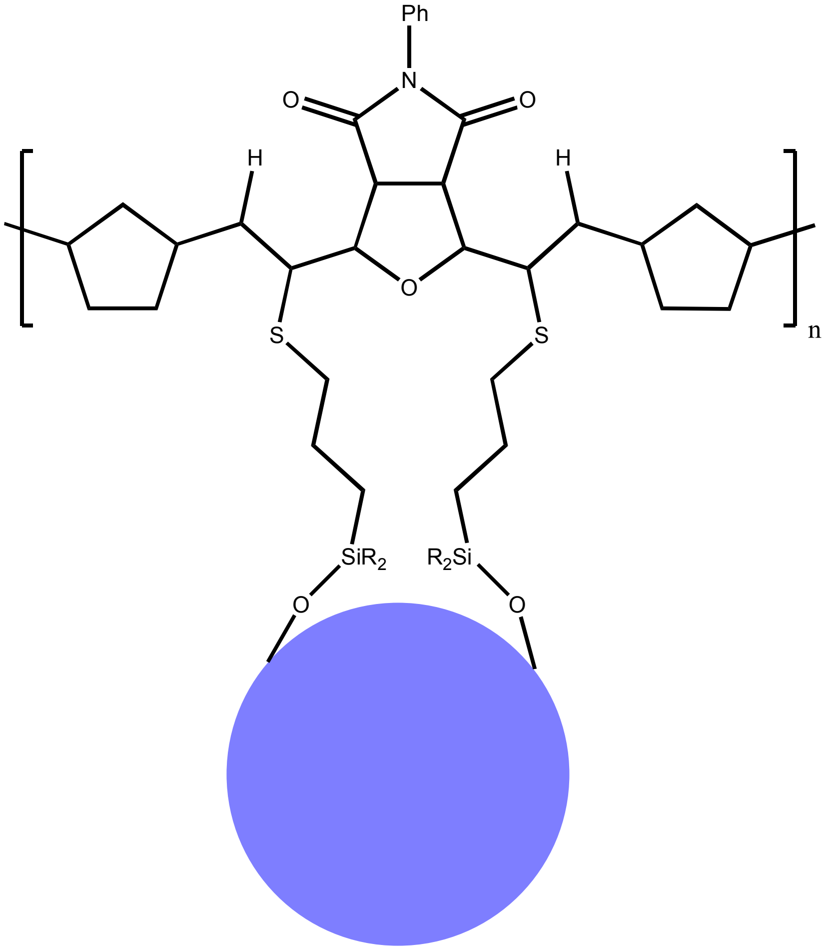
SAND2010-6030P

Functionalized Polymers for Dielectric Materials

Leah N. Appelhans

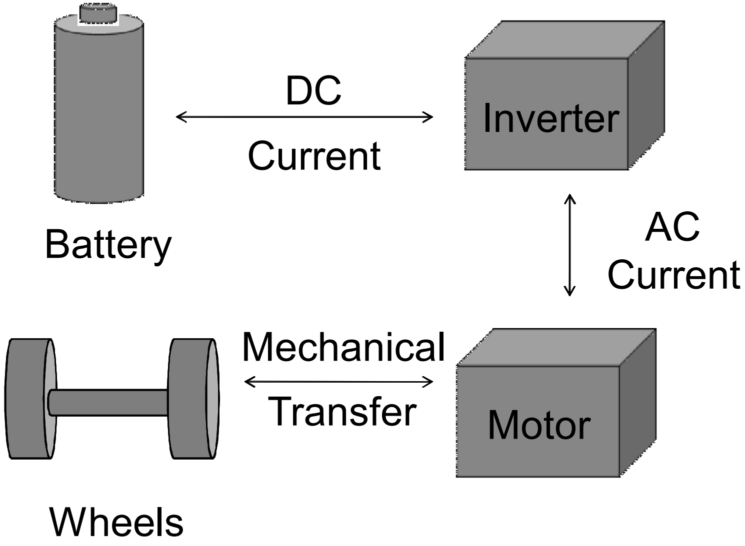


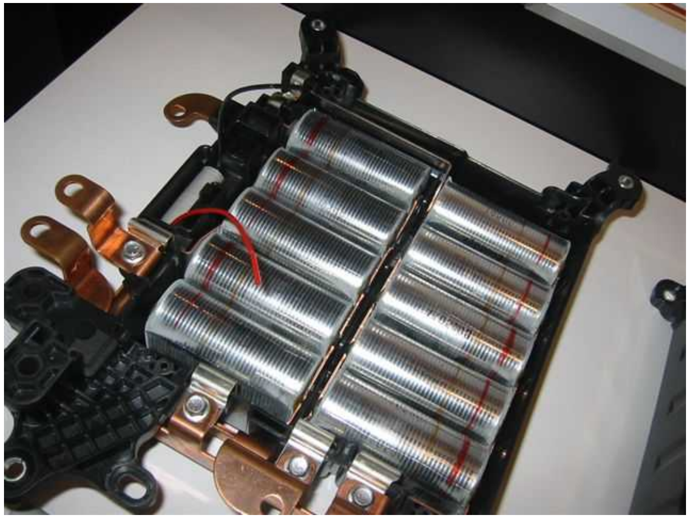
High Energy Density Capacitors

- electric trains
- solar, wind and water power generation systems
- hybrid and electric vehicles
- electric planes/ships
- pulsed-power applications

New dielectric materials needed with improved:

- energy density *increase*
- breakdown strength *increase*
- dissipation factor *decrease*
- dielectric permittivity *increase*
- cost *decrease*
- operating range (T) *increase*





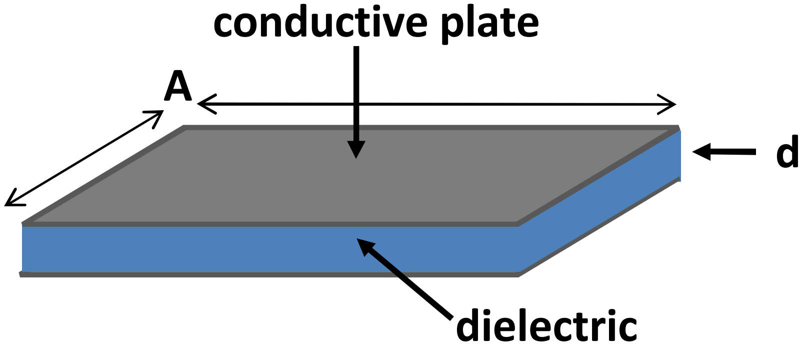
Bank of 138 µF Polymer Dielectric Film Capacitors in 2004 Prius Inverter provide >1000 µF

Parallel Plate Capacitors

capacitance: *The amount of charge stored at a given potential difference* $C = Q/V$.

breakdown strength: *The electric field strength at which the failure of insulating properties occurs* $(E_b = V_b/d)$

dissipation factor: *the rate at which stored charge dissipates in a dielectric material due to electron conduction and dipole relaxation*



$$C = \varepsilon_0 \varepsilon_r A/d$$

energy density: *the energy stored per unit volume* $U_e = \frac{1}{2}\varepsilon_r \varepsilon_o E^2$

The maximum energy density is $U_{e,max} = \frac{1}{2}\varepsilon_r \varepsilon_o E_b^2$ *where* E_b *is the breakdown field strength.*

Polymer Dielectric Materials

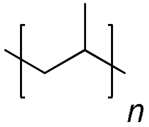
Advantages of Polymer Dielectrics

- high breakdown voltages
- soft failure
- cost
- flexibility
- ease of processing
- control of properties

but…

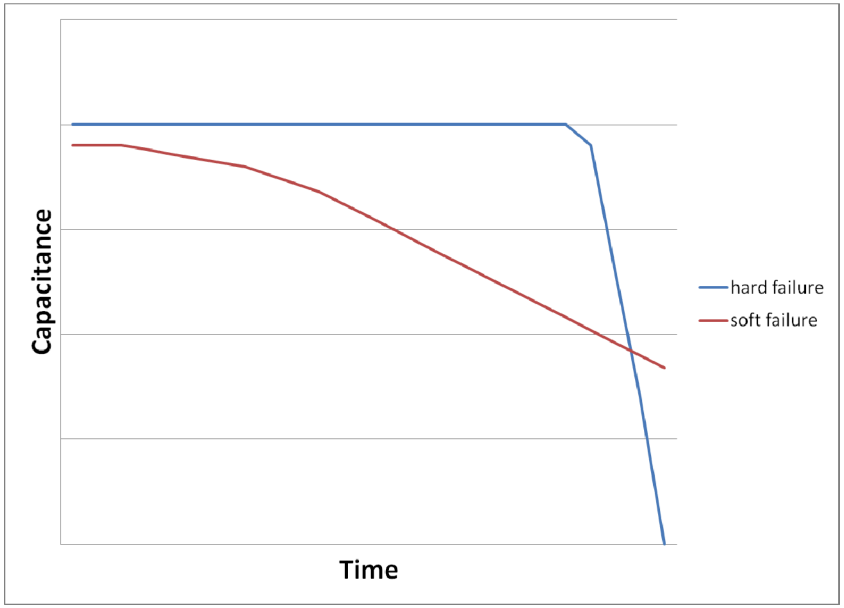
- low dielectric permittivities
- low energy densities
- low T ranges

Biaxially Oriented Poly(propylene) (**BOPP**)
energy density 1-1.5 J/cm^3
max temperature 105 °C



Nur noch eine rauchende Ruine blieb gestern von dieser Windkraftanlage in Tüttendorf bei Rendsburg übrig. Durch Blitzschlag hatte sich die Gondel in 60 Meter Höhe entzündet und brannte aus. Foto: dpa

J. Bond, ECI, High Energy and Temperature Capacitors for Advanced Power Systems, 2007, Penn State University



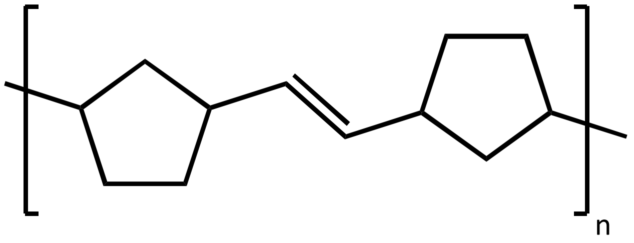
Increasing Energy Density

$$U_e = \tfrac{1}{2}\,\varepsilon_r \varepsilon_o E^2$$

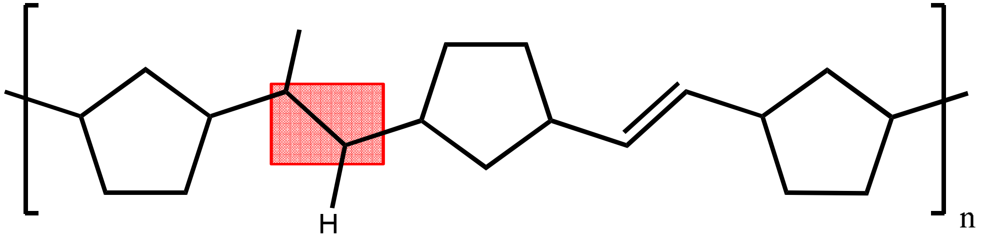
-Increase breakdown strength

- remove reactive functional groups

poly(norbornene)



functionalized poly(norbornene)



thermoset

thermoplastic

n

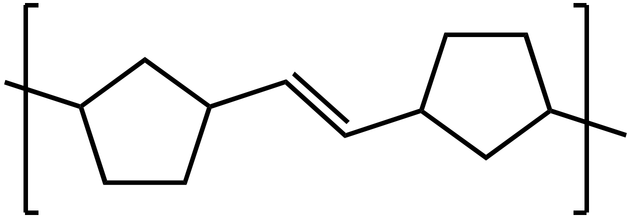
Increasing Energy Density

$$U_e = \frac{1}{2} \varepsilon_r \varepsilon_o E^2$$

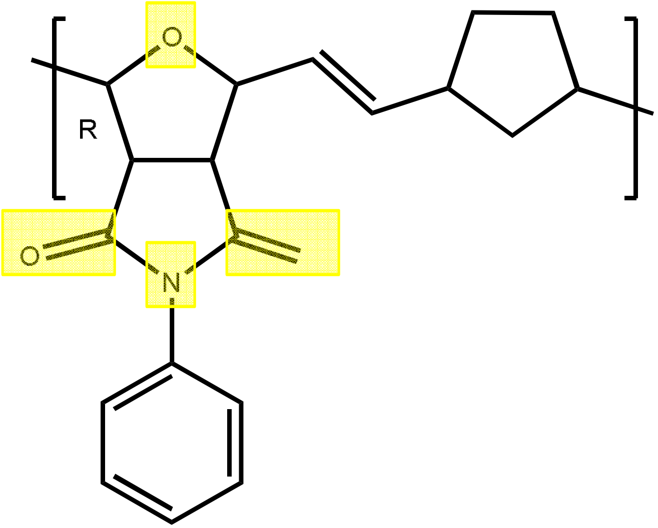
-**Increase relative permittivity**

- add polarizability

poly(norbornene)



poly(norbornene)-co-poly(PhONDI)

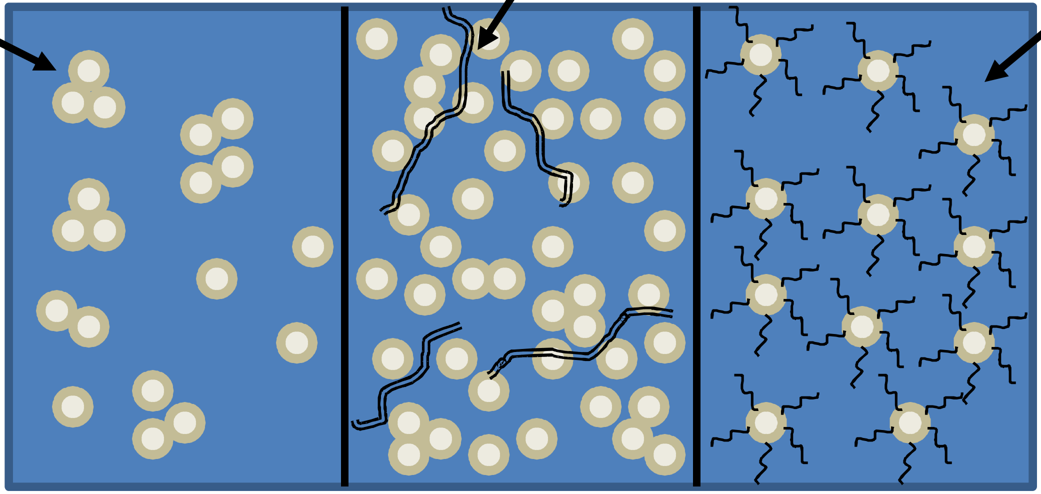


Increasing Energy Density: Composites

$$U_e = \tfrac{1}{2}\,\varepsilon_r \varepsilon_o E^2$$

-**Increase relative permittivity**

- composites of high κ inorganic dielectric materials and polymers can significantly increase permittivity relative to polymers alone



unfunctionalized particles can agglomerate

high loadings cause poor film quality

functionalization can reduce agglomeration and improve film quality

New Polymer Dielectric Materials

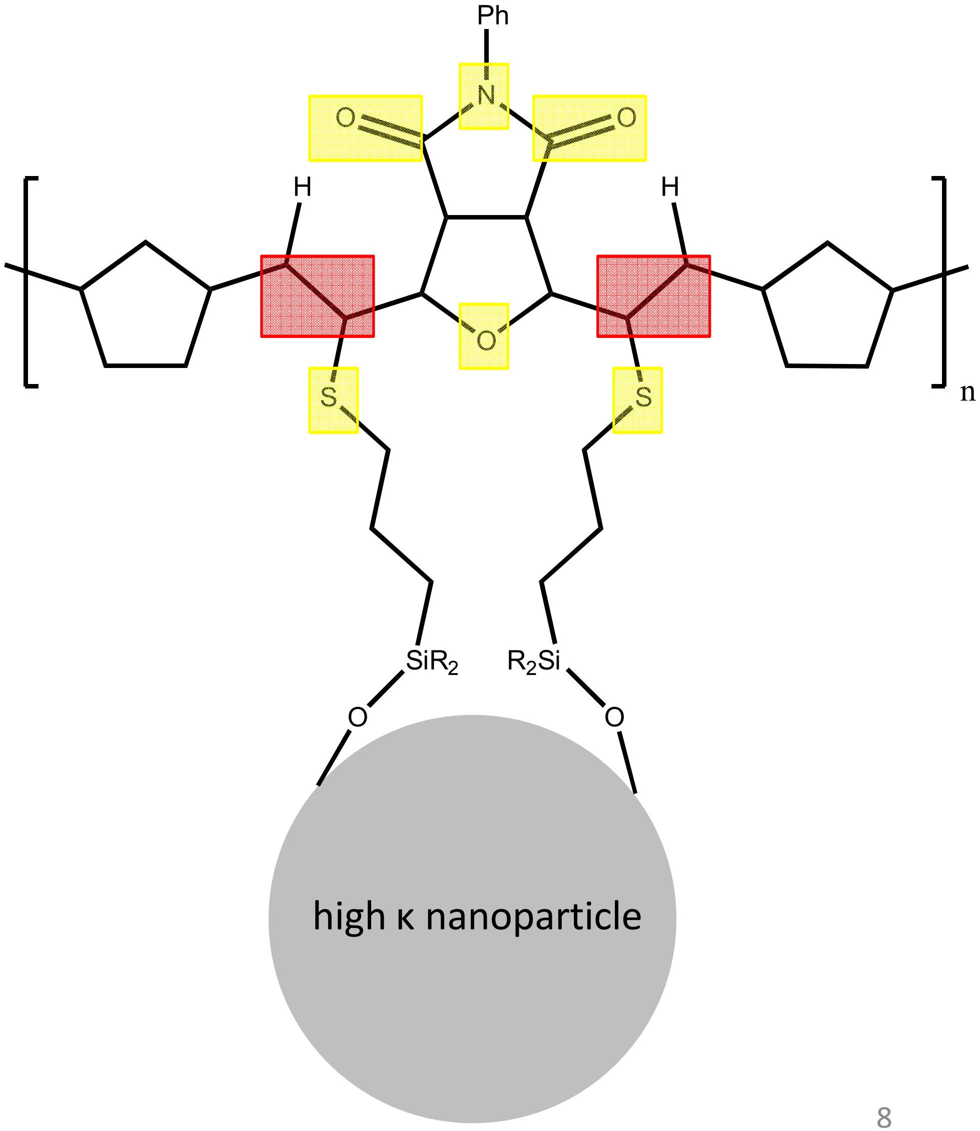
$$U_e = \tfrac{1}{2}\,\varepsilon_r \varepsilon_o E^2$$

- Increase breakdown strength by removing reactive double bonds

- Increase relative permittivity by adding polarizable groups

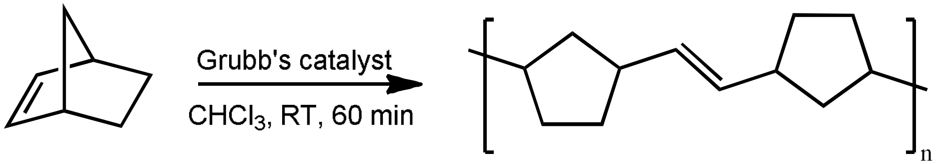
- Increase relative permittivity by incorporating functionalized np's *covalently* into polymer matrix

