Convex Solubility Parameters for Polymers
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Introduction

- Solution: solute dissolved in solvent
- Based on the concept of “like dissolves like” - e.g., polar solvents dissolve polar solutes
- Additive combinations of good solvents should also be good solvents
- Hildebrand model: solubility is based on thermodynamics
- Hansen model: solubility is based on intermolecular forces

Hansen Solubility Parameters

- Difference between solubility parameters of solvent and solute give “solubility distance” $R_d$:
  \[ R_d = 4(\delta_1 - \delta_d)^2 + (\delta_2 - \delta_d)^2 + (\delta_3 - \delta_d)^2 \]
- HSP taken to be center of sphere
- Better solvents are closer to center
- Issues:
  - Spheres can be largely extrapolated - overestimates solubility region
  - Portions of sphere outside physical parameter range
  - Hydrogen Bonding is a sort of “catch all” for every force not listed above
  - Good solvents may lie outside sphere and poor solvents may be inside sphere

New Approach: Convex Solubility Parameters

- Convex hull: smallest region in space that contains a given set of points and all line segments between those points
- Solubility region of polymer defined by the convex hull $Q$ of all good solvents $x_1, x_2, \ldots, x_t$

  \[ Q = \left\{ x \left| x = \sum_{i=1}^{t} \lambda_i x_i, \sum_{i=1}^{t} \lambda_i = 1, \lambda_i \geq 0, i = 1, \ldots, t \right. \right\} \]

- Several candidate “centers” of the hull could serve as the Convex Solubility Parameter (CSP) of the polymer
- Determining if a solvent is inside the hull can be done by solving a linear feasibility problem:
  \[ \begin{align*}
  \text{Find } q, \text{ such that } q = \sum_{i=1}^{t} \lambda_i x_i, \sum_{i=1}^{t} \lambda_i = 1, \lambda_i \geq 0, i = 1, \ldots, t \\
  \end{align*} \]

Methods for Computing the Convex Solubility Parameter

Method 1: Center of mass of the solubility region, treating the surface of the region with uniform density as an empty shell

Method 2: Center of mass of the solubility region, treating the region as a solid with uniform density

Method 3: Mean coordinates of all good solvents that lie on the boundary of the solubility region

Method 4: Mean coordinates of all good solvents on the boundary and within the solubility region

Method 5: Center of the largest sphere completely contained within the solubility region (known as the Chebyshev center)

Method 6: Midpoint of the range of each of the good solvents

Solubility region generated using convex hull of coordinates of good solvents in parameter space. A reasonable choice for Convex Solubility Parameter is the center of mass of the hull when treated as a solid of uniform density. These results are the product of an independent study course in Spring 2015 and have been submitted to the Journal of Polymer Science Part B: Polymer Physics.

References


Acknowledgements

The authors acknowledge the financial support of the College of Charleston Office of Undergraduate Research and Creative Activities (MAYA Grant No. 62062400) and the Howard Hughes Medical Institute, Pre-College and Undergraduate Science Education Program (HHMI Grant No. 52007537).

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