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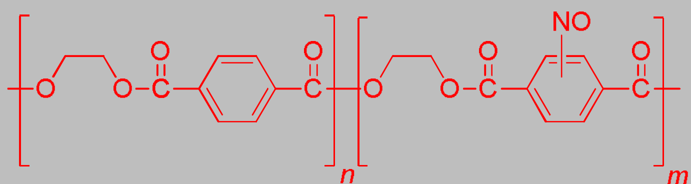

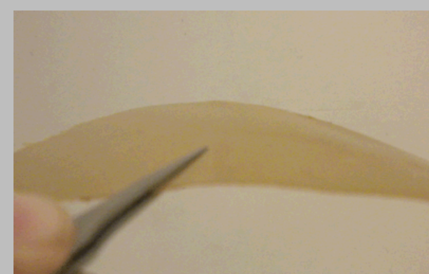

Nitrated Poly(ethylene terephthalate) as a Dielectric Material for Capacitors

Victor Piñón III, Brent E. Dial, Shawn Dirk, and Benjamin J. Anderson

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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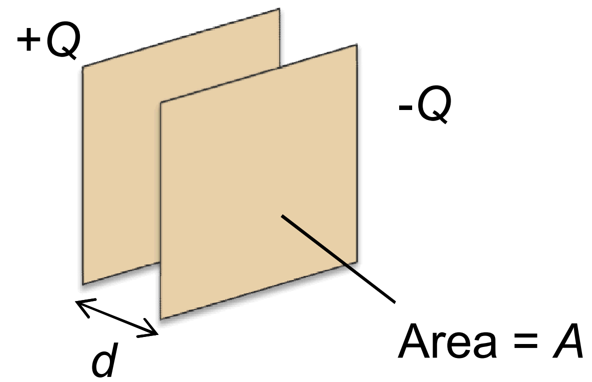
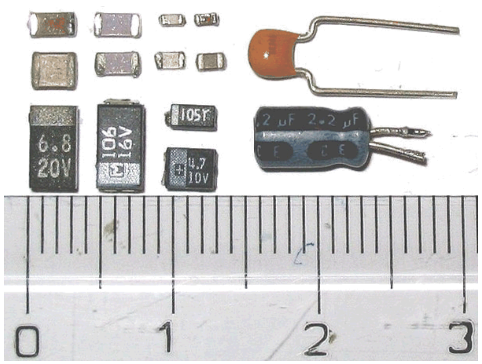
Capacitors

- Device to store an electrostatic charge in an electric field
- Two conductive components separated by a dielectric material
- Capacitance is greatest when there is a narrow separation between two conductors of large area
- BOPET (Mylar®) is a common dielectric used



$$C = \frac{\varepsilon_0 A}{d}$$

ε_0=permittivity of air



$$C \equiv \frac{Q}{\Delta V}$$

C= capacitance
Q= charge
ΔV= potential difference

Serway, R. A.; Jewett, Jr., J. W. *Physics for Scientists and Engineers*; Belmont, CA, 2010.
Image from http://en.wikipedia.org

Why Nitrate PET?