- stable to 140 °C
- good solution stability
- good mechanical properties
- inexpensive



ROMP Polymers

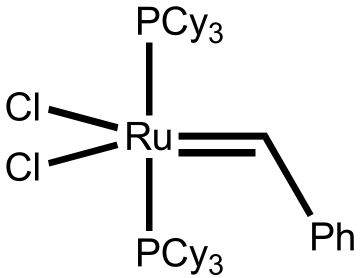
Ring-opening metathesis polymerization

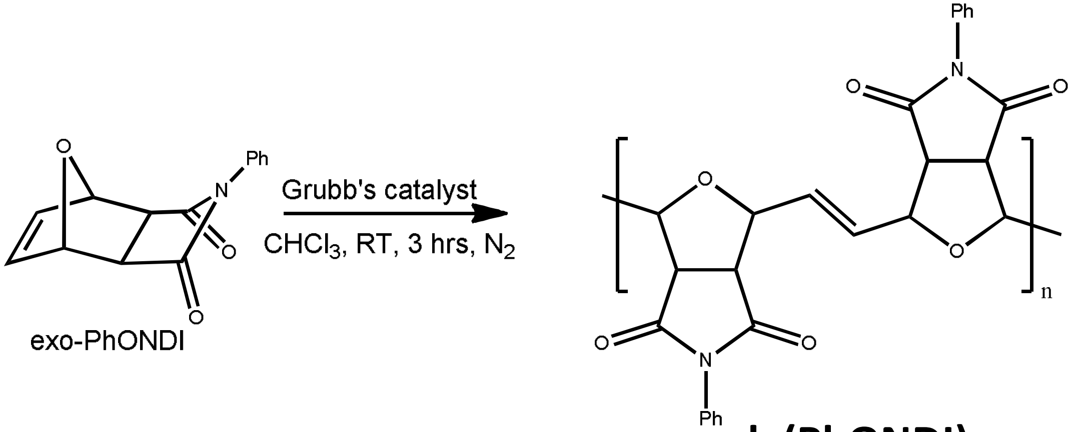


norbornene

poly(nbe)

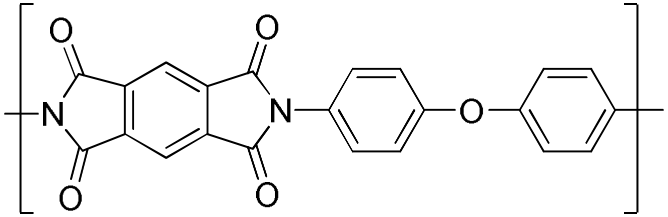
simple
inexpensive
$T_g \approx 45$ °C



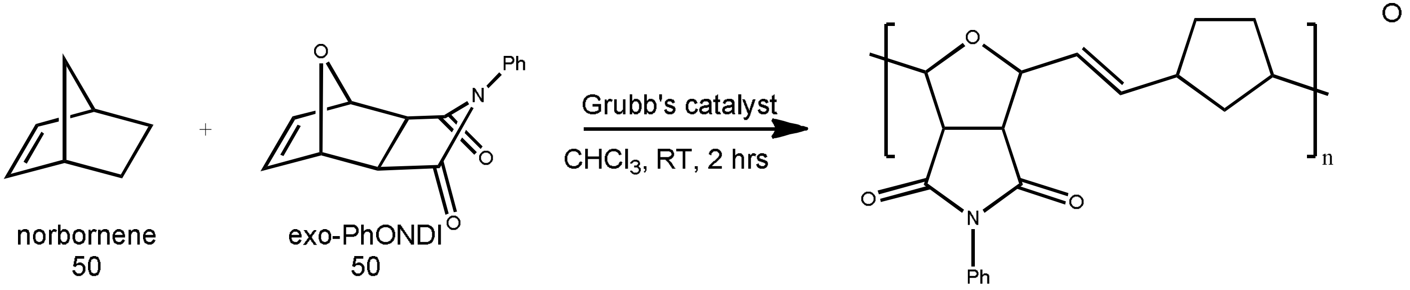


exo-PhONDI

poly(PhONDI)



Kapton: κ=4.0, low DF, stable to 180 °C



norbornene
50

exo-PhONDI
50

PhONDI
40

nbe
60

co-poly(nbe)-poly(PhONDI)

best mechanical properties
$T_g \approx 170$ °C

Increasing Energy Density

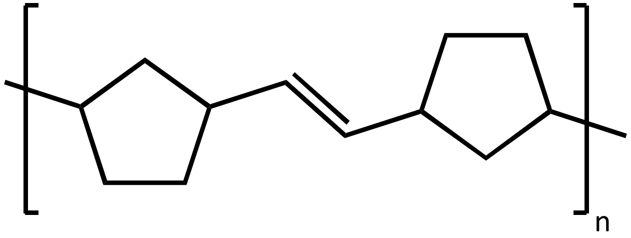
$$U_e = ½\, \varepsilon_r \varepsilon_o E^2$$

-**Increase breakdown strength**

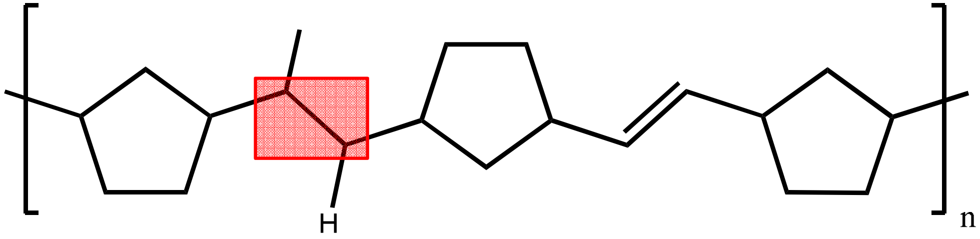
  - remove reactive functional groups

n

poly(norbornene)

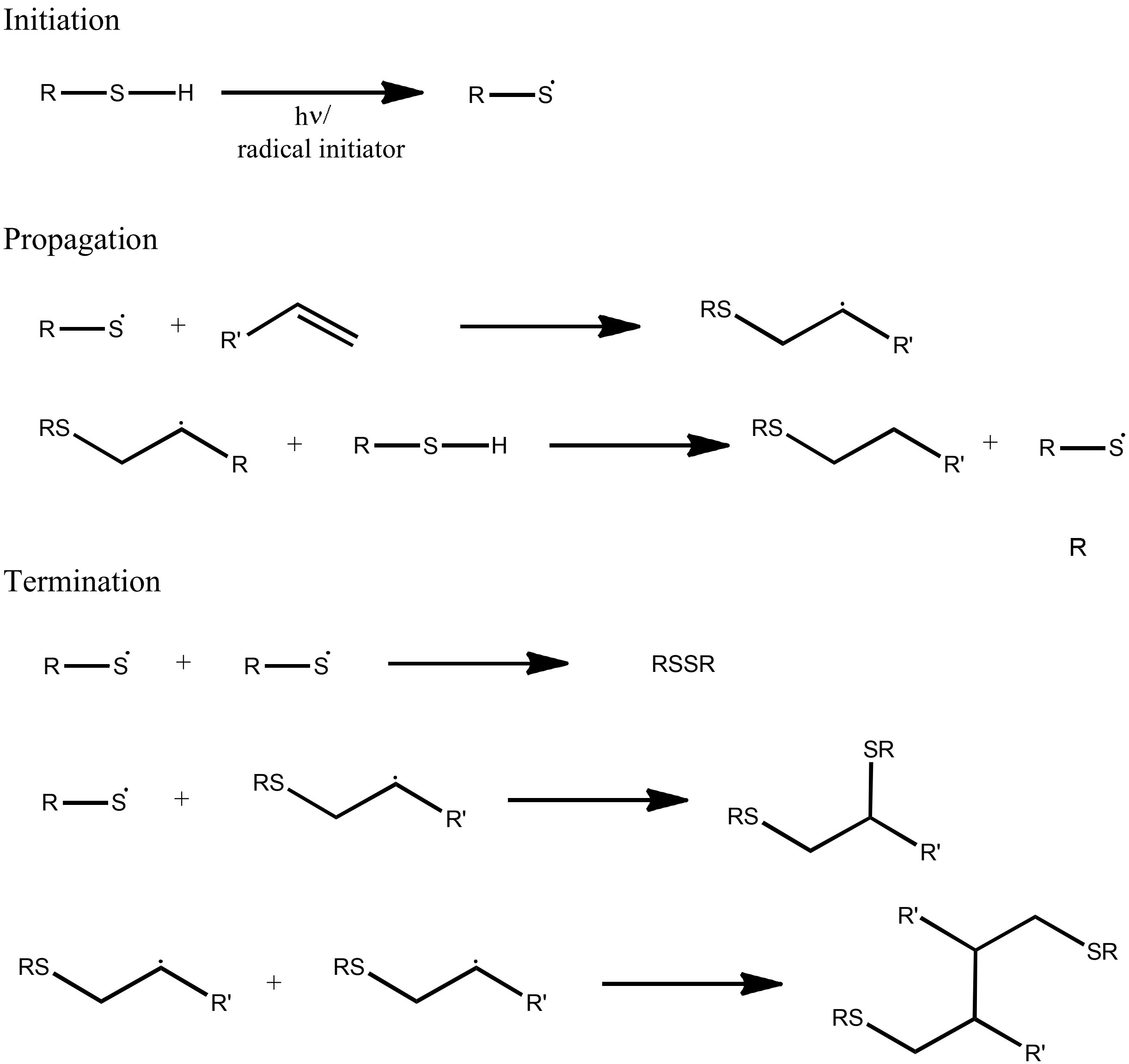


functionalized poly(norbornene)



Alkene Functionalization:

Radical Thiol-Ene Reaction

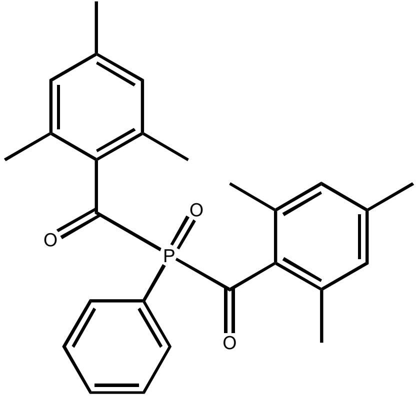


Initiation

Propagation

Termination

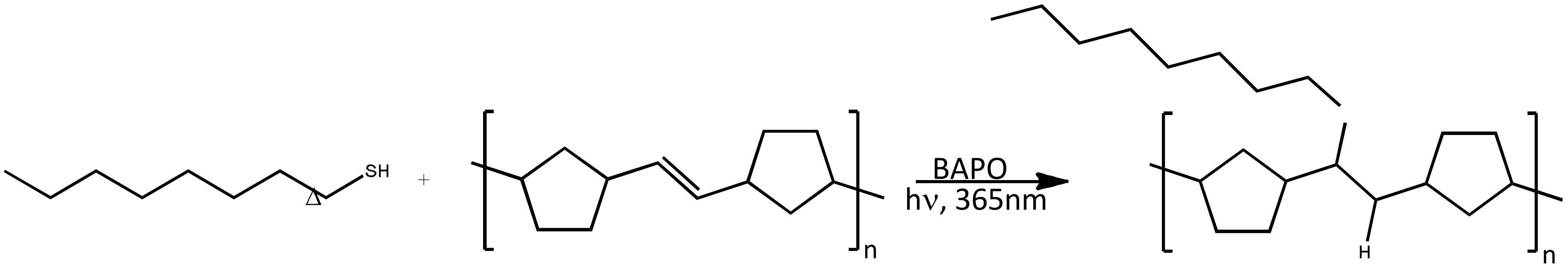
BAPO



phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide

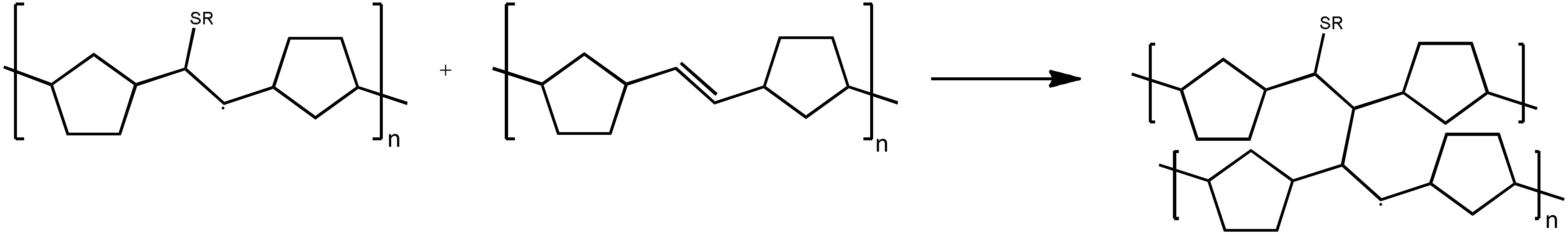
C.E. Hoyle, et.al. J. Poly. Science: Part A, **2004**, 42, 5301–5338

Poly(nbe) Thiol-ene



yields insoluble GEL

Crosslinking?

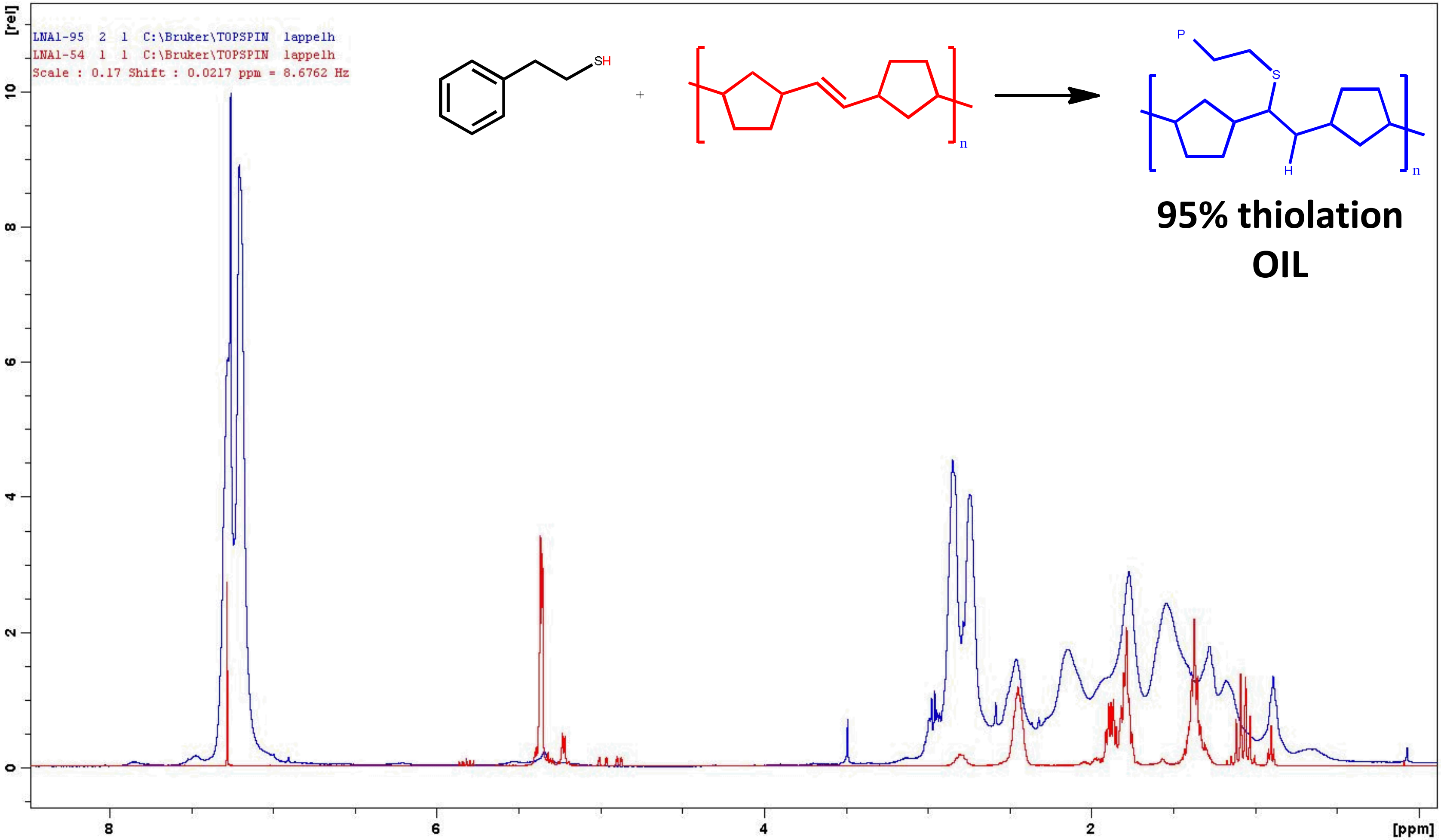


Poly(nbe) Thiol-ene: low M_N

-polymerization with a chain transfer agent yields a low M_N polymer (~3000)

S

-reaction of low M_N polymer in neat thiol yields non-crosslinked highly thiolated polymers but…. they are oils.

