3). PEO/MoO$_3$ shows a single phases with expansions of about 0.6 or 0.8 nm, corresponding to the formation of monolayers and bilayers, respectively.$^{14}$ LPEI/MoO$_3$ (ref. 18) and PANI/MoO$_3$ (ref. 19) both show a single phase with $\Delta d \approx 0.5$ nm, corresponding to monolayer formation.
Table A2. PXRD repeat distances (d) and derived interlayer expansions (Δd) of PAMAM/MoO$_3$ nanocomposites at different reactant ratios.

<table>
<thead>
<tr>
<th>Reactant ratio</th>
<th>G0</th>
<th>G2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d (nm)</td>
<td>Δd (nm)</td>
</tr>
<tr>
<td>0.1</td>
<td>1.20</td>
<td>0.51</td>
</tr>
<tr>
<td>0.2</td>
<td>1.21</td>
<td>0.52</td>
</tr>
<tr>
<td>0.3</td>
<td>1.20</td>
<td>0.51</td>
</tr>
<tr>
<td>0.4</td>
<td>1.20</td>
<td>0.51</td>
</tr>
<tr>
<td>0.5</td>
<td>1.20</td>
<td>0.51</td>
</tr>
<tr>
<td>0.6</td>
<td>1.19</td>
<td>0.50</td>
</tr>
<tr>
<td>0.7</td>
<td>1.20</td>
<td>0.51</td>
</tr>
<tr>
<td>0.8</td>
<td>1.18</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table A3. Comparison of PAMAM/MoO$_3$ with other polymer/MoO$_3$ nanocomposites.

<table>
<thead>
<tr>
<th>Intercalate</th>
<th>Organic mass %</th>
<th>Δd (nm)</th>
<th>Type</th>
<th>Packing fraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>10*</td>
<td>0.60</td>
<td>Monolayer</td>
<td>0.46*</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>21*</td>
<td>0.83</td>
<td>Bilayer</td>
<td>0.74*</td>
<td></td>
</tr>
<tr>
<td>LPEI</td>
<td>16</td>
<td>0.47</td>
<td>Monolayer</td>
<td>0.96*</td>
<td>18</td>
</tr>
<tr>
<td>PANI</td>
<td>17*</td>
<td>0.54</td>
<td>Monolayer</td>
<td>0.71*</td>
<td>19</td>
</tr>
<tr>
<td>G0 PAMAM</td>
<td>12-14</td>
<td>0.51</td>
<td>Monolayer</td>
<td>0.55-0.69</td>
<td>This work</td>
</tr>
<tr>
<td>G2 PAMAM</td>
<td>22-25</td>
<td>0.79</td>
<td>Bilayer</td>
<td>0.77-0.95</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from the compositional and structural data provided in the reference indicated.
Figure A1. PXRD patterns of $\text{[Na(H}_2\text{O)}_2\text{]}_{0.25}\text{MoO}_3$ and PAMAM/MoO$_3$ nanocomposites with G0 (a) or G2 (b) PAMAM at different reactant ratios.

Figure A2. Proposed schematic structure of obtained nanocomposites. (a) G0/MoO$_3$ monolayer and (b) G2/MoO$_3$ bilayer.
Figure A3. Interlayer expansions (Δd) obtained at different reactant ratios for PAMAM/MoO$_3$ nanocomposites using PAMAM G0 (Δ) and G2 (■).

Figure A4. Thermographs of [Na(H$_2$O)$_2$]$_{0.25}$MoO$_3$ (a), and the nanocomposites G0-0.5 (b) and G2-0.5 (c).
Figure A4 shows the thermographs of [Na(H₂O)₂]₀.₂₅MoO₃ and two representative nanocomposites. [Na(H₂O)₂]₀.₂₅MoO₃ shows a dehydration mass loss of about 5% below 150 °C, and is then thermally stable up to about 700 °C. Both nanocomposites also show a mass loss attributed to dehydration at low temperatures, and a larger mass loss from 200 to 400 °C attributed to the decomposition and volatilization of PAMAM. From these mass loss events, the compositions of PAMAM, H₂O, and Na₀.₂₅MoO₃ in each material were obtained. These compositions are reported in Table A4.

As can be seen in Figure A3 and Table A4, the nanocomposites where PXRD data indicate a single bilayer phase, G₂-0.5 to G₂-0.8, contain 22-25 mass % PAMAM. The G₀ PAMAM nancomposites, which all show a single monolayer phase, contain a PAMAM content of 12-14 mass %. This approximate 2:1 ratio of PAMAM content for the two phases supports their assignments as bilayer and monolayer intercalate structures as described above, and agrees with the organic content observed previously for polymer/MoO₃ nanocomposites (10-17% for monolayer and 21% for bilayer structures) as shown in Table A3. Compositions G₂-0.2 to 0.4 are mixed phase products containing about 22-28 mass % PAMAM.
Table A4. Compositional data for different reactant ratios using PAMAM G0 and G2.