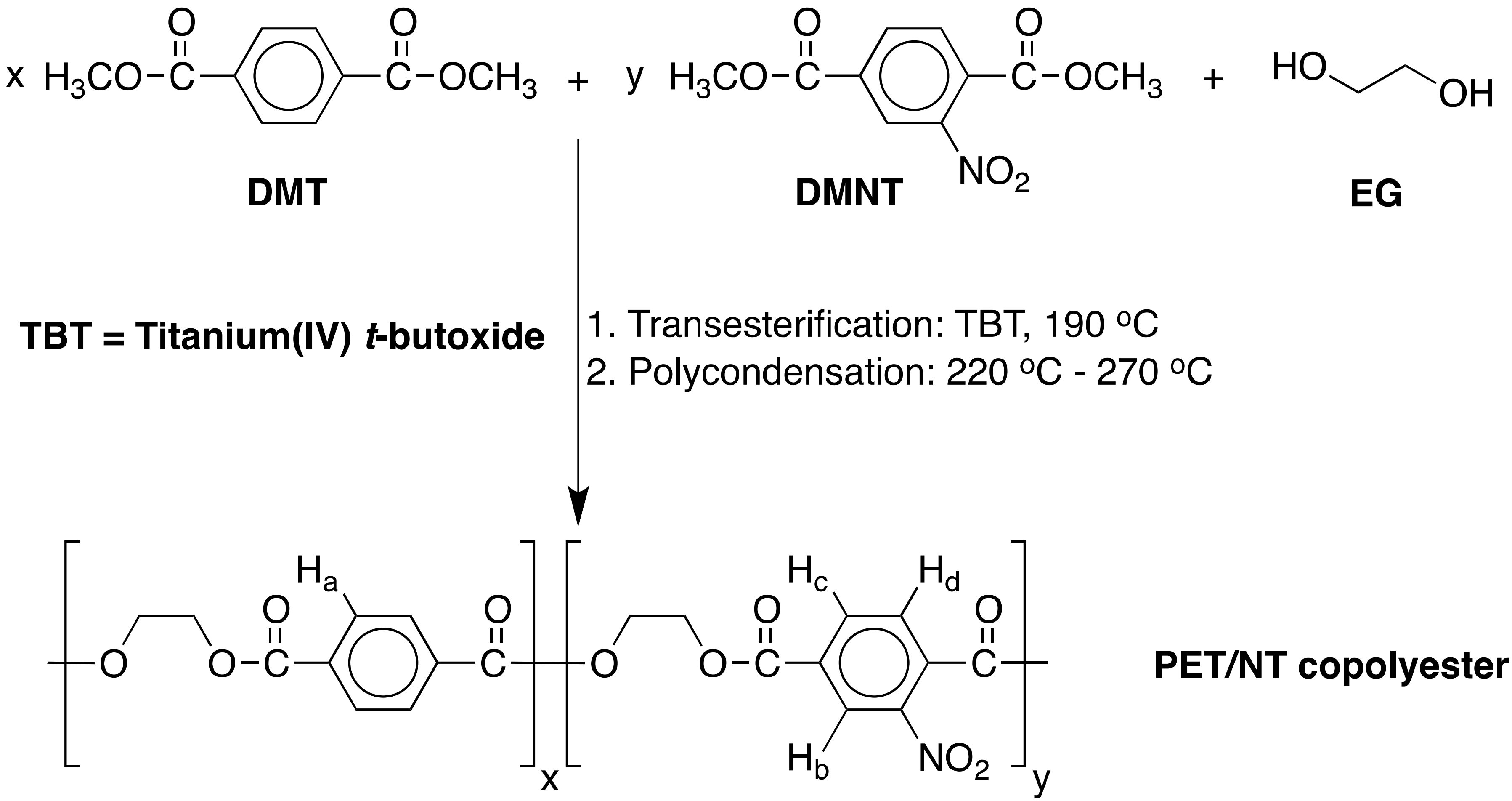
- Nitration of aryl groups shown to depress melting point (T_g unaltered)
  - Thermal failsafe
  - Processing advantages
  - T_m tunable
- Nitro groups serve as radical-traps
  - Radicals often the source of degradation in PET
  - Stability in extreme environments (i.e. radiation in outer space)

Polyester	T_g (°C)[a]	T_m (°C)[b]
PET	80	258
$PET_{95}NT_5$	82	248
$PET_{90}NT_{10}$	82	235
$PET_{85}NT_{15}$	84	223
$PET_{80}NT_{20}$	84	214
$PET_{70}NT_{30}$	83	180
$PET_{50}NT_{50}$	81	—
$PET_{25}NT_{75}$	85	—
PENT	88	—