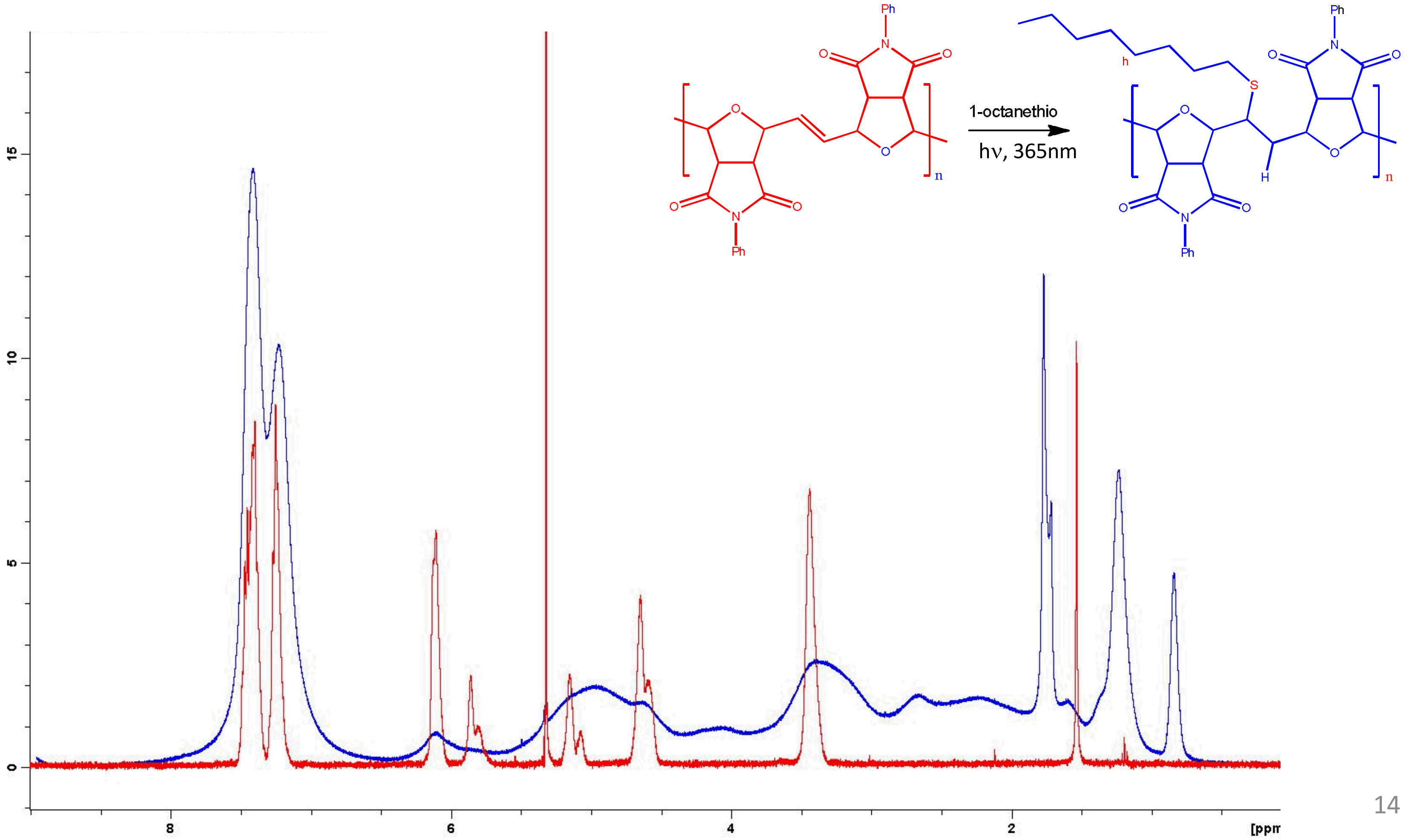


95% thiolation
OIL

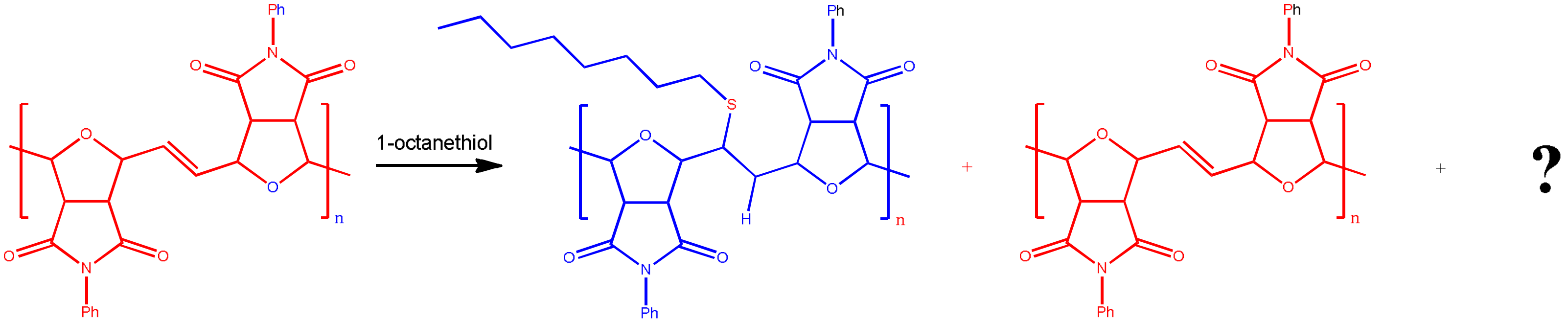
Poly(PhONDI) Thiol-ene

- poly(PhONDI) more stable than poly(nbe), less crosslinking?

- thiol-ene reaction yields a soluble polymer with ~15-25% thiolation



Poly(PhONDI) Thiol-ene

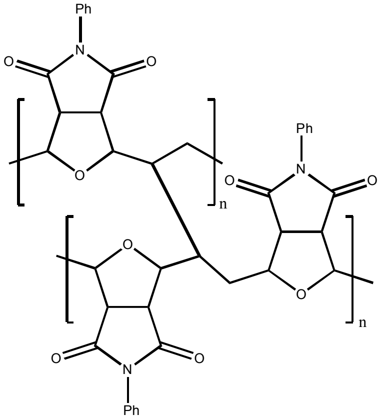


thiolation
15-25%

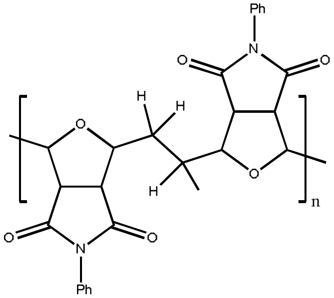
unreacted
10-20%

unknown
60-70%
(no olefin)

crosslinking?



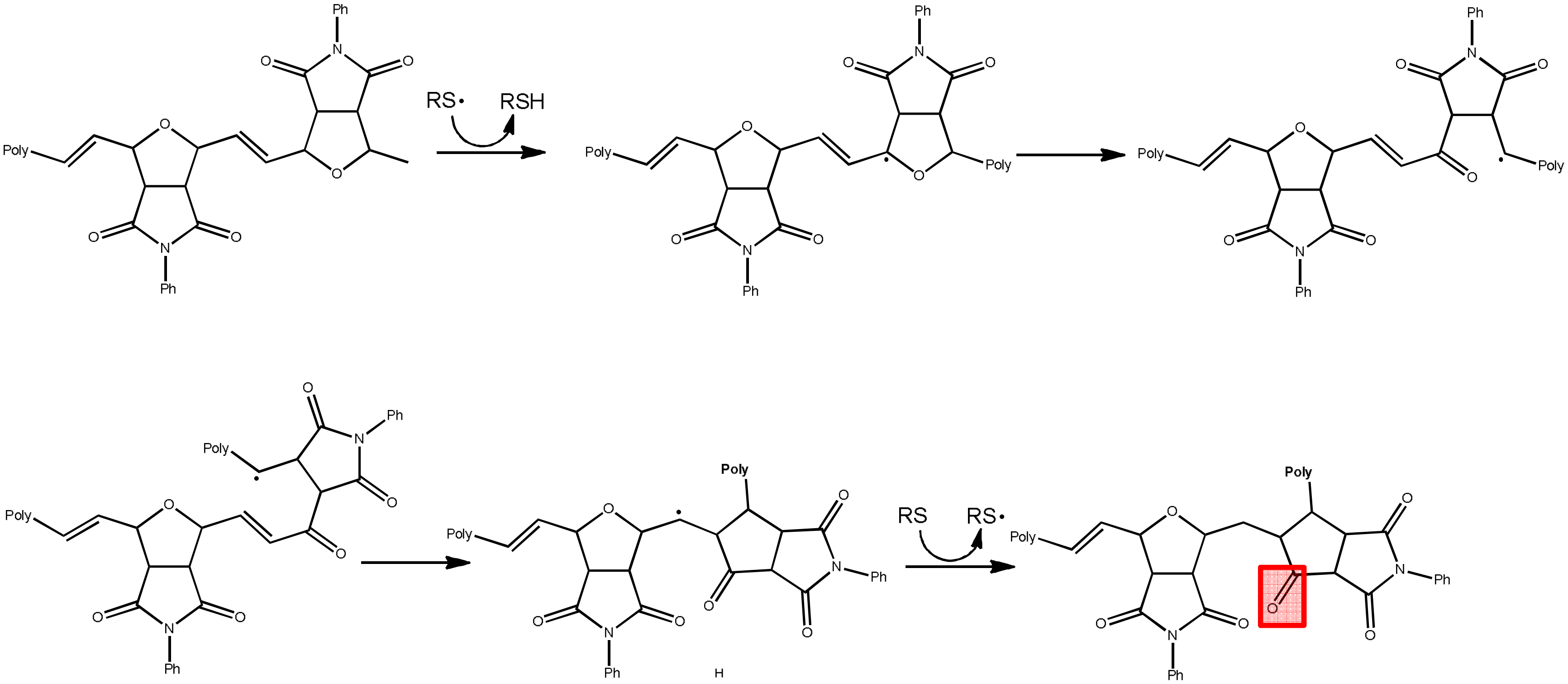
hydrogenation?



- -insoluble in $CHCl_3$
- -brittle films
- -higher T_g
- -soluble in CH_2Cl_2

Poly(PhONDI) Thiol-ene

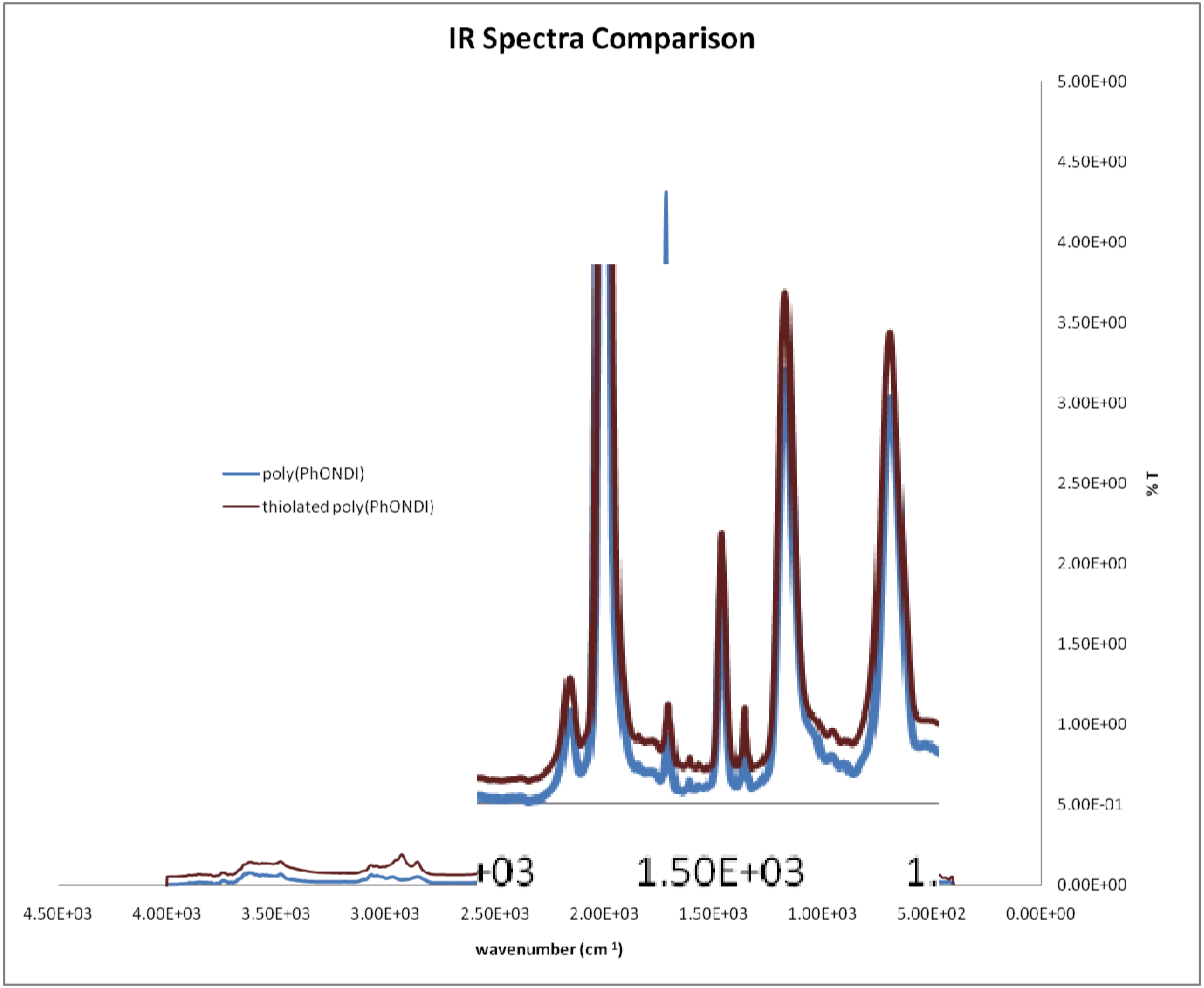
- radical H-abstraction at the stable allylic position rather than the olefin



5-exo-trig

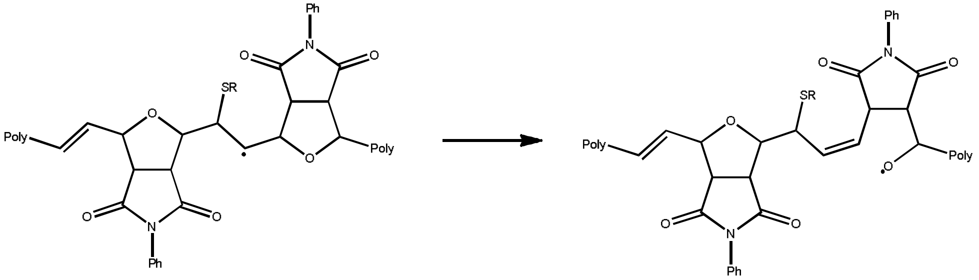
ketone = 1725-1705 cm^{-1}
amide = 1690-1650 cm^{-1}

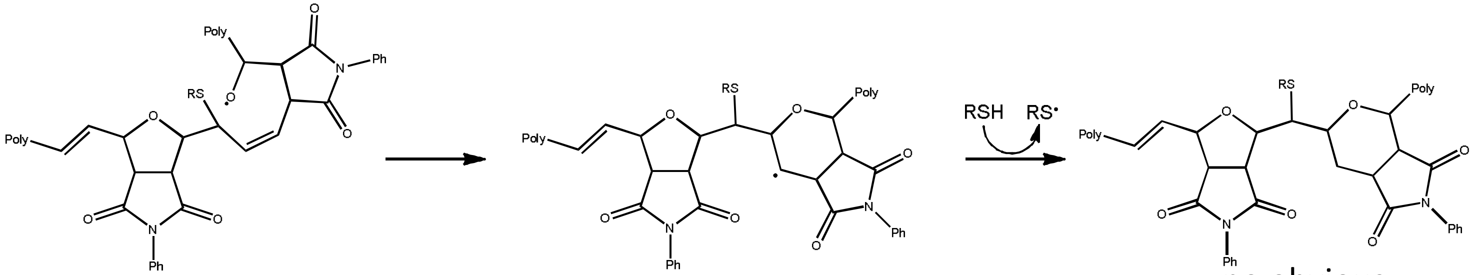
Poly(PhONDI) Thiol-ene



Poly(PhONDI) Thiol-ene

- formation of an O-centered radical leading to 6-endo-trig cyclization



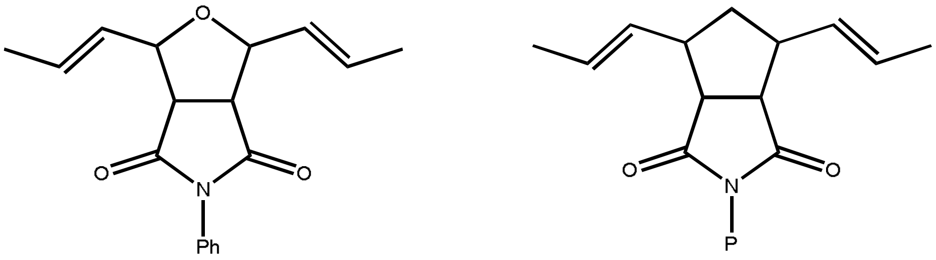


6-endo-trig

no obvious
NMR or IR tags

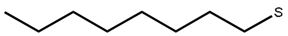
H

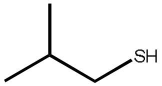
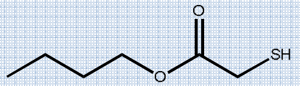
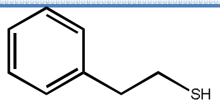
- model compounds



Poly(PhONDI) Thiol-ene Reaction

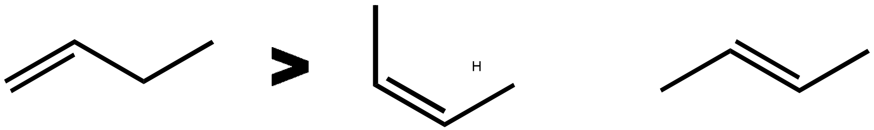
- **thiol-ene reaction variability**

 	% unreacted	% thiolated	% unknown	total % olefin consumed
1	22	15	63	78
2	27	12	61	73
3	16	16	69	85
4	20	13	67	80

Thiol	% unreacted	% thiolated	% unknown	total % olefin consumed
 	20	13	67	80
 	14	16	70	86
 	6	21	73	94
 	6	26 h	68	94

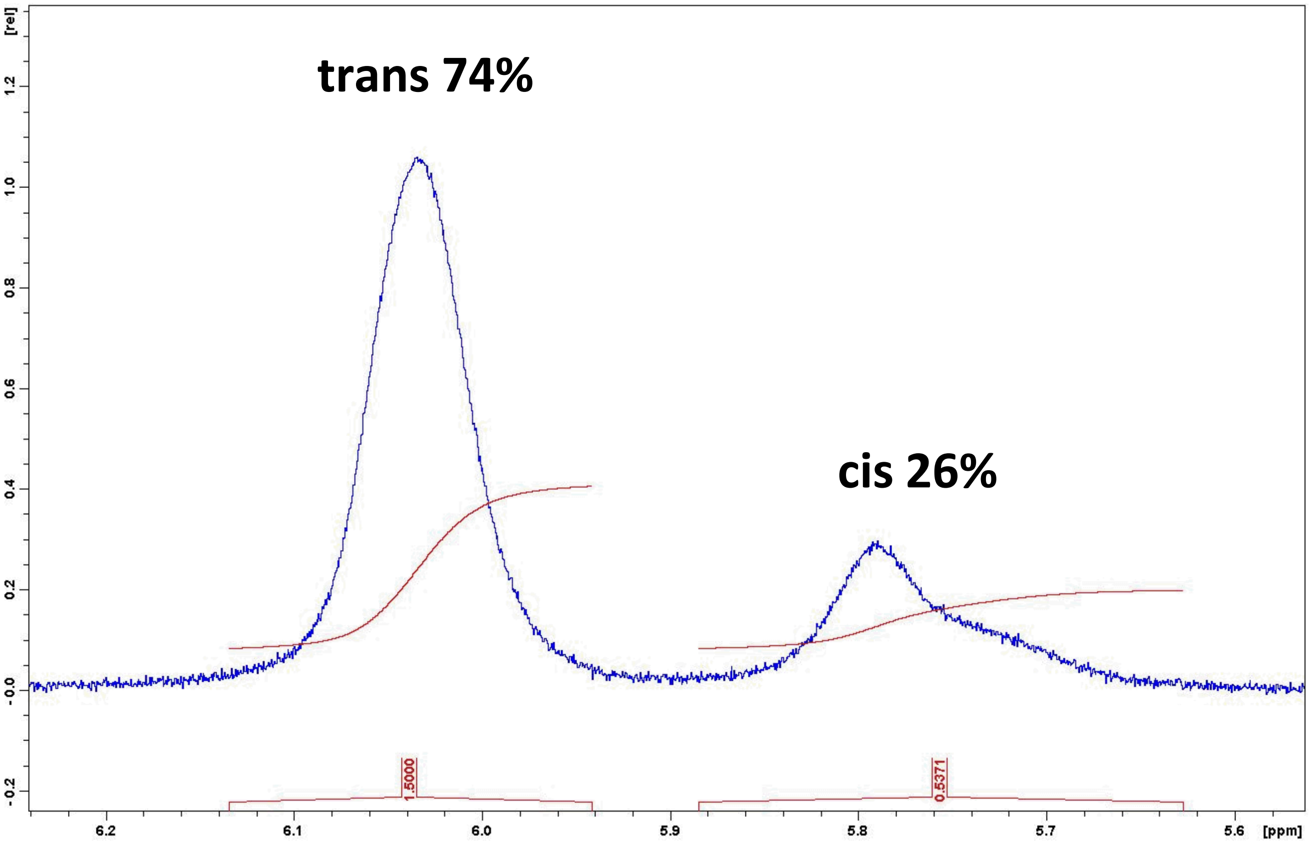
Poly(PhONDI) Thiol-ene Reaction

Thiol-ene activity



C.E. Hoyle, et.al. J. Poly. Science: Part A, **2004**, 42, 5301–5338

Cis:trans selectivity in PhONDI ROMP

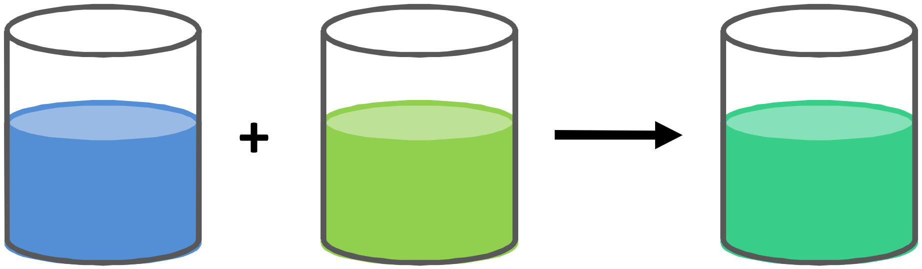


% thiolated
13
26
21
16

Poly(PhONDI) Polyblend Films

- pure thiolated polymers are too brittle to make a film
- blend with poly(PhONDI) to improve mechanical characteristics
- measure dielectric permittivity and breakdown strength