<table>
<thead>
<tr>
<th>Reactant ratio</th>
<th>Mass %</th>
<th>Mole ratio, $r_i$</th>
<th>Packing fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$O</td>
<td>PAMAM</td>
<td>Na$_{0.25}$MoO$_3$</td>
</tr>
<tr>
<td>G0-0.1</td>
<td>3.0</td>
<td>11.5</td>
<td>85.1</td>
</tr>
<tr>
<td>G0-0.2</td>
<td>3.6</td>
<td>13.0</td>
<td>83.4</td>
</tr>
<tr>
<td>G0-0.4</td>
<td>3.6</td>
<td>12.1</td>
<td>84.3</td>
</tr>
<tr>
<td>G0-0.5</td>
<td>3.5</td>
<td>11.6</td>
<td>84.9</td>
</tr>
<tr>
<td>G0-0.6</td>
<td>2.7</td>
<td>12.3</td>
<td>84.9</td>
</tr>
<tr>
<td>G0-0.7</td>
<td>3.6</td>
<td>13.5</td>
<td>80.0</td>
</tr>
<tr>
<td>G0-0.8</td>
<td>2.9</td>
<td>12.6</td>
<td>84.5</td>
</tr>
<tr>
<td>G2-0.1</td>
<td>3.9</td>
<td>11.5</td>
<td>84.6</td>
</tr>
<tr>
<td>G2-0.2</td>
<td>4.5</td>
<td>21.8</td>
<td>73.7</td>
</tr>
<tr>
<td>G2-0.3</td>
<td>4.2</td>
<td>26.8</td>
<td>69.0</td>
</tr>
<tr>
<td>G2-0.4</td>
<td>5.1</td>
<td>28.0</td>
<td>66.9</td>
</tr>
<tr>
<td>G2-0.5</td>
<td>4.3</td>
<td>22.0</td>
<td>73.7</td>
</tr>
<tr>
<td>G2-0.6</td>
<td>3.4</td>
<td>24.2</td>
<td>72.4</td>
</tr>
<tr>
<td>G2-0.7</td>
<td>6.2</td>
<td>24.8</td>
<td>69.0</td>
</tr>
<tr>
<td>G2-0.8</td>
<td>4.3</td>
<td>22.6</td>
<td>73.1</td>
</tr>
</tbody>
</table>

Where interlayer expansions and phase compositions are known, the packing fraction of PAMAM in the interlayer galleries can be determined as follows (equation (1)):\textsuperscript{23}

\[
Packing\ fraction = \frac{Z r_i V_{vdw}}{a c \Delta d}\] (1)
where \( Z = 2 \) (the number of MoO\(_3\) units per half unit cell), \( r_i \) = mole ratio of PAMAM to Na\(_{0.25}\)MoO\(_3\), \( V_{vdw} \) is the van der Waals volume of PAMAM according to Ref. 24, and \( a \) and \( c \) are MoO\(_3\) unit cell parameters: \( a = 0.396 \) nm, \( c = 0.370 \) nm.\(^{21}\) Packing fractions therefore represent the relative filling by guest intercalate of available volume in the expanded galleries. For comparison, \( V_{vdw} \) and packing fractions of PEO, LPEI and PANI in MoO\(_3\) were also estimated by a literature method.\(^{23}\) As shown in Table A3, packing fractions obtained for PEO/MoO\(_3\), LPEI/MoO\(_3\), PANI/MoO\(_3\) monolayers and the PEO/MoO\(_3\) bilayer are 0.46, 0.96, 0.71 and 0.74 respectively. The packing fraction calculated for all the compositions studied was in the range of 0.77-0.95 for G2 and 0.55-0.69 for G0. The present results demonstrate that starting compositions have little or no effect on the product packing fraction, and that G2 PAMAM packs more densely in the intercalate galleries than does G0 PAMAM.

The effect of reaction temperature was examined by preparing a series of G2-0.3 nanocomposites under different heating conditions. At 20 °C, a mix of [Na(H\(_2\)O)\(_2\)]\(_{0.25}\)MoO\(_3\) and a bilayer phase are obtained with \( \Delta d = 0.72 \) nm (Figure A5). At 40 °C, a single-phase product with \( \Delta d = 1.44 \) nm was obtained. This phase is also obtained as part of the mixed-phase product at 60 °C with G2-0.2, G2-0.3, and G2-0.4. Above 40 °C, there is a gradual decrease in the \( \Delta d = 1.44 \) nm phase and increase in a bilayer PAMAM phase (\( \Delta d = 0.72 \) nm) similar to that obtained for G2-0.3 at 60 °C. At the highest temperatures, the packing fractions (Table A5) are greater than 1, indicating that non-intercalated PAMAM is present in the samples.
Calculations of packing fractions indicate that the very highly expanded phase must be stage 1 (with all galleries occupied). Unusually higher expansion (\(d = 3.8\) nm, \(\Delta d = 3.1\) nm) has been reported previously for PVP/Li\(_{0.25}\)MoO\(_3\) and PAM/Li\(_{0.25}\)MoO\(_3\) nanocomposites.\(^{20}\) The actual PAMAM arrangement or conformational changes to form these very large galleries has yet to be established.

