Development of High Energy Polymers Systems - 12th Monthly Status Report

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DEVELOPMENT OF HIGH ENERGY POLYMERIC SYSTEMS

TWELFTH MONTHLY STATUS REPORT

PERIOD ENDING 69 DEC 31

Air Force Contract F08635-69-C-0121

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A final series of attempts were made to prepare polyesters of respectable molecular weights ($M_n = 2000+$) from the following materials:

- **DNPCl**: Dinitropimelic acid, diacid chloride of
- **AFN-25Cl**: Dinitrofluoroethoxyfumaric acid, diacid chloride of
- **DINOL**: 2,2,8,8-Tetranitro-4,6-dioxa-1,9-nonane diol
- **REX-18**: 3-(Dinitrofluoroethoxy)-1,2 propane diol

Results of the aforesaid attempts are tabulated below. In all cases, the mole ratio of diol to acid chloride was 6/5, aiming for hydroxyl termination.

<table>
<thead>
<tr>
<th>Acid Chloride</th>
<th>Diol</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFN-25Cl</td>
<td>DINOL</td>
<td>Refluxing heptane, 60 hrs.</td>
<td>$M_n = 900$</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>REX-18</td>
<td>Same as above</td>
<td>Major fraction ($MeCl_2$ soluble) $M_n = 1250$; Minor fraction ($MeCl_2$ insoluble) $M_n = 1500$</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>DINOL</td>
<td>$AlCl_3$ catalysis in methylene chloride</td>
<td>Primarily recovery of starting materials.</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>REX-18</td>
<td>Same as above</td>
<td>Same as above</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>DINOL</td>
<td>$K_2CO_3$ in refluxing tetrahydrofuran</td>
<td>Degradation: all products soluble in $H_2O$.</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>REX-18</td>
<td>Same as above</td>
<td>Same as above</td>
</tr>
<tr>
<td>DNPCl</td>
<td>REX-18</td>
<td>Refluxing heptane, 9 days</td>
<td>$M_n = 1350$, very viscous, gummy mass.</td>
</tr>
<tr>
<td>AFN-25Cl</td>
<td>REX-18</td>
<td>Same as above</td>
<td>$M_n = 1450$, hard, almost a glass.</td>
</tr>
</tbody>
</table>
In the previous Status Report, contradictory results (quantitative yield, but low molecular weight) were noted for the DMPCl/REX-18 combination after reaction in the presence of K2CO3. Solvent fractionation of this material subsequently showed that unreacted diol was present, accounting for the apparent anomaly. Removal of 10% of the original weight as REX-18 starting material only increased the $\bar{M}_n$ of the residue from 700 to 800, so fractionation was not pursued further.

Reviewing this and prior months' results allow us to reach the following conclusions:

1. The classical techniques do not readily yield high molecular weight polyesters with these materials; the simplest technique, a melt polymerization wherein HCl is thermally eliminated under refluxing heptane, gave the best results.

2. The best (most reactive, highest molecular weight) combination is AFN-25Cl/REX-18 which is a little surprising, since both the diacid and the diol are asymmetrical. However, this best combination only polymerized to the extent of about 6 units (3 each of diacid and diol) on the average.

3. At molecular weights of 2000+, these combinations would probably yield solid prepolymer.

This program is now complete. The final report is being drafted.