- cast by drawdown machine from dichloroethane/dichloromethane
- ensure films are free of small molecules (solvents)
- sputter coat 50nm Au back electrode
- sputter coat 50nm Au front electrodes, 6.3mm diameter



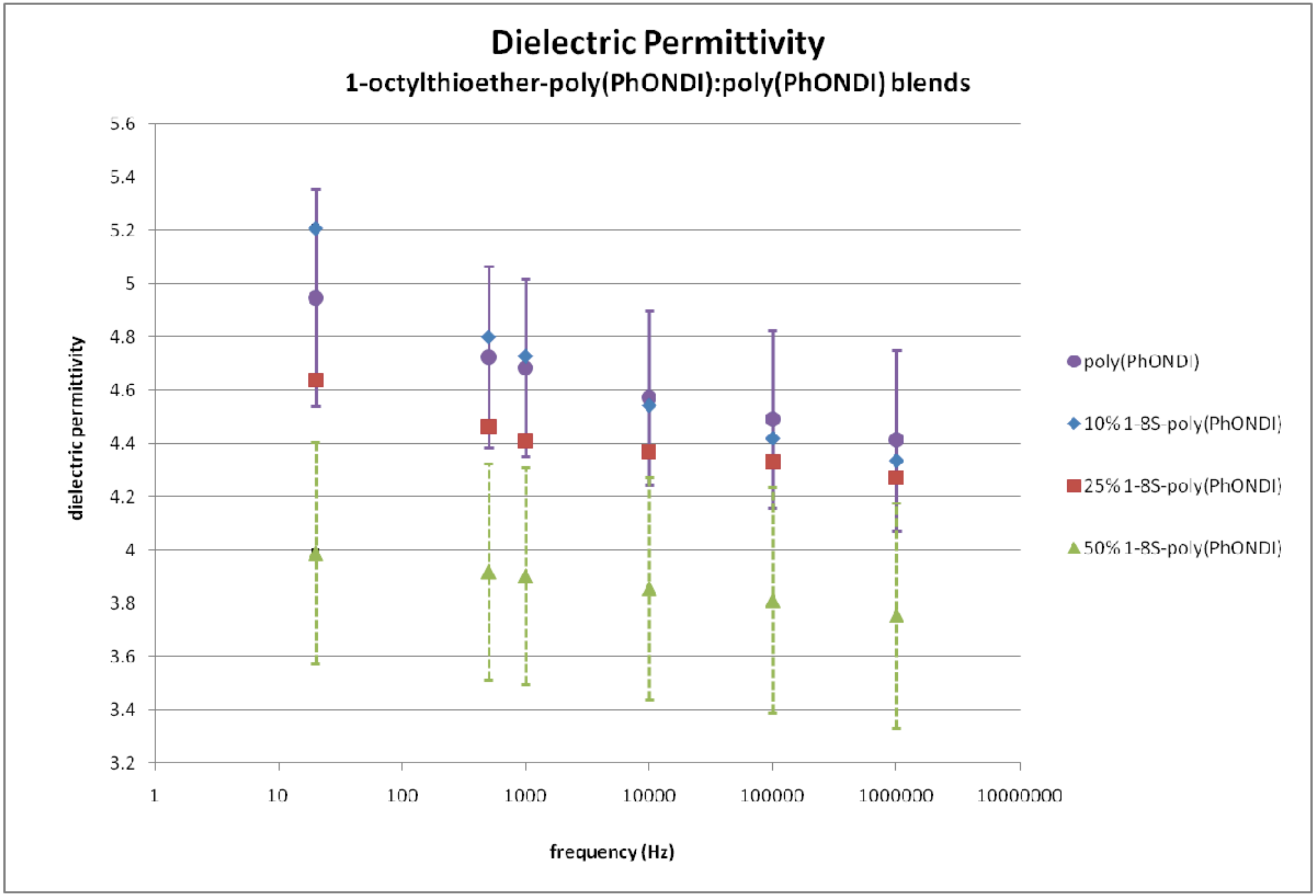
thiolated poly(PhONDI) + poly(PhONDI) → polyblend

brittle films

poor sol’n stability
lower breakdown

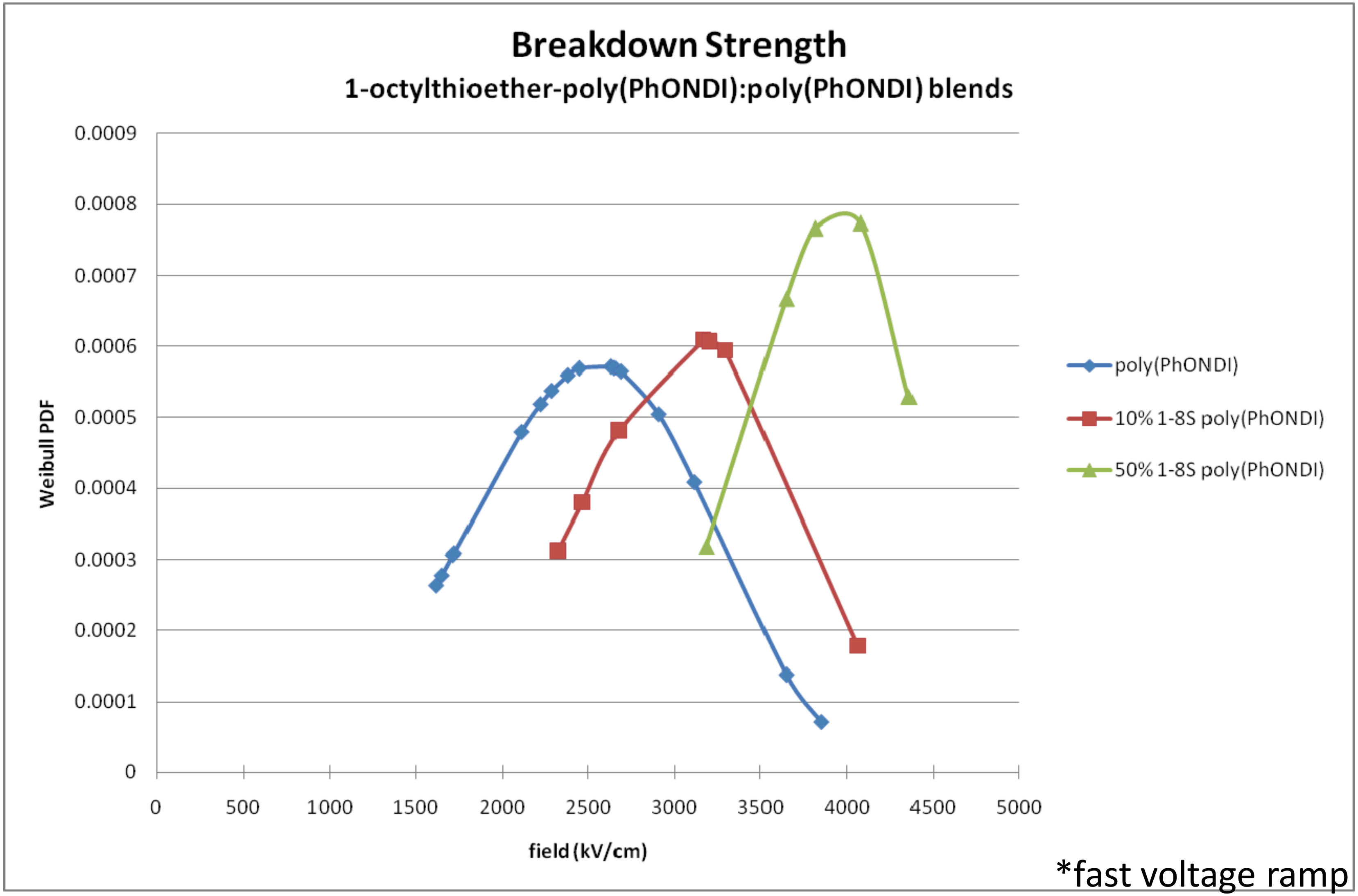
better films
better breakdowns
better sol’n stability

Poly(PhONDI) Polyblend Films



- dielectric permittivity decreases with increasing % thiolated polymer due to removal of double bonds, but not substantially
- addition of thioether functionality may compensate for loss of olefins

Poly(PhONDI) Polyblend Films



*fast voltage ramp

- breakdown strength increases with increasing % thiolated polymer due to removal of double bonds

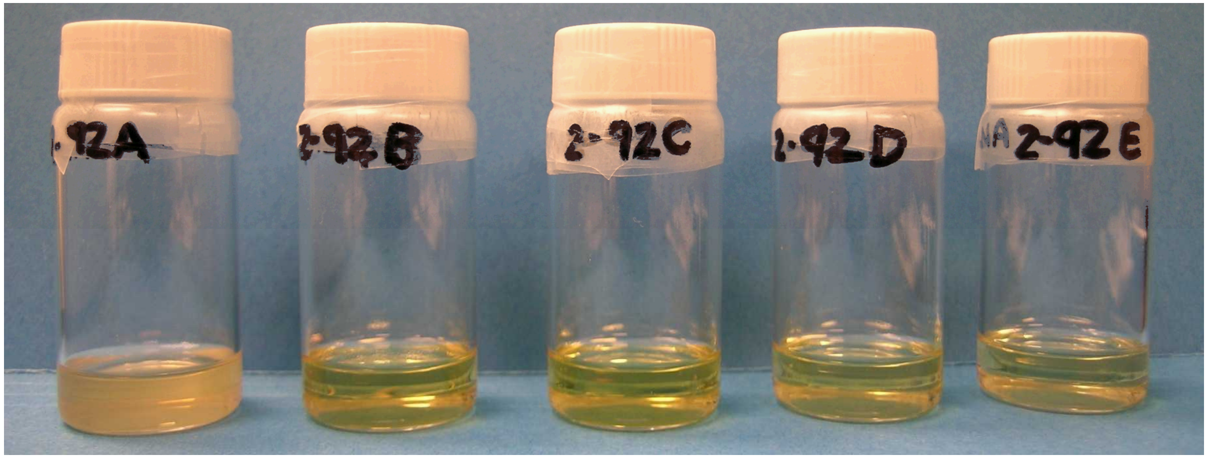
Poly(PhONDI) Polyblend Films

Energy Density 1 kHz

film	E_b (kV/cm)*	ε_r (1 kHz)	U_o (J/cm^3)
poly(PhONDI)	2729.95	4.57	3.02
10% 1-8S	3276.89	4.54	4.32
50% 1-8S	4017.25	3.86	5.52

*fast voltage ramp

7wt% in dichloromethane, 21 days

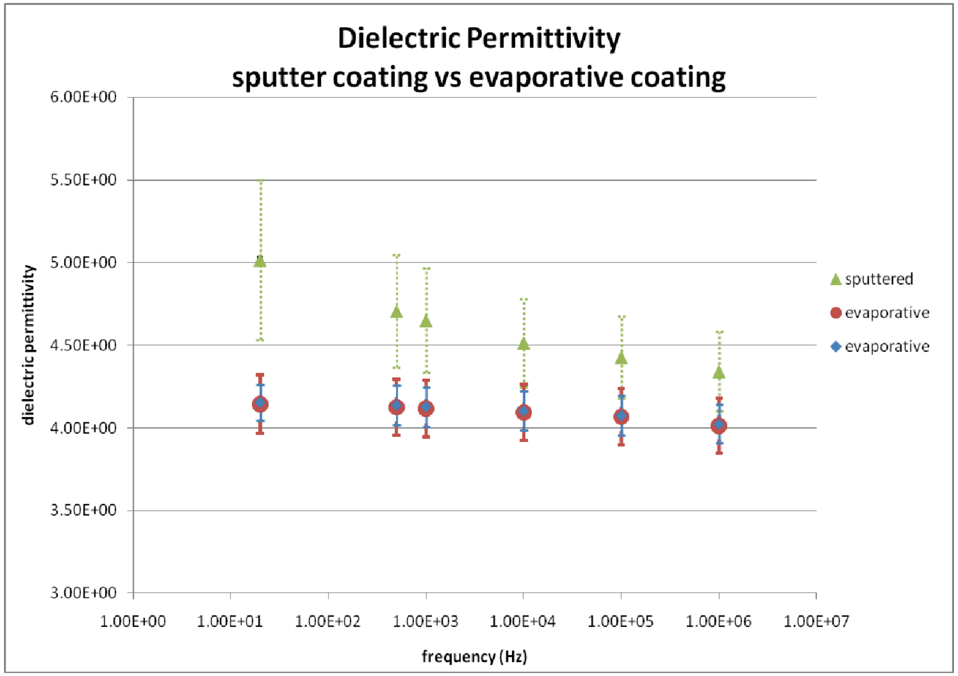


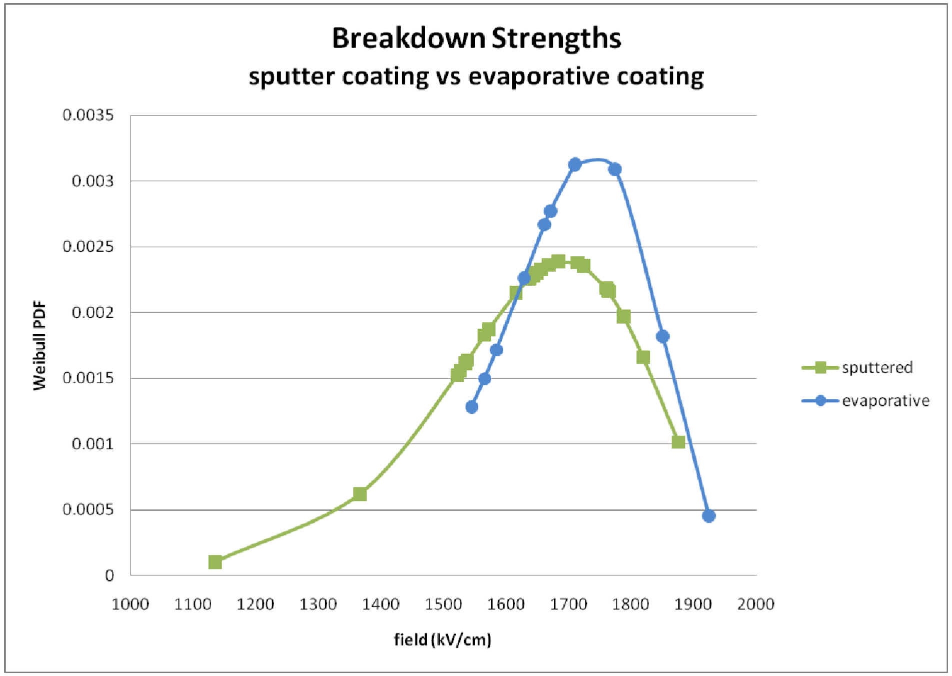
poly(PhONDI) 75:25 50:50 25:75 1-8S-poly(PhONDI)

- polyblends have higher breakdown strengths/energy densities
- polyblends are significantly more stable in solution
- high % films are still brittle

Coating Methods

- sputter coating
- e-beam evaporative coating

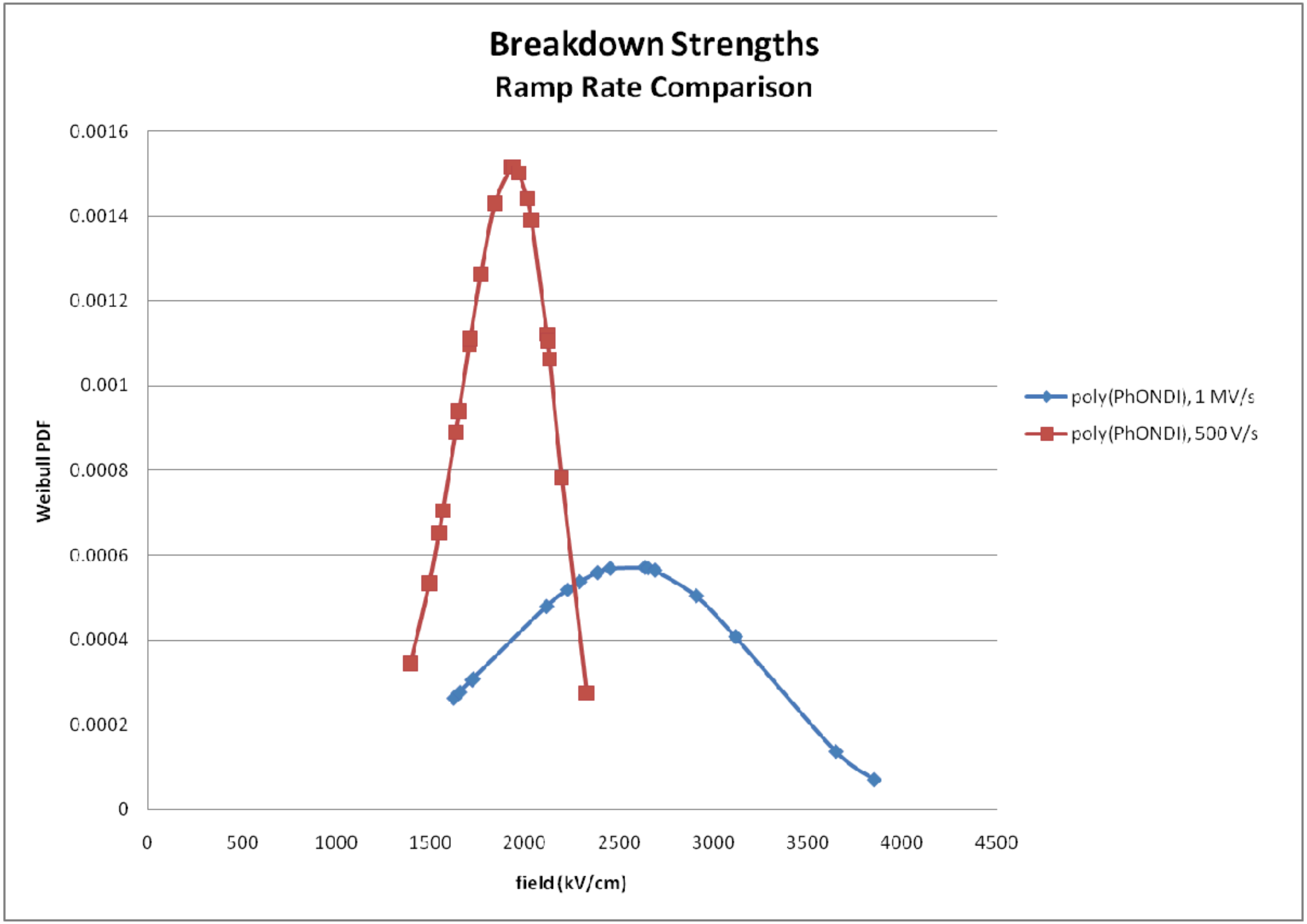




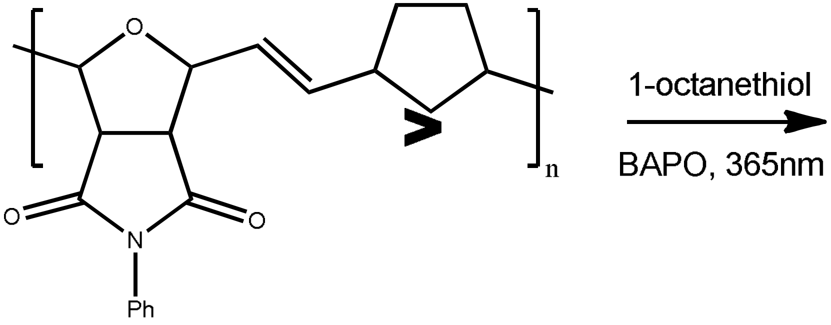
- sputter coating can lead to Au or Ar atom implantation in the film, affecting dielectric properties

