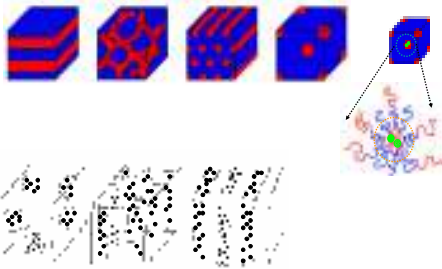


Block Copolymer Nanostructures



- Blocks of sequences of repeat units of one homopolymer **chemically linked** to blocks of another homopolymer sequence.
- **Microphase separation** due to block incompatibility
- **Templates** for synthesis of **metal oxide nanoparticles**
- Nanoparticles selectively dispersed within one of the block domains but excluded by the other.

Motivation



- Develop high dielectric constant (K) polymer-based dielectric for capacitor applications such as embedded capacitors for microelectromechanical systems and supercapacitors as the next generation of energy storage system.
- Polymeric materials: weight and space efficient, shape-flexible, cost effectiveness with good processibility.



Block Copolymer Matrix

---Norbornene/norbornene dicarboxylic acid (NOR/NORCOOH) diblock copolymer



---Sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (PSS/PEB/PSS) triblock copolymer



Increase K of Polymer Matrix

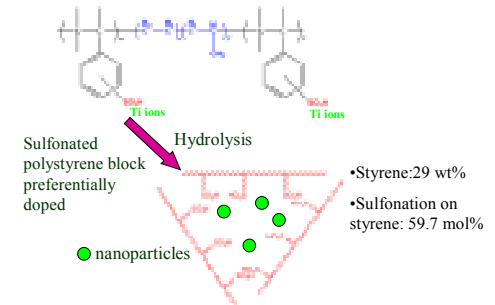
- $K_{\text{composite}} = \text{Function}(K_{\text{polymer}}, K_{\text{filler}}, \text{Filler volume fraction})$
- K_{filler} and filler volume fraction increase $\rightarrow K_{\text{composite}}$ increases



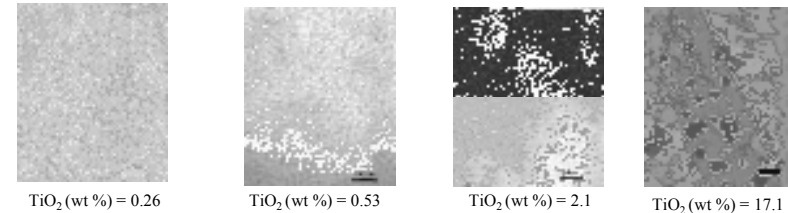
Dielectric constant of materials directly proportional to their polarizability

- Atomic (ionic) polarization
- Orientation polarization
- Interface polarization

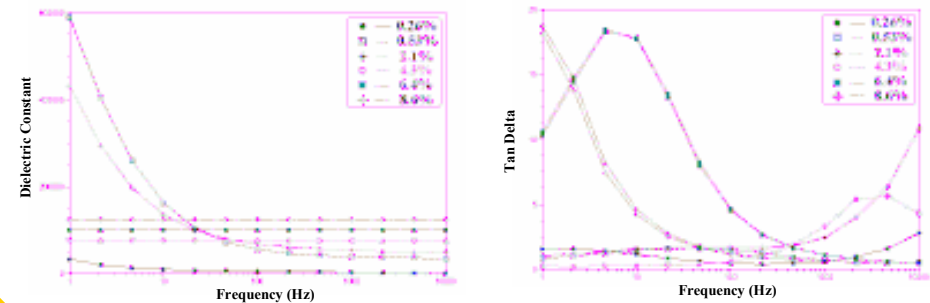
Templating TiO₂ Nanoparticles within the Triblock Matrix



Effect of Dopant Concentration

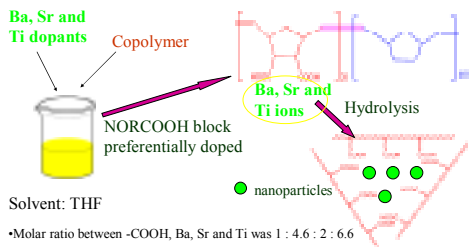


Nanoparticles were templated within the block copolymer pattern. High dopant concentrations resulted in non-uniformly dispersed particle clusters.



The permittivity is high, however, the loss is also high due to the SO₃H groups.

Templating Nanoparticles within the Diblock Matrix

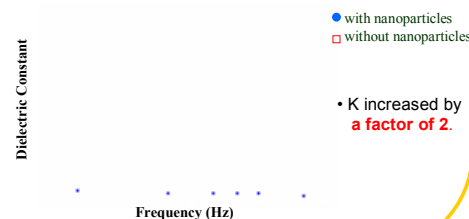


XPS Investigation

- From Ba 3d_{5/2}, Ti 2p_{3/2} and O 1s \rightarrow BaTiO₃ was formed.
- From Sr 3d_{5/2} and O 1s \rightarrow other metal oxides were formed.

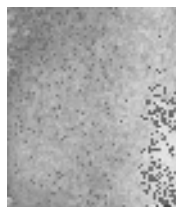
	Ba3d _{5/2}	Ti2p _{3/2}	Sr3d _{5/2}	O1s	
This work	780.2	458.5	134.3	530.1	BaTiO ₃
Literature (BaTiO ₃)	779.65 [#]	458.3 [#]	*	529-530 [#]	other metal oxides
Literature (SrTiO ₃)	*	458.1%	132.7%	529.2%	

Dielectric Analysis



Morphology of Copolymer with Nanoparticles

- Nanoparticles were formed within the matrix



Conclusions

- The diblock copolymers acted as nanotemplates to form well-dispersed nanoparticles within the polymer matrix.
- NOR/NORCOOH composites: electrical property tests showed that the nanoparticles within the copolymer significantly increased the dielectric constant of the nanocomposite.
- PSS/PEB/PSS composites: the polarizability from the SO₃H groups enhanced the dielectric constant, however, these groups also caused higher dielectric loss.

Acknowledgements

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