Volume Expansion Polymerizations

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Outline

- Background
- Dilatometry
- Expanding monomers
  - Different monomers
  - Temperature dependence
- Possible Explanation
- Is there proof...?
- Applications
- Conclusion
“Normal” Behavior

- Polymerization leads to better organization of molecules
- Organization packs monomer closer together
- Result is a higher density polymer than monomer

Salmone, Polymeric Materials Encyclopedia p.7550
Expansion

- Why is this counter intuitive?
- Solids usually more dense than liquids:
  - Aluminum ($\rho_s=2.548 \text{ g/cm}^3 \rho_L=2.368 \text{ g/cm}^3$)
  - Copper ($\rho_s=8.350 \text{ g/cm}^3 \rho_L=7.937 \text{ g/cm}^3$)
- Polymers more dense than monomers
  - Ethylene - 66% Shrinkage
  - Styrene – 14.5% Shrinkage
- BUT everyone has seen one thing that does expand on freezing
ICE!

http://campaignprojects.wordpress.com/2008/12/22/back-soon/

Dilatometry

Definition: The measurement and study of dimensional changes in polymers as a function of temperature, fluid absorption, mechanical stress or chemical reaction.

Applications
- % Crystalline (Presented by Brandon)
- Extent of reaction
- Thermal expansion
Dilatometry – Thermal Devices

- Thermal expansion most common thing to measure by dilatometry
- TMA: Thermo Mechanical Analysis
  - Older technique
  - Only good for temperature
- Bulb dilatometer
  - Uncommon
  - Uses mercury

Dilatometry – Expansion Devices

- Measure capillary fluid height as a function of time
- Track volume expansion of sample
- In ‘normal’ polymerizations the fluid level goes down (increased density)
- Can also be used if fluid level goes up due to polymer expansion

Stuart, Polymer Analysis p. 91
Polymers That Supposedly Expand

- Early work done by Bailey (Univ. of Maryland) and Endo (Tokyo Inst. of Tech.)
- First published as “Monomers that Expand on Polymerization” (1976)
- First materials were theorized to do this were:
  - Spiro ortho esters
  - Spiro ortho carbonates
- Most volume changes were very small as measured
  - (-0.1%-0.5%)
  - Measured by “density gradient tube method”

William J. Bailey

Spiro-Ortho Carbonates (SOCs)

- **General Scheme:**

- Catalyzed by Lewis Acids
- Double ring opening polymerization
- Sometimes either cationically or anionically
Density Results

- These are some examples of monomers that studies have shown expand on polymerization.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Volume Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>1, 4, 6, 10, 12, 15, 17, 19-Octaoxatríspiro [4.2.2.4.2.2] nonane (m.p. 215°C)</td>
<td>+3.0 @ 145°C</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>2, 3, 7, 8-Di(9, 10-anthrylene) - 1, 4, 6, 9-tetraoxaspiro [4.4] nonane</td>
<td>+7.6 @ 60°C +17.9 @ 190°C</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>Spiro-7, 9-dioxacyclo [4.3.0] nonane-8, 2'-1' - oxacyclo-pentane (b.p. 57°C/0.01 mm)</td>
<td>+3.0 @ 25°C +1.3 @ 100°C</td>
</tr>
</tbody>
</table>

Sadhir, and Luck, Expanding Monomers (various pages)
Density of both polymer and monomer are temperature dependent.

Temperature dependence is different function.

This is data by Endo on 8,10,19,20-Tetraoxatrispiro-[5.2.2.5.2.2]heneicosane.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Monomer Density (g/cm³)</th>
<th>Polymer Density (g/cm³)</th>
<th>Percent Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.150</td>
<td>1.110</td>
<td>3.48</td>
</tr>
<tr>
<td>50</td>
<td>1.145</td>
<td>1.070</td>
<td>6.55</td>
</tr>
<tr>
<td>78</td>
<td>1.144</td>
<td>1.010</td>
<td>11.71</td>
</tr>
<tr>
<td>84</td>
<td>1.011</td>
<td>0.991</td>
<td>1.98</td>
</tr>
<tr>
<td>100</td>
<td>0.997</td>
<td>0.975</td>
<td>2.21</td>
</tr>
<tr>
<td>120</td>
<td>0.975</td>
<td>0.940</td>
<td>3.59</td>
</tr>
</tbody>
</table>

Endo et al, Makrom. Chem. 1976
Other Examples of Potential Volume Expansion

- Cyclic sulfates:
- Cyclic carbonates:
- Bicyclo-ortho esters:
- Spyro-ortho esters:

Salmone, Polymeric Materials Encyclopedia p.7551
An Explanation – Bond Distances

- When molecules (monomers) are in solution they are kept apart by van der Walls forces
- Polymers, by definition are held together by covalent bonds
- Van der Waals distance always bigger than covalent distance

*FIGURE 2. Mechanism of volume change on polymerization of vinyl, monocyclic, and bicyclic monomers.*

Salmone, *Polymeric Materials Encyclopedia* p.7551
Polymerization - General

- A van der Waals bond (between monomers) is replaced by a covalent bond
- Covalent < van der Waals => Overall Shrinkage

Polystyrene
No bonds broken, new bond formed between each monomer
Note: For condensation polymerization net effect is same
Polymerization – Single Ring Opening

- Normally one van der Waals bond is replaced with one covalent bond.
- In single ring opening one bond is broken and a van der Waals bond shifts to a covalent bond.
  - One covalent broken in opening ring
  - van der Waals between monomers is replaced by covalent bond
- Net result is still shrinkage
  - New covalent bond makes whole network more dense

Bond broken

Poly(ethylene oxide)
Overall shrinkage

Bond formed
Polymerization – Double Ring Opening

- For every bond involving a shift from van der Waals to covalent, two covalent bonds are broken.
- Net result is that the reduction in density is counteracted, leading to minimal, or no shrinkage, or potentially expansion.
Is There Proof?

- It appears so however…
  - Most changes are very small
  - Dilatometry isn’t always very accurate
  - Sometimes minor structure changes made the difference between shrinkage and expansion

- Explanations not always satisfactory
  - Near van der Waals distances are bigger than covalent distances
  - Why does is breaking two bonds enough?
  - Why does temperature dependence vary?
  - Explanation could be as simple as ring strain release

- So dispute continues…
Applications

- Expansion materials: Stuff that fills cracks
  - Precision moldings
  - Dental fillings
  - Rock cracking materials

- Zero expansion materials: Stuff that stays the same
  - Strain-free composites
  - Potting resins
  - Binders for solid propellants
Conclusion

- “Normal” monomers shrink on polymerization
- Dilatometry is an effective tool for monitoring density changes
  - Also good for thermal changes
  - Can be used for extent of reaction in most systems
- Double-ring opening polymerizations seem to show expansion on polymerization
- An explanation for this phenomenon might be bond-distances
- Still dispute of explanation and whether or not this phenomenon really happens
References

- Stuart, Barbara. *Polymer Analysis*. 2002
Thank you!

Any questions...?