Breakdown Measurements

- ramp rate can make breakdown strengths appear artificially high
- changed ramp rate for measurements from 1 MV/s to 500 V/s



Co-poly(PhONDI)-poly(nbe) Polyblends



insoluble gel

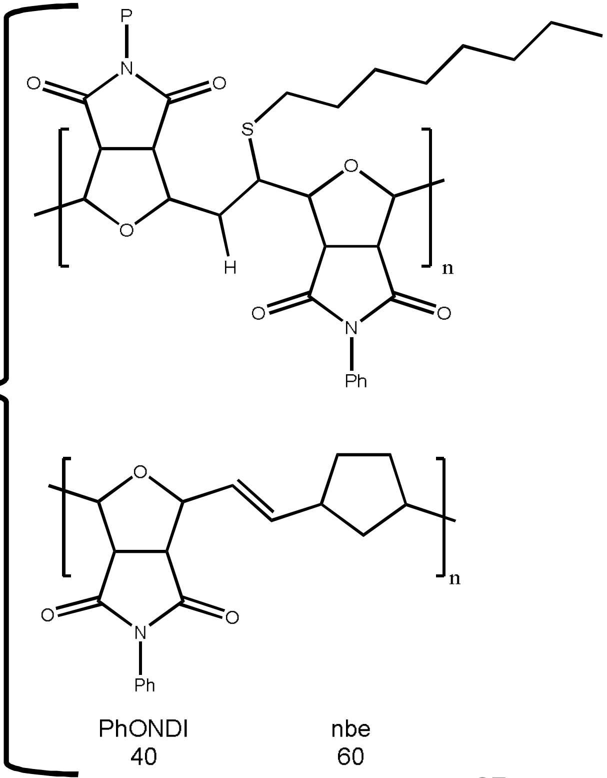
PhONDI
40

nbe
60

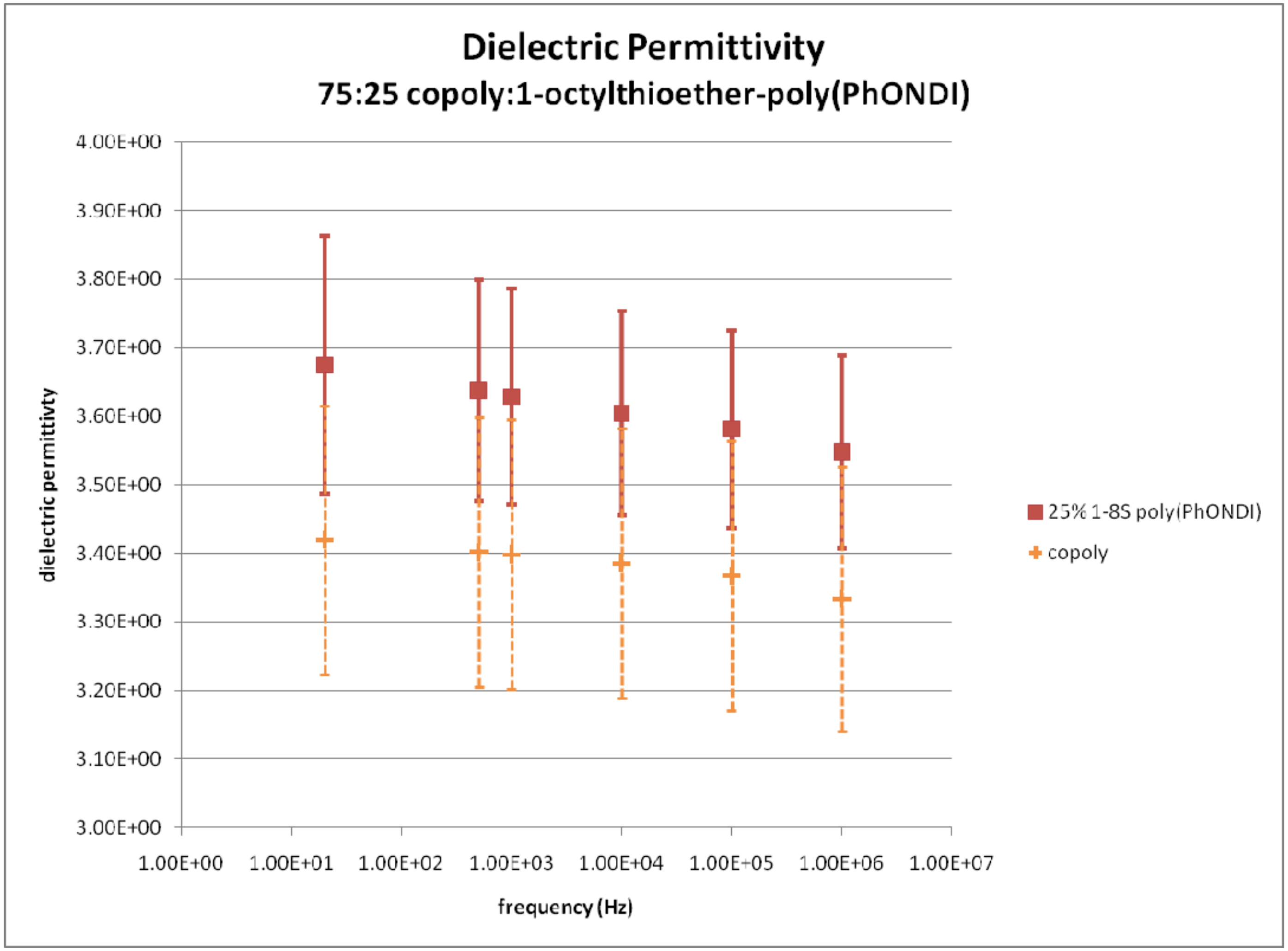
co-poly(nbe)-poly(PhONDI)

- copoly also crosslinks in UV thiol-ene reaction
- make polyblends with thiolated poly(PhONDI) and copolymer
- improved mechanical properties vs poly(PhONDI) polyblends

copoly/S-PhONDI polyblend

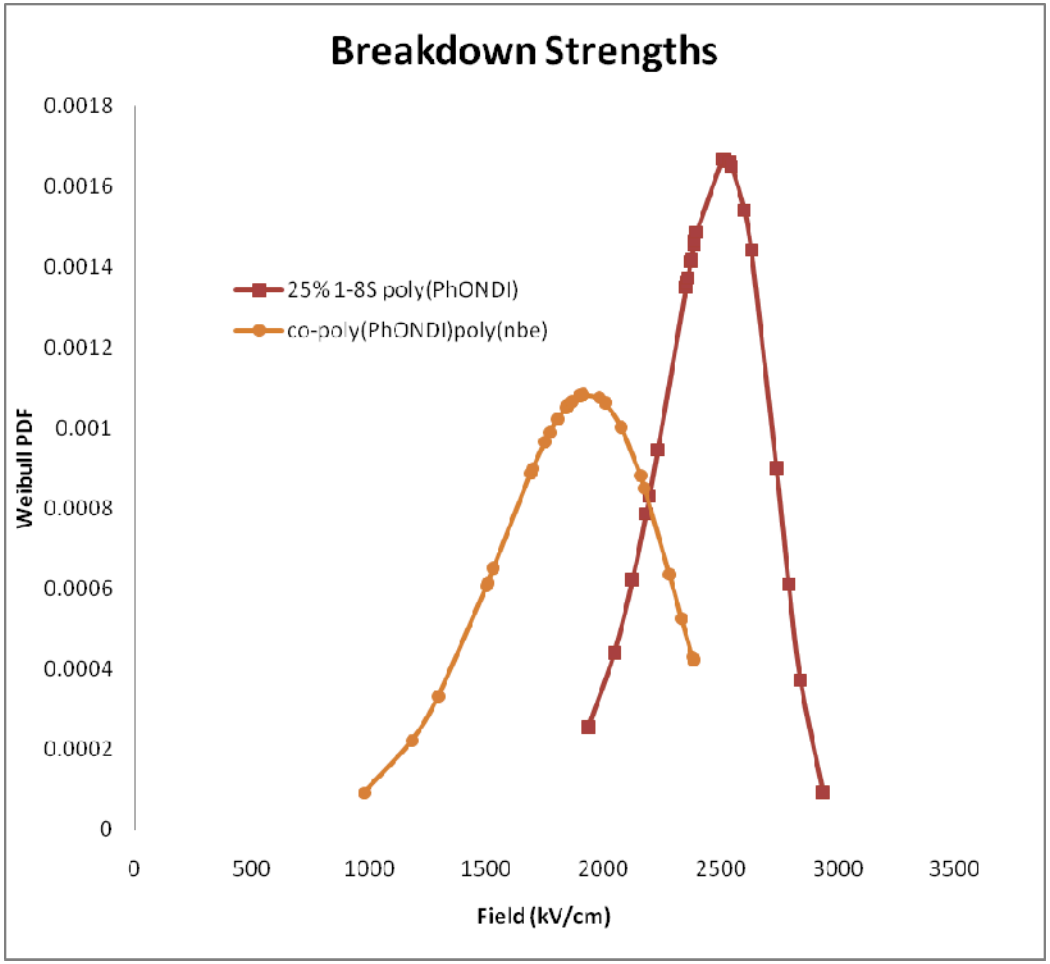


Co-poly(PhONDI)-poly(nbe) Polyblends



- dielectric permittivity is approximately the same for the blend compared to the unmodified copolymer
- the addition of thioether functionalities and a % of unreacted poly(PhONDI) compensates for the decrease expected due to removal of olefins

Co-poly(PhONDI)-poly(nbe) Polyblends



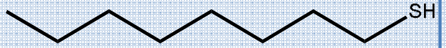
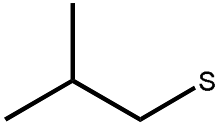
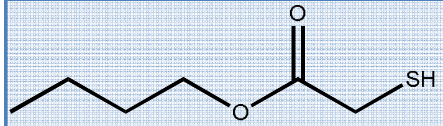
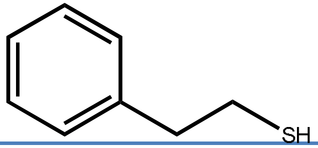
- breakdown strengths of the polyblend increase relative to the unmodified copolymer
- increased breakdown strengths combined with similar dielectric permittivity yield increased energy density

Energy Density 1 kHz

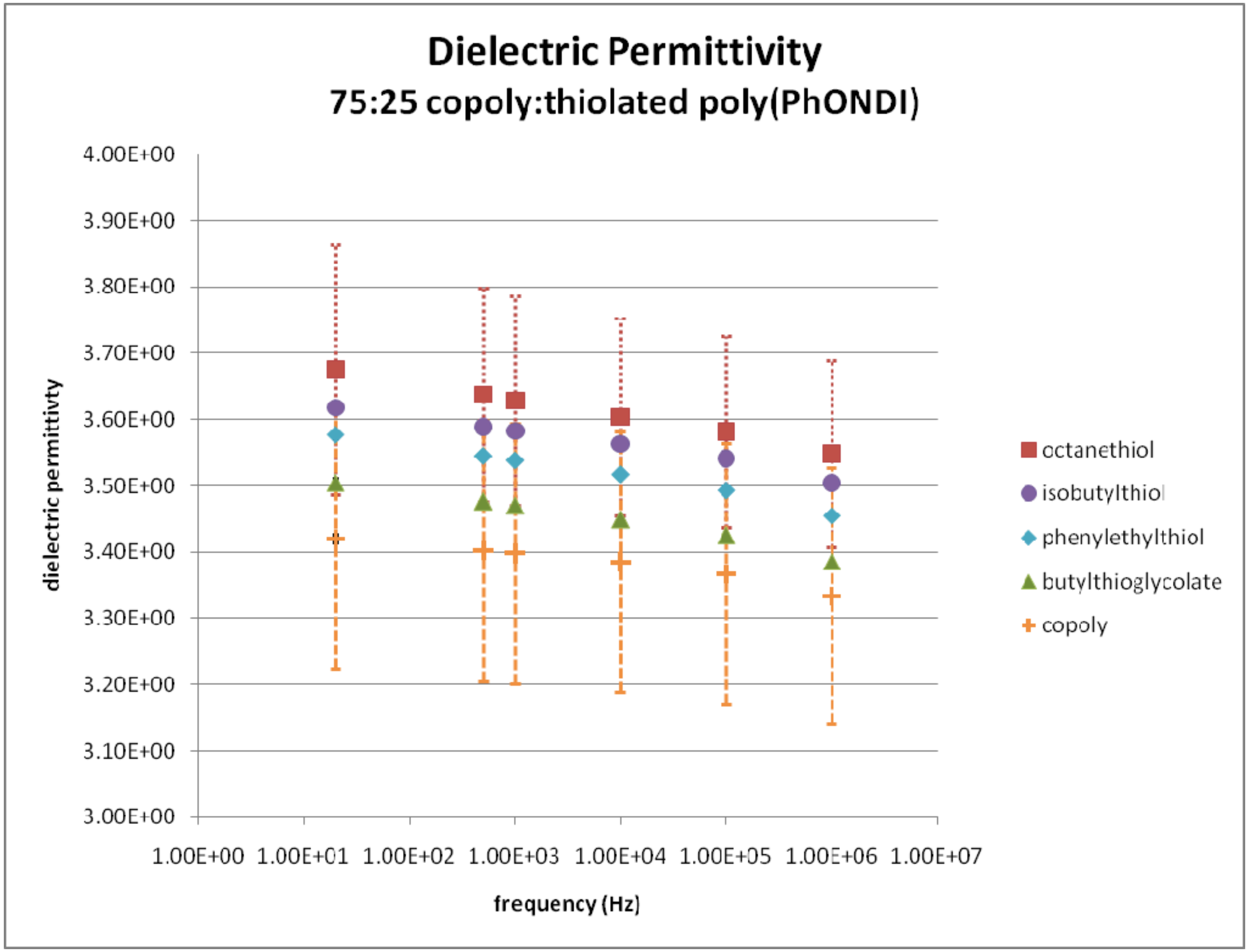
film	E_b (kV/cm)	ε_r (1 kHz)	U_o (J/cm^3)
copolymer	1999.96	3.39	**1.20**
octanethiol	2535.61	3.57	**2.03**

Co-poly(PhONDI)-poly(nbe) Polyblends

- make polyblend films with thiolated polymers of a variety of thiols to see if there is an effect on dielectric properties

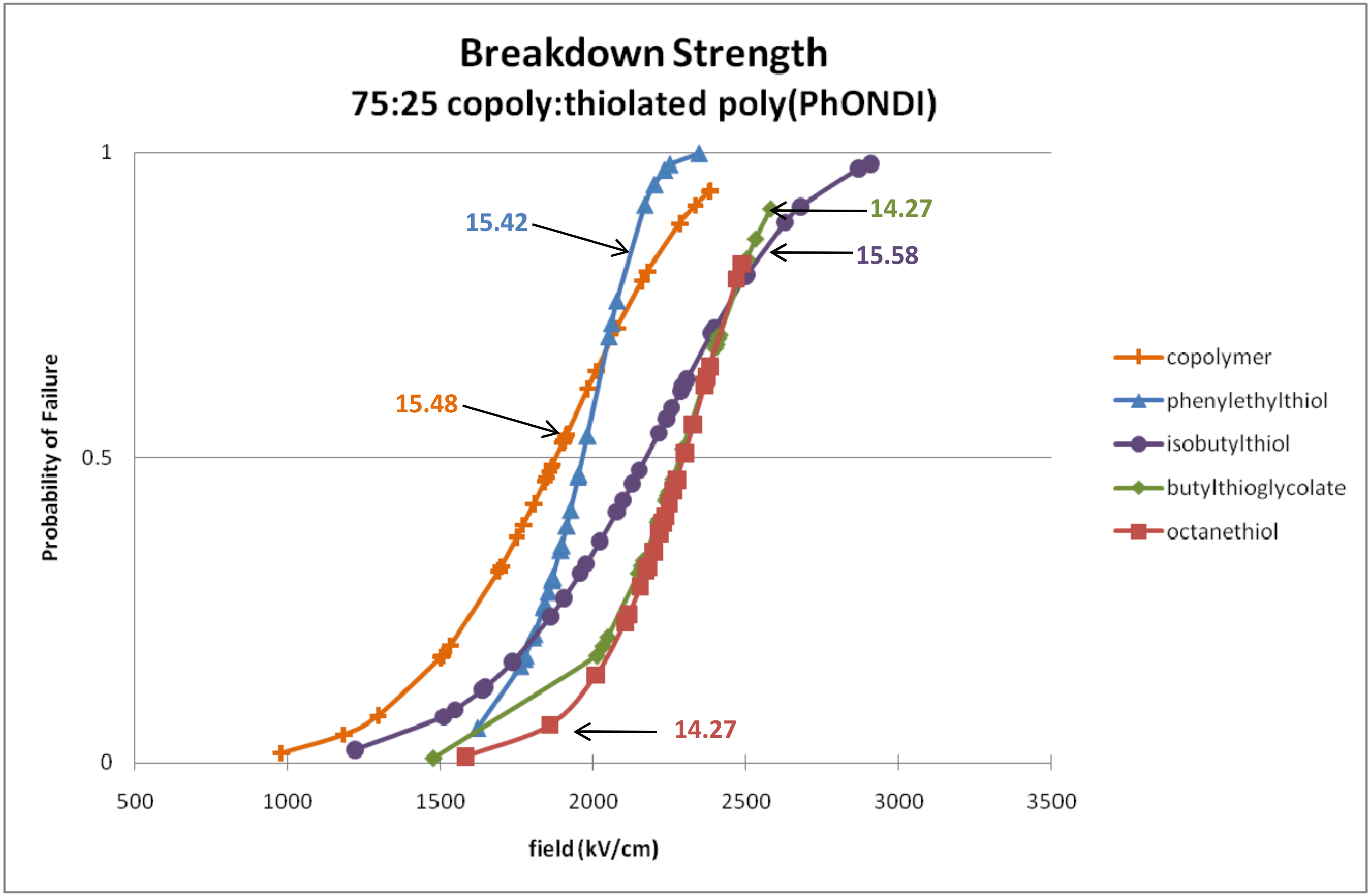
Thiol	% unreacted	% thiolated	% unknown	total % olefin consumed
	20	13	67	h 80
	14	16	70	86
	6	21	73	94
	6	26	68	94