Table A5. Effect of temperature on the structure of G2-0.3 nanocomposites.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Mass %</th>
<th>Mole ratio, (r_i)</th>
<th>(d) (nm)</th>
<th>(\Delta d) (nm)</th>
<th>Packing Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H(_2)O</td>
<td>PAMAM</td>
<td>Na(_{0.25})MoO(_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
<td>14.1</td>
<td>82.3</td>
<td>0.008</td>
<td>0.97; 1.43</td>
</tr>
<tr>
<td>40</td>
<td>3.7</td>
<td>24.2</td>
<td>72.1</td>
<td>0.015</td>
<td>2.13</td>
</tr>
<tr>
<td>60</td>
<td>4.1</td>
<td>26.8</td>
<td>69.1</td>
<td>0.018</td>
<td>1.32; 2.12</td>
</tr>
<tr>
<td>80</td>
<td>5.5</td>
<td>30.0</td>
<td>64.5</td>
<td>0.021</td>
<td>1.12; 1.40</td>
</tr>
<tr>
<td>100</td>
<td>4.9</td>
<td>30.6</td>
<td>64.5</td>
<td>0.022</td>
<td>1.42</td>
</tr>
<tr>
<td>120</td>
<td>5.0</td>
<td>26.4</td>
<td>68.6</td>
<td>0.018</td>
<td>1.44</td>
</tr>
</tbody>
</table>
Figure A5. PXRD patterns showing the effect of temperature on G2 PAMAM/MoO$_3$ nanocomposites.

Figure A6. SEM micrographs of (a) MoO$_3$, (b) Na$_x$MoO$_3$ and (c) the nanocomposite G2-0.8.
SEM images of the starting materials, MoO₃, [Na(H₂O)₂]₀.₂₅MoO₃ and the PAMAM/MoO₃ nanocomposite (G2-0.8) are presented in Figure A6. Particles clearly retain their macroscopic features but show exfoliation and fragmentation during the nanocomposite formation.

Figure A7. IR spectra of G2 PAMAM (a), nanocomposite G2-0.7 (b) and MoO₃ (c).

The IR spectra of PAMAM and its nanocomposites are presented in Figure A7. The amidic groups (HNC=O) groups present on the dendrimer give absorption bands at 1623-35 cm⁻¹ (amide I, mainly C=O stretching) and 1551-67 cm⁻¹ (amide II, combination of N-H in-plane bending and C-N stretching).²⁵ In the G2-0.7 nanocomposite, which is representative, the amide I band has shifted to a slightly higher value of 1655 cm⁻¹ while the amide II band shifted to a lower value of 1548 cm⁻¹. The positions of the amide bands arising from the intercalate are close to those of native PAMAM as has been observed previously for a PVP/MoO₃ nanocomposite.²⁰ A band at 3086 cm⁻¹ corresponding to N-H amide stretching mode was also present for the nanocomposites.²⁶ The spectrum for MoO₃ shows bands at
966 and 816 cm\(^{-1}\), corresponding to M=O and M-O stretching vibrations, respectively,\(^{17}\) which shift to 974, 938 and 894 cm\(^{-1}\) in the nanocomposites. The shift to higher wavenumber absorbances suggests that the anionic MoO\(_3\) layers in the nanocomposite are less reduced than in Na\(_{0.25}\)MoO\(_3\).\(^{20}\)

### A.5 CONCLUSION

This study indicates that PAMAM dendrimers can be intercalated into MoO\(_3\) as monolayers or bilayers. The intercalate arrangement is strongly dependent on the PAMAM generation. Bilayers of G2 PAMAM can be formed in MoO\(_3\) gallery even at low PAMAM composition. This is a new observation, which is contrary to the observation with other polymer guests that bilayers are formed only at higher compositions.

Reaction temperature was observed to affect the structure of the obtained nanocomposites. Pure bilayers with different levels of expansion were obtained at 40 and 120 °C, whereas mixed phases were obtained at 60 °C.

### A.6 REFERENCES


APPENDIX B

SUPPLEMENTARY DATA: SYNTHESIS AND CHARACTERIZATION OF LOW-GENERATION POLYAMIDOAMINE (PAMAM) DENDRIMER – SODIUM MONTMORILLONITE (Na-MMT) CLAY NANOCOMPOSITES

Amila U. Liyanage, Esther U. Ikhuoria, a Adeniyi A. Adenuga,
Vincent T. Remcho, and Michael M. Lerner

Department of Chemistry
Oregon State University
Corvallis, OR 97331-4003, USA

a Fulbright visiting scholar, Oregon State University, 2011/2012. Permanent address: Department of Chemistry, University of Benin, Benin City, Nigeria.

B.1 SUPPLEMENTARY DATA

Figure B1. PXRD data for (a) G(0.0), (b) G(1.0), and (c) G(2.0)/Na-MMT nanocomposites synthesized at room temperature and 60 °C. Reactant ratios were 0.3 g/g PAMAM/Na-MMT.

Figure B2. FTIR spectrum of dehydrated Na-MMT.
Figure B3. FTIR spectrum of a 0.4 PAMAM G(2.0)/Na-MMT nanocomposite. The 2850-3500 cm\(^{-1}\) region is intensified x10 for clarity.