The Specific Refractive Index Increments for POSS Polymers in Solution

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15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:
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The Specific Refractive Index Increments for POSS Polymers in Solution.

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Best Available Copy  Distribution A: Approved for public release, distribution unlimited
Goal: Develop High Performance Polymers that REDEFINE material properties
POSS – Polyhedral Oligomeric Silsesquioxanes

- Hybrid Plastics bridge the differences between ceramics and polymers

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Introduction to POSS

- Retain optical clarity
- Increased gas permeability

- Fire Retardancy
- Mechanicals
- Increased HDT

- Viscosity Reduction
- Decreased Dielectric

- Drug delivery
- Biological scaffolds

- Catalysis supports
- Monomers
- Crosslinkers

- Silane replacements

- Corrosion resistant coatings

- Lubricants
- Compatibilizers

As Additives
As Reagents
As Surface Modifiers

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Anatomy of a POSS Nanostructure

R-Groups
- Cyclohexyl
- Phenyl
- Cyclopentyl
- Ethyl
- isoButyl

Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

May possess one or more functional groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

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POSS Polymer Incorporation

Cross-linker  Pendant Polymer  Bead Polymer

Blending

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POSS Styrene Monomer Synthesis

- High-yield syntheses
- Phenyl derivative requires inverse addition


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POSS Styrene Copolymer Synthesis

- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble

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IR = Aromatic Integral
   Aliphatic Integral

Mole fraction POSS-styrene
   = (5 - 3*IR)
   (63*IR + 1)

R = cyclohexyl

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• The Specific Refractive Index Increment, \( \frac{dn}{dc} = \frac{(n-n_0)}{c} \), is the change in RI with change in concentration.

• It is a constant value for a dilute polymer in solution at constant temperature, pressure and wavelength.

• It is useful for determining the Mw of a polymer by light scattering (GPC).

• For copolymers composed of two monomers, the \( \frac{dn}{dc} \) is an additive function of the individual weight fractions.
Why Find the \( \frac{dn}{dc} \) Value?

- To accurately determine the weight average molecular weights of various POSS-polymers.

- To generically parameterize each POSS type (\( R = \) cyclohexyl, isobutyl, phenyl etc.) in order to predict POSS-polymers \( \frac{dn}{dc} \) values.

- To provide a quick and accurate method to determine POSS \% incorporation in any polymer system.
R vs. Concentration of BuPOSS-PS copolymer

wt.% POSS-Styrene

Slope = dn/dc

0 wt.%

Y = 0.1428x + 1.4435
R² = 0.9958

6 wt.%

Y = 0.1327x + 1.4436
R² = 0.9929

15 wt.%

Y = 0.1159x + 1.4437
R² = 0.9976

30 wt.%

Y = 0.0954x + 1.4439
R² = 0.9996

50 wt.%

Y = 0.0636x + 1.444
R² = 0.9962

75 wt.%

Y = 0.0402x + 1.444
R² = 0.9976

100 wt.%

Y = 0.0000x + 1.444
R² = 1.0000

R = isobutyl

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RI vs. Concentration of CyPOSS-PS copolymer

wt.% POSS-Styrene

Slope = dn/dc

0 wt.%

Y = 0.1386x + 1.4437
R² = 0.9975

6 wt.%

Y = 0.1488x + 1.4437
R² = 0.9949

15 wt.%

Y = 0.1352x + 1.4439
R² = 0.9985

30 wt.%

Y = 0.1270x + 1.4438
R² = 0.9995

50 wt.%

Y = 0.1104x + 1.4434
R² = 0.9989

75 wt.%

Y = 0.0894x + 1.444
R² = 0.9998

100 wt.%

Y = 0.0676x + 1.4442
R² = 0.9959

g/ml of CHCl₃

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Clearly, dn/dc is linear with respect to weight % POSS not mole % POSS; changes in refractive index are proportional to the volume occupied by the polymeric components. A typical POSS monomer is about 10X more massive than a typical organic monomer.

Note that the dn/dc value decreases with increasing POSS incorporation.
• There is a linear relationship between weight % POSS and the dn/dc of a styrene copolymer.

• To graph a dn/dc / weight % POSS relationship for any new POSS polymer it is reasonable to just measure the dn/dc values of the 0 and 100 % POSS polymer.

• We intend to prove this concept for other glassy (Acrylics) and rubbery (Norbornenes) POSS copolymers.
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