Co-poly(PhONDI)-poly(nbe) Polyblends

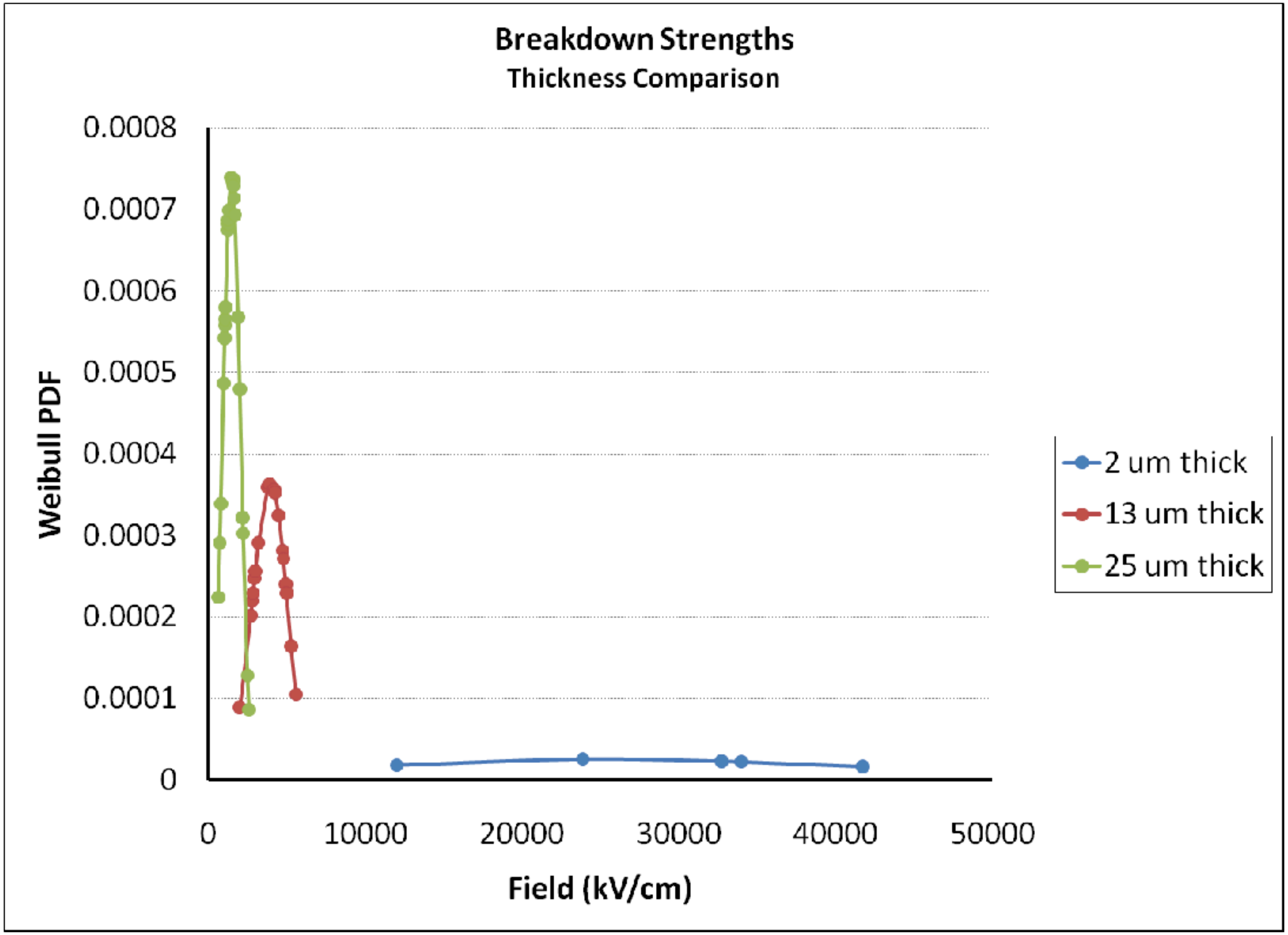


- dielectric permittivity approximately the same for polyblends and unmodified copolymer
- higher % olefin consumption correlates with lower dielectric, but differences are not greater than standard deviation

Co-poly(PhONDI)-poly(nbe) Polyblends

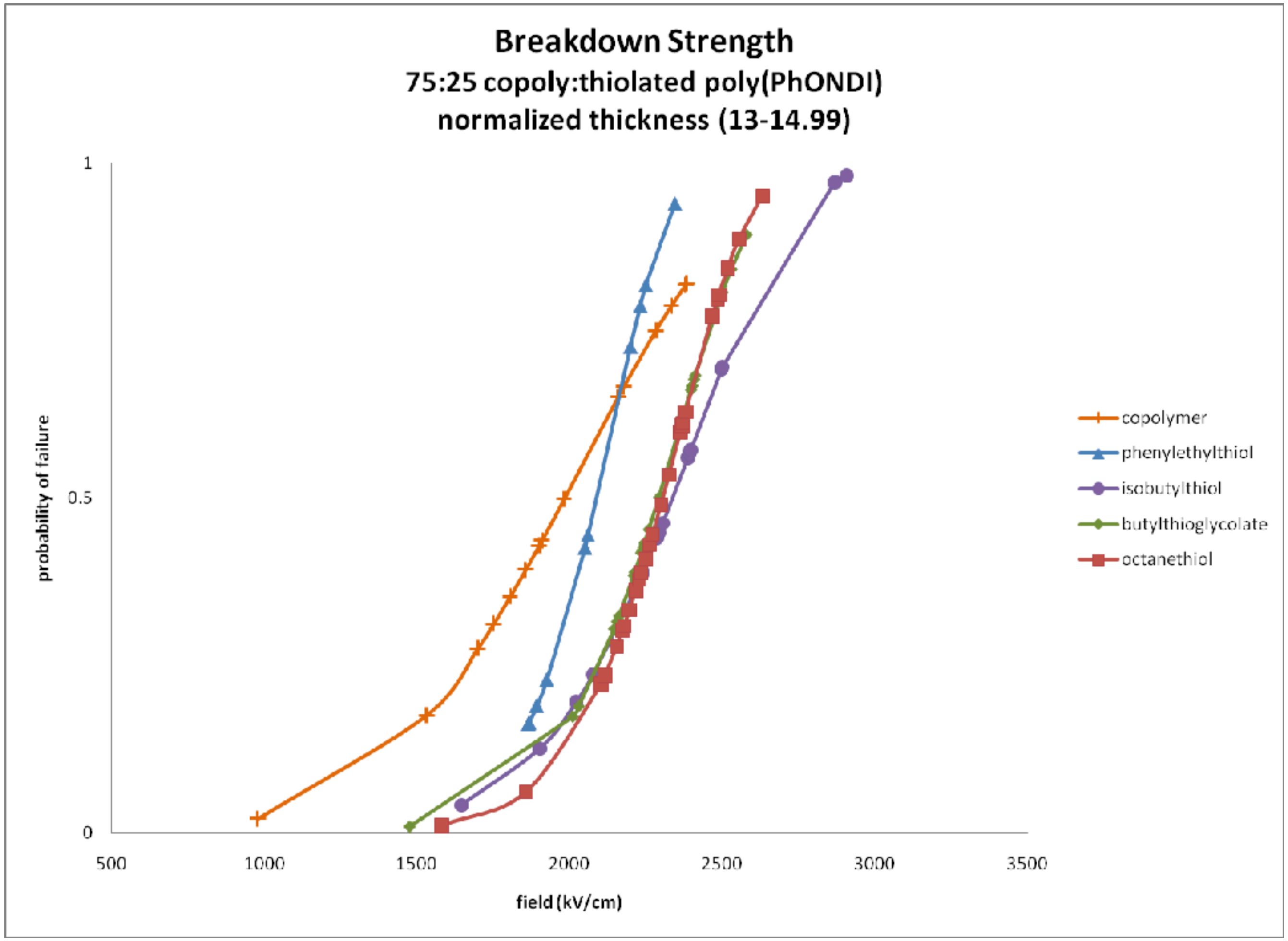


Co-poly(PhONDI)-poly(nbe) Polyblends



- breakdown strength is sensitive to film thickness, with thinner films having higher breakdown strengths due to higher relative contribution of interface

Co-poly(PhONDI)-poly(nbe) Polyblends



- breakdown strength increases in the polyblends relative to the unmodified copolymer
- inclusion of aromatic group lowers breakdown strength

Co-poly(PhONDI)-poly(nbe) Polyblends

Energy Density 1 kHz (thickness normalized)

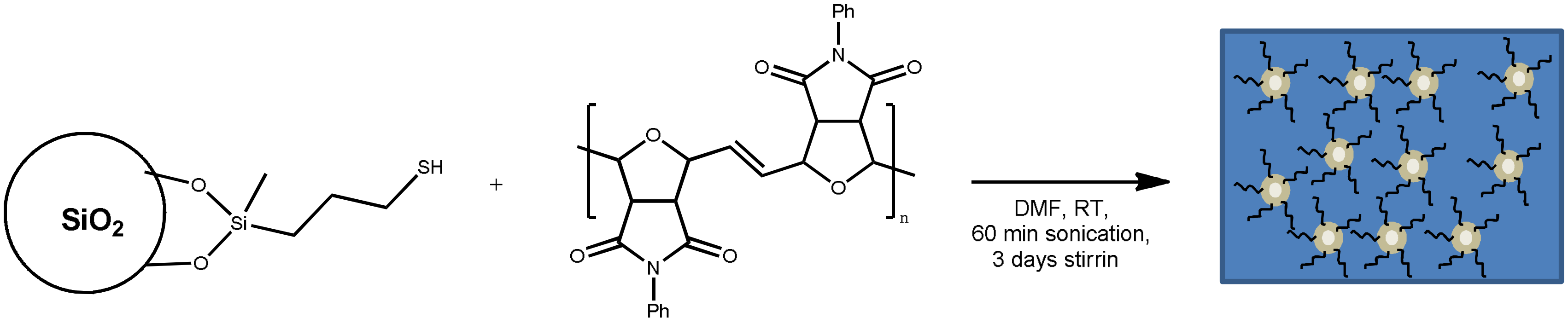
film	E_b (kV/cm)	ε_r (1 kHz)	U_o (J/cm^3)
copolymer	2136.32	3.39	1.37
phenylethylthiol	2152.11	3.52	1.44
butylthioglycolate	2378.39	3.45	1.73
octanethiol	2382.67	3.57	1.79
isobutylthiol	2446.55	3.56	1.89

- copoly blends show improved breakdown strengths and energy densities relative to copolymer alone
- improved mechanical properties vs poly(PhONDI) polyblends
- decreased breakdown strength with aromatic functionality, but otherwise no trends with varying thiols

BOPP: energy density = **1-1.5 J/cm^3** temp stability = **105 °C**

thiolated polyblend: energy density = **1.4-1.9 J/cm^3** temp stability* ≈ **150 °C**

Composites: Blending Only

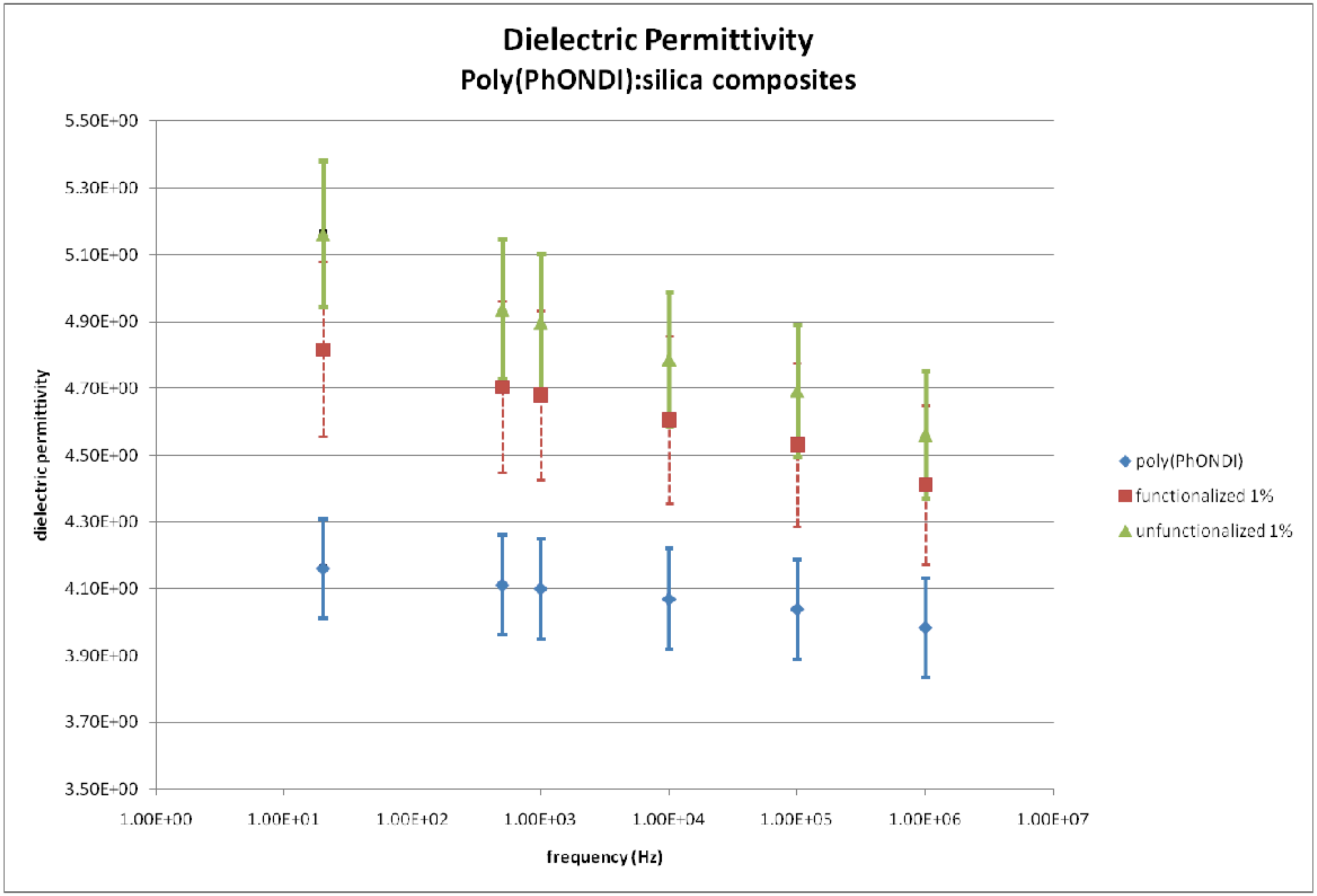


H

polymer	nanoparticles	wt %
poly(PhONDI)	functionalized	1
poly(PhONDI)	unfunctionalized	1
poly(PhONDI)	functionalized	3.5
poly(PhONDI)	unfunctionalized	3.5

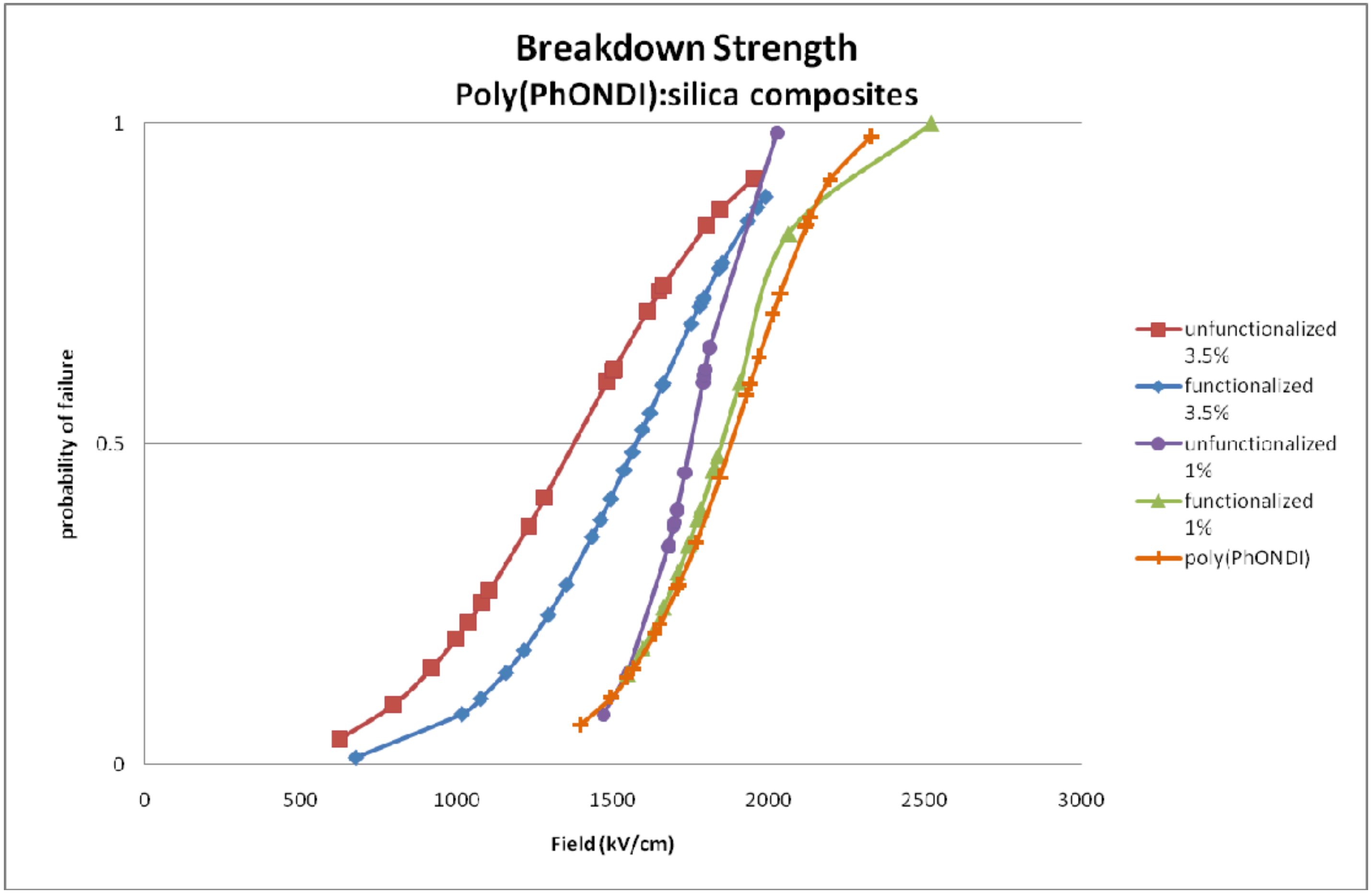
unfunctionalized functionalized

Composites: Blending Only



- dielectric permittivity increases in the composites relative to unmodified polymer
- dielectric permittivity is approximately the same between functionalized and unfunctionalized composites

Composites: Blending Only

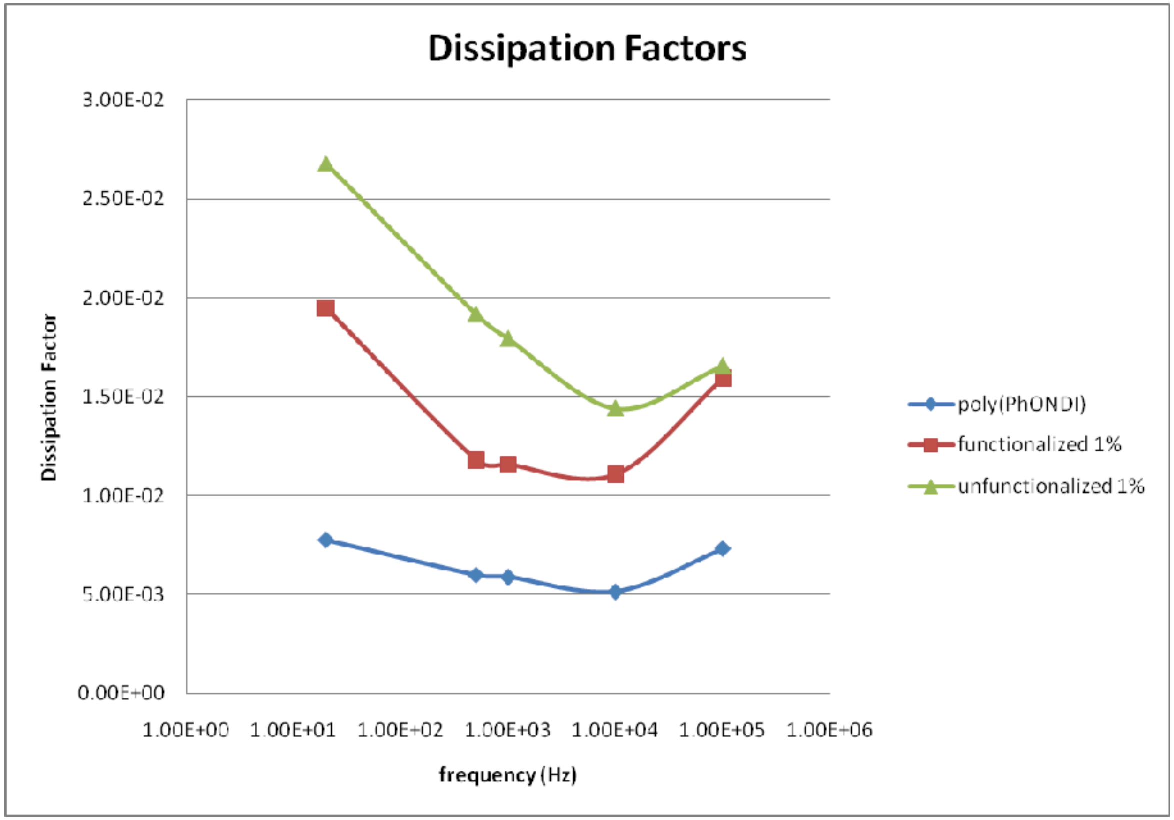


- breakdown strength for unfunctionalized composites is **lower** than functionalized composites and unmodified polymer
- breakdown strength for the higher loadings is **lower** than for lower loadings, for both functionalized and unfunctionalized composites
- functionalized 1% composite has approximately the same breakdown strength as unmodified polymer

Composites

Energy Density 1 kHz

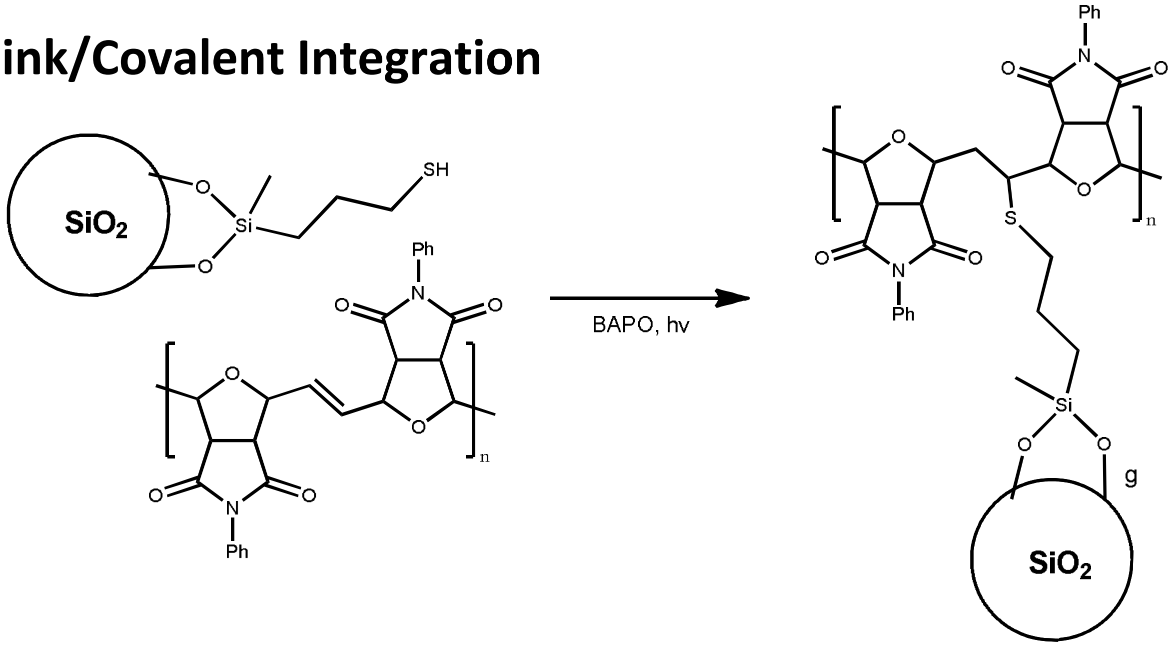
film	E_b (kV/cm)	ε_r (1 kHz)	U_o (J/cm^3)
poly(PhONDI)	1963.6	4.07	1.39
functionalized 1%	1926.8	4.61	1.51
unfunctionalized 1%	1801.29	4.79	1.38



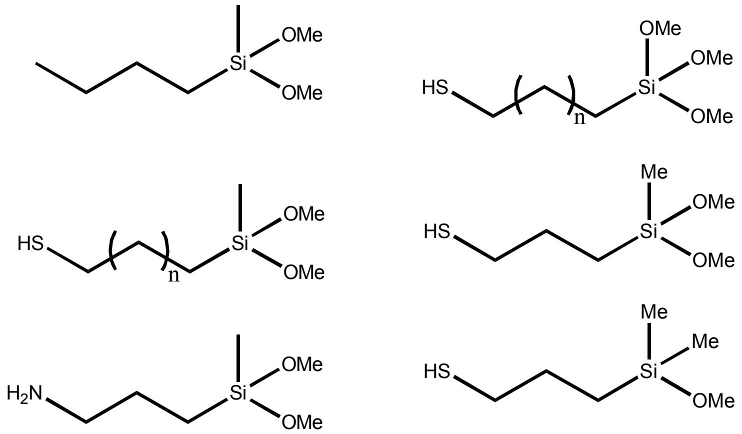
- functionalized composite has a higher breakdown strength and energy density vs unfunctionalized
- functionalized composite has a higher energy density vs unmodified polymer
- functionalization improves dissipation factor relative to unfunctionalized composite

Composites: Future Work

Crosslink/Covalent Integration



Functional Group Comparison

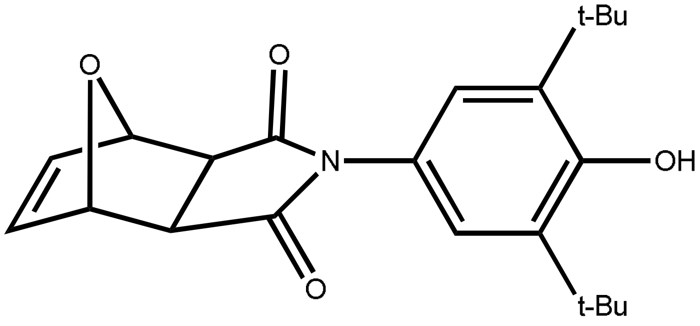


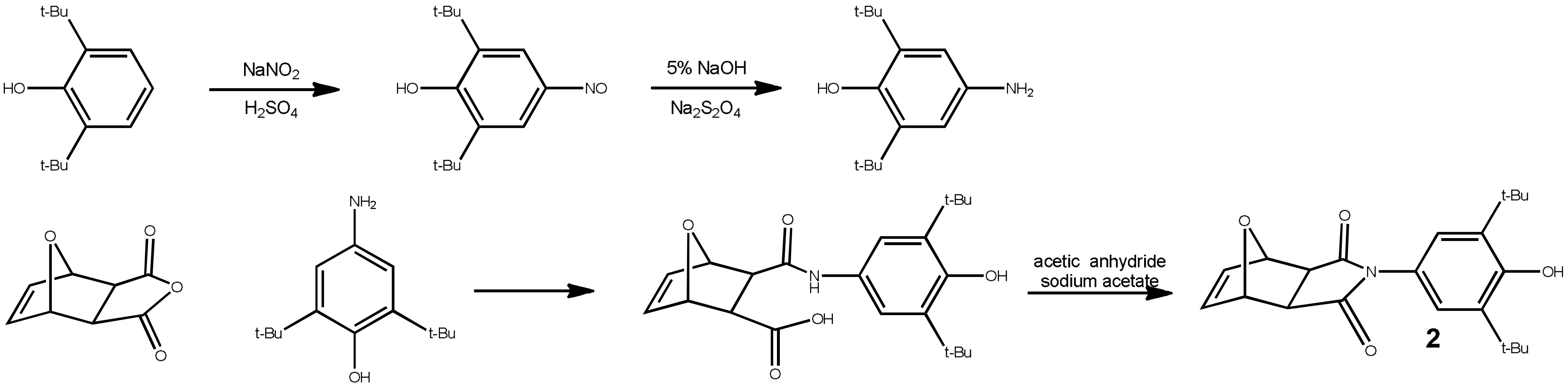
Higher κ Inorganics

κ ≈ 4	κ ≈ 9	κ ≈ 41
SiO_2	Al_2O_3	TiO

Functionalized Polymers: Future Work

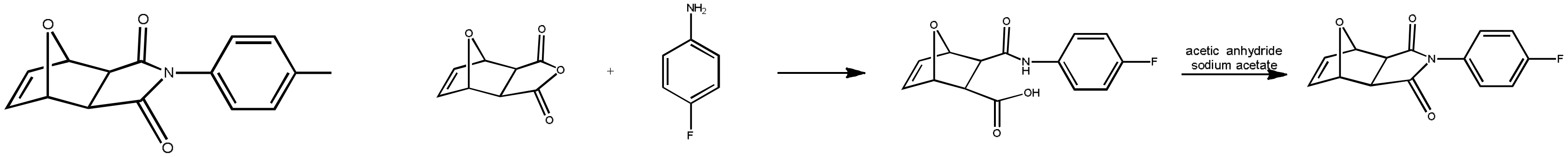
- BHT addition increases solution stability and breakdown strength
- make a BHT-PhONDI monomer for BHT incorporation into polymers





Functionalized Polymers: Future Work

- p-fluoroPhONDI improve dielectric characteristics, NMR tag



- improve % thiolation in thiol-ene reaction
  - cis/trans ratio in poly(PhONDI)?
  - addition of $ArS(ArSSAr)^{+}$?
- determine identity of unknown product in thiol-ene
  - model reactions

Summary

- Poly(nbe) forms crosslinked gels under UV thiol-ene conditions, except at very low MW weights.
- Poly(PhONDI) can be functionalized via the thiol-ene reaction up to ~25%, but also undergoes an unidentified side reaction. Films have poor mechanical properties.
- Blends of thiolated poly(PhONDI) with poly(PhONDI) and copolymer show improved solution stability and dielectric and mechanical properties.
- Polymer/silica composites have higher dielectric permittivity, but lower breakdown strengths than polymer alone. Functionalization increases the breakdown strengths yielding higher energy density materials. Covalent integration of nanoparticles is expected to improve breakdown strength and dissipation factors even more.

Selective modification of dielectric properties via polymer functionalization is successful in creating new dieletric materials with higher overall performance than current standards.

BOPP: energy density = **1-1.5 J/cm^3** temp stability = **105 °C**
thiolated polyblend: energy density = **1.4-1.9 J/cm^3** temp stability* ≈ **150 °C**
functionalized composite: energy density = **1.5 J/cm^3** temp stability* ≈ **150 °C**

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Dirk Group

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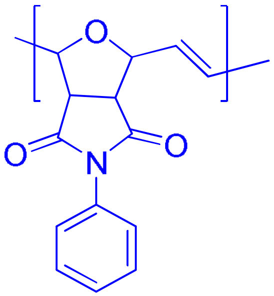
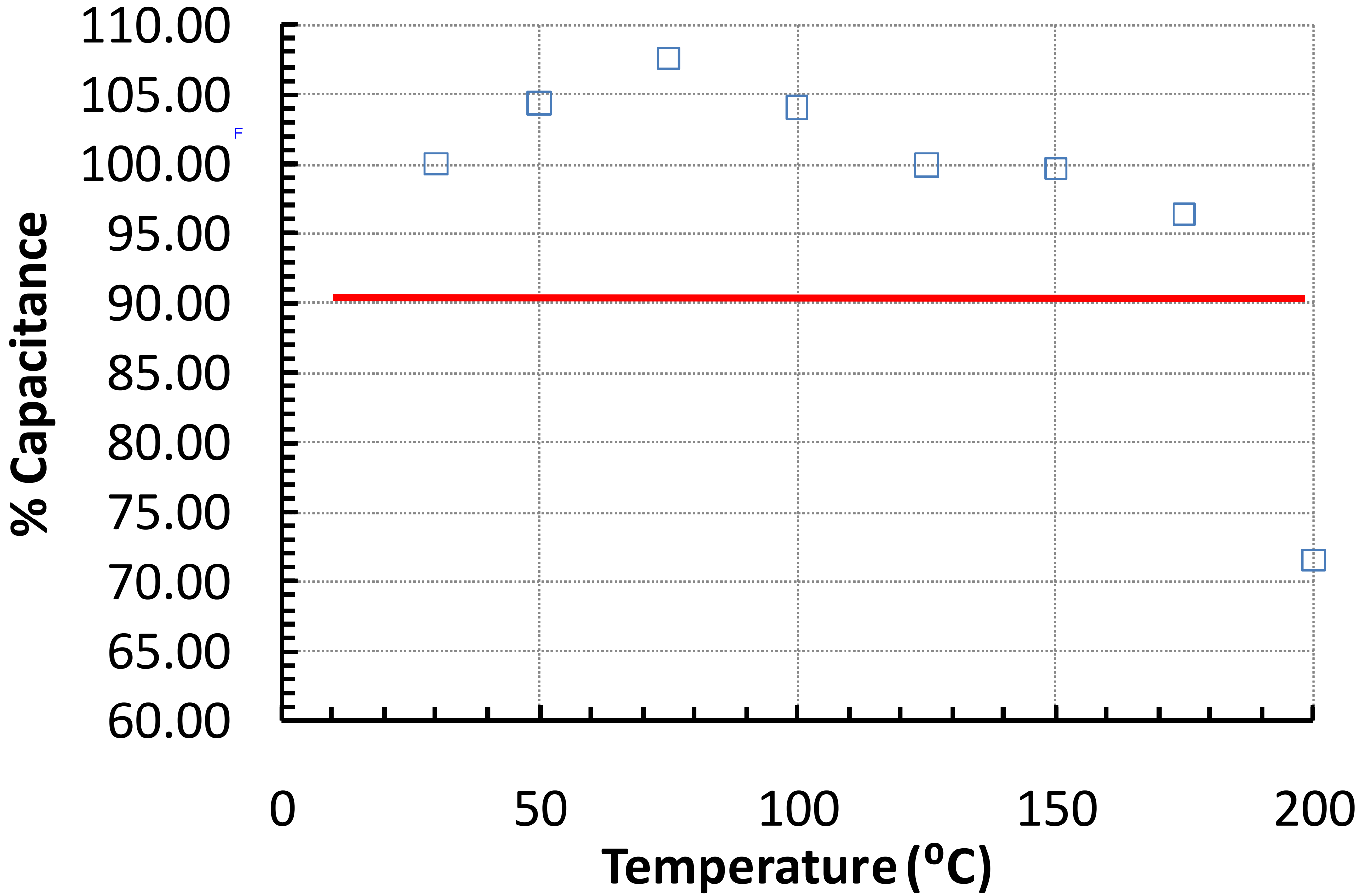
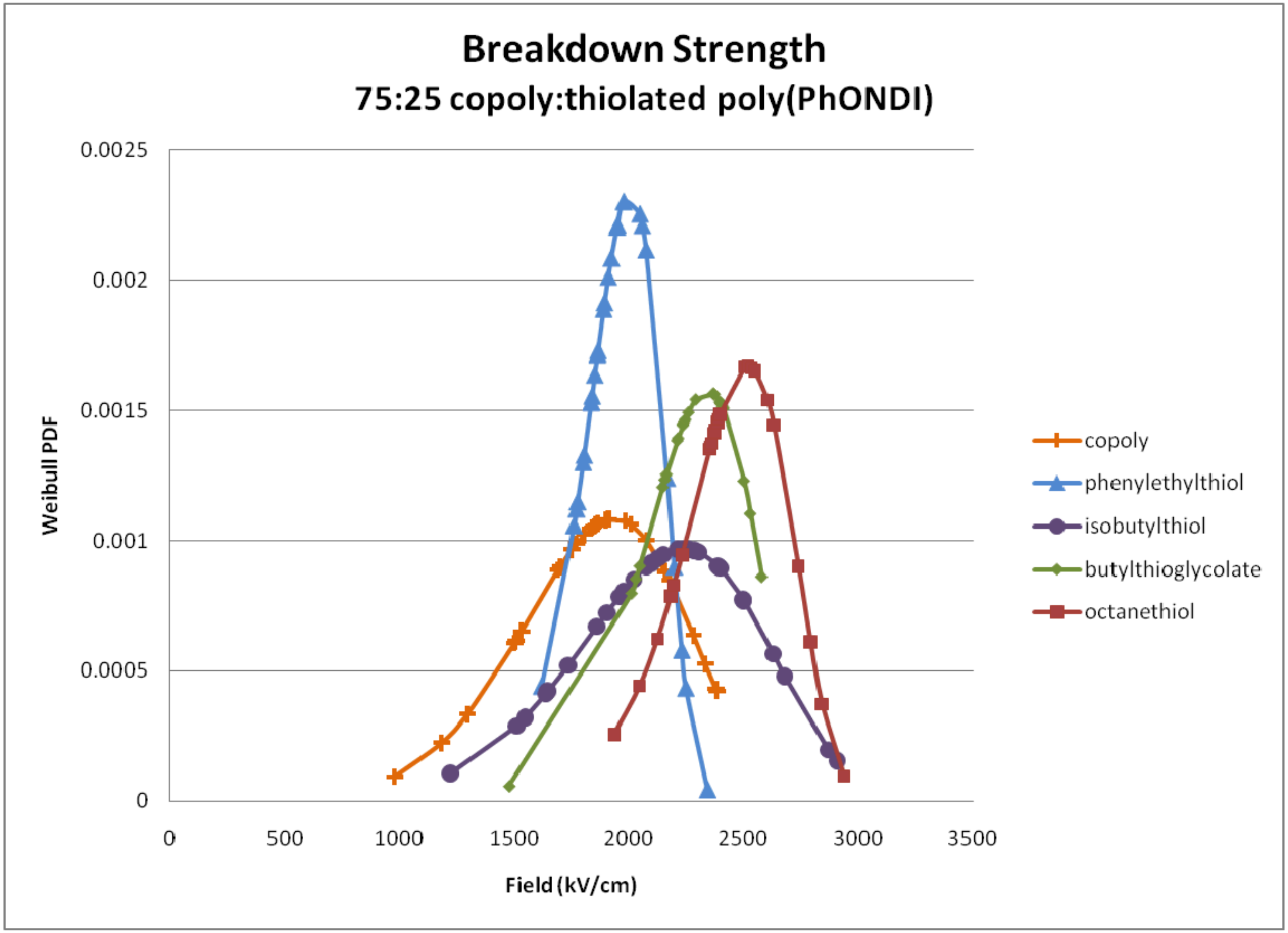
Sandia National Labs
Freedom Car



High Temperature Homopolymer
Measured at 10 kHz



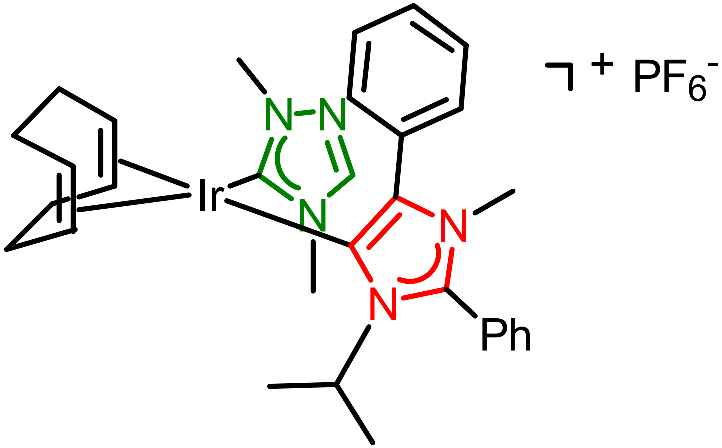
Co-poly(PhONDI)-poly(nbe) Polyblends

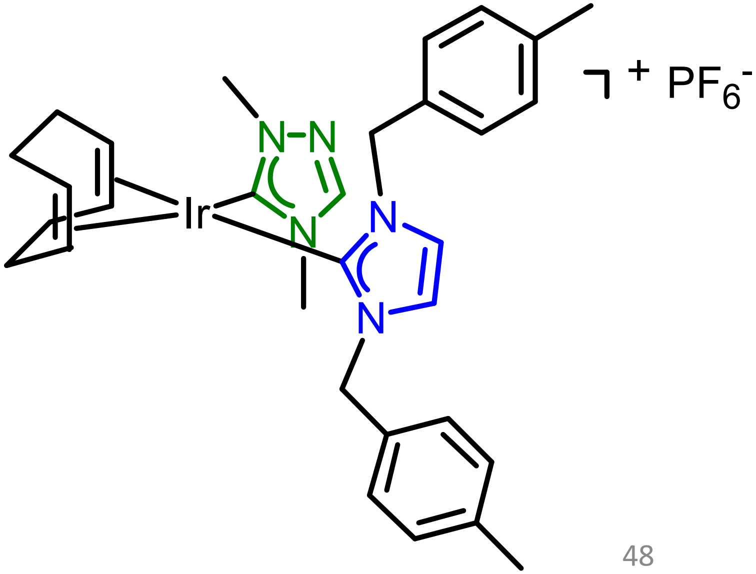


Fischer and N-Heterocyclic Carbene Complexes of Rh and Ir: Synthesis and Reactivity

Bob Crabtree, Yale University

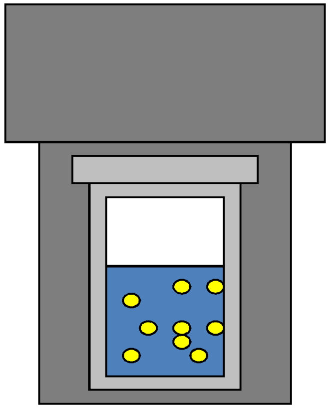
- Synthesis of new carbene ligands and transition metal carbene complexes
- Study of reactivity of new complexes: C-H activation, C-C couplings, electronic and steric effects of ligands, anion effects
- Determine reaction mechanisms with combination of computation and experiment
- Applications in catalysis based on understanding of properties



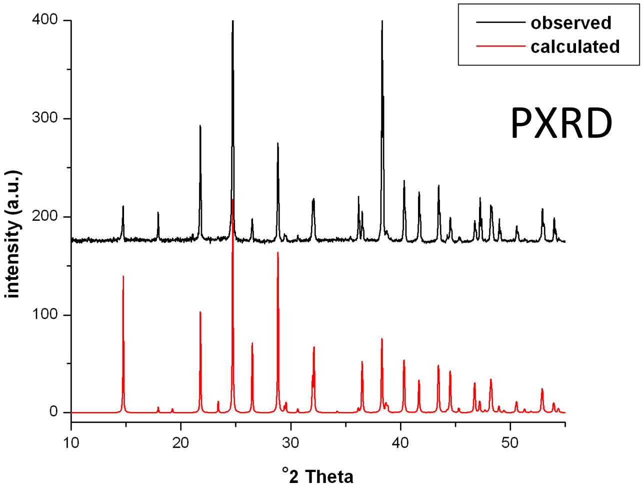


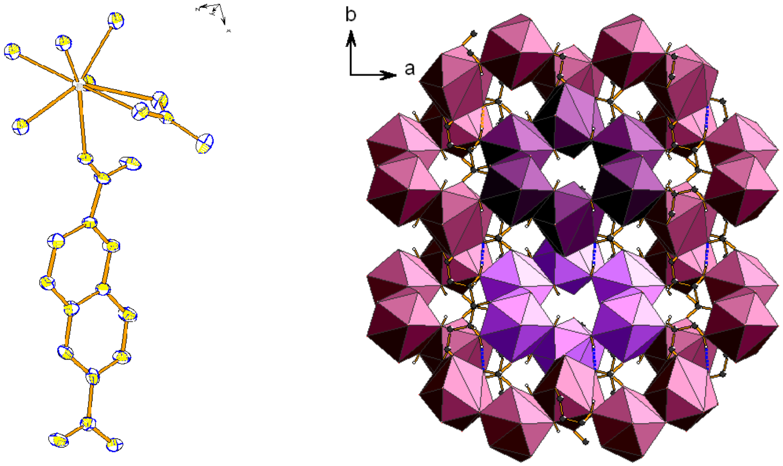
Metal-Organic Frameworks of Chiral Alkaline Earth Tartrates

Tony Cheetham,UCSB

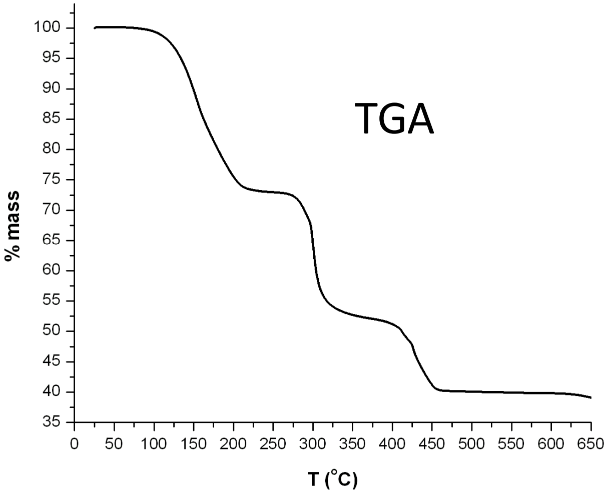


hydrothermal synthesis





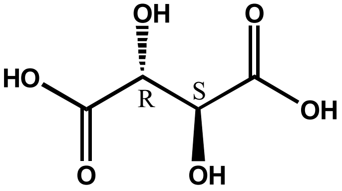
single crystal XRD



Alkaline Earth Tartrates

Goals

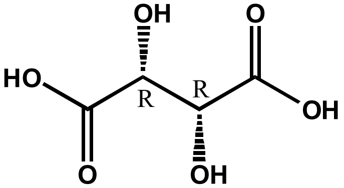
- **What variables control dense structure formation?**
  - **thermodynamics**
  - **kinetics**
  - **both?**
- **What is the role of chirality?**
- **Are dense consistent with porous framework trends?**
  - **hydration**
  - **connectivity**



L-tartaric acid

noncentrosymmetric
chiral

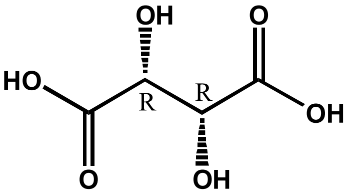
Ca

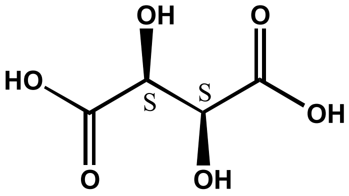


meso-tartaric acid

centrosymmetric
achiral

Sr





Ba

D,L-tartaric acid

racemic mixture

Alkaline Earth Tartrates

	RT	60 °C	100 °C	125 °C	150 °C	180 °C	200 °C	220 °C
Ca + LTar	$Ca(L)(H_2O)_2.2H_2O$	$Ca(L)(H_2O)_2.2H_2O$	mix	$Ca(L)$	$Ca(L)$	$Ca(L)$	$Ca(L)$	$Ca(L)$
Ca + mTar	$Ca(\mathit{m}).3H_2O$	$Ca(\mathit{m}).3H_2O$	$Ca(\mathit{m}).2H_2O$	$Ca(\mathit{m})$	$Ca(\mathit{m})$	$Ca(\mathit{m})$	$Ca(\mathit{m})$	$Ca(\mathit{m})$
Ca + DLTar	$Ca(DL)(H_2O)_4$	$Ca(DL)(H_2O)_4$	$Ca(DL)(H_2O)_4$	$Ca(DL)(H_2O)_4$	mix	mix	$[Ca(D,L)]_2.H_2O$	$[Ca(D,L)]_2.H_2O$

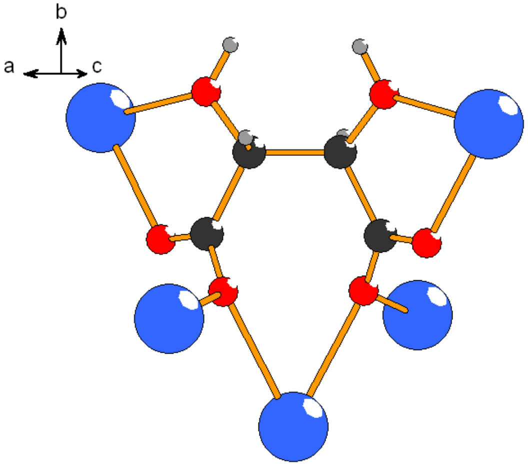
Sr + LTar	$Sr(L)(H_2O)_2.2H_2O$ $Sr(L)(H_2O)_3$	$Sr(L)(H_2O)$ $Sr(L)(H_2O)_3$	mix	$Sr(L)$	$Sr(L)$	mix	$Sr(\mathit{m})$	$Sr(\mathit{m})$
Sr + mTar	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$	$Sr(\mathit{m})$
Sr + DLTar	$Sr(DL)(H_2O)_4$	$Sr(DL)(H_2O)_4$	$Sr(DL)(H_2O)_4$	mix	mix	mix	$Sr(\mathit{m})$	$Sr(\mathit{m})$

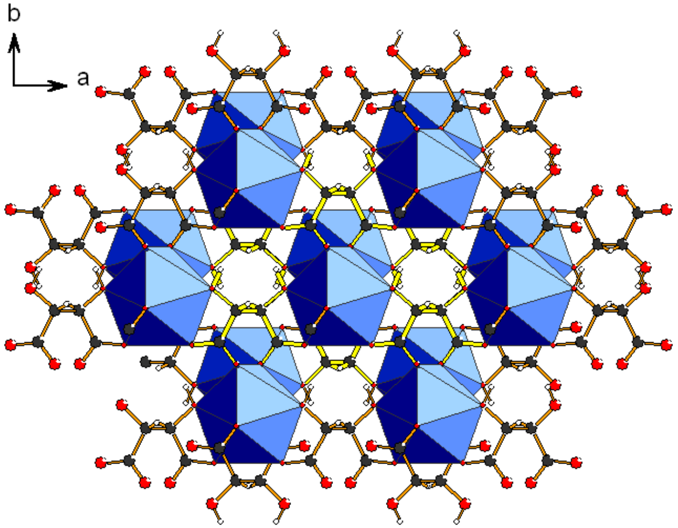
Ba + LTar	$Ba(L)$	$Ba(L)$	$Ba(L)$	$Ba(L)$	$Ba(L)$	$Ba(L)$	$Ba(L)$	$Ba(DL)$
Ba + mTar	$Ba(\mathit{m})(H_2O)$	$Ba(\mathit{m})(H_2O)$	$Ba(\mathit{m})(H_2O)$	$Ba(\mathit{m})(H_2O)$	$Ba(\mathit{m})(H_2O)$	$Ba(\mathit{m})(H_2O)$	mix	$Ba(DL)$
Ba + DLTar	$Ba(DL)(H_2O)_2$ $[Ba(DL)]_2(H_2O)_3$	$Ba(DL)$	$Ba(DL)$	$Ba(DL)$	$Ba(DL)$	$Ba(DL)$	$Ba(DL)$	$Ba(DL)$

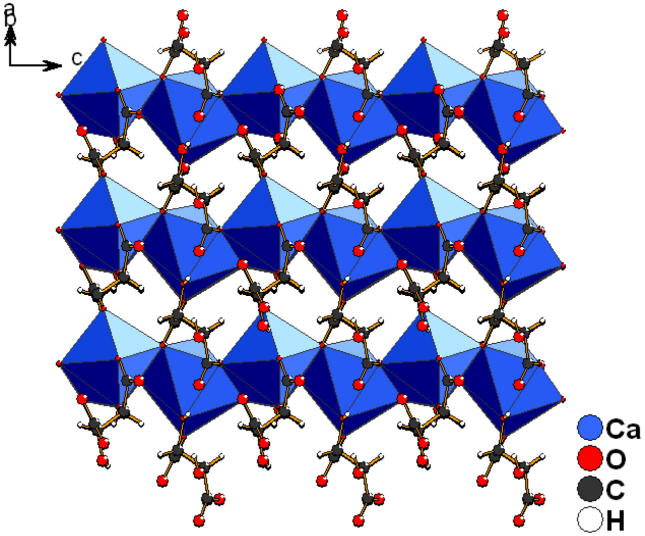
each color represents a unique phase

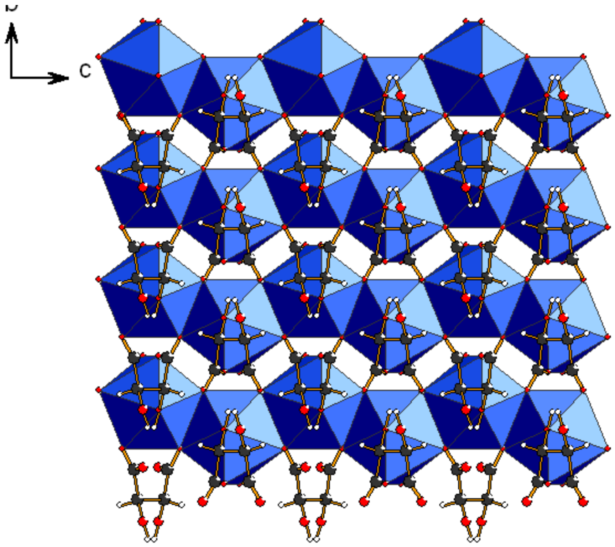
identical colors between metals indicate isostructural phases

Ca(L-Tartrate)









Summary

- **Phase behavior in alkaline earth tartrates is controlled by both thermodynamic and kinetic factors and is different for each cation, even isostructural Ca and Sr.**

- **Ca**: The **Ca(*m*)** phase is the most **thermodynamically** stable phase. Because relative stability differences between the phases are small no phase transformations are observed up to 220 °C.

- **Sr**: The **Sr(*m*)** phase is the most **thermodynamically** stable phase. The larger relative stability difference between phases creates a greater driving force promoting phase transformations to the more stable *meso* phase at 180 °C and above. Phase transformation is not observed at lower temperatures due to a **kinetic** barrier to the racemization of tartaric acid.

- **Ba**: The **Ba(DL)** phase is the most **thermodynamically** stable phase at high temperatures. The **Ba(L)** phase is likely the most **thermodynamically** stable at lower temperatures. However, **kinetic** factors favor the formation of the DL phase from racemic solutions.

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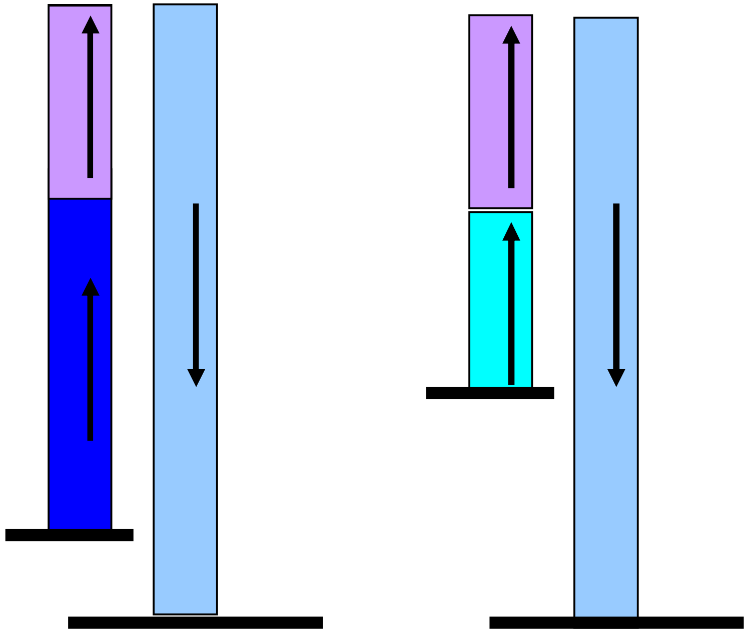
calorimetry



🟦 breaking solute-solute bonds (endo)

🟪 breaking solvent-solvent bonds (endo)

□ forming solute-solvent bonds (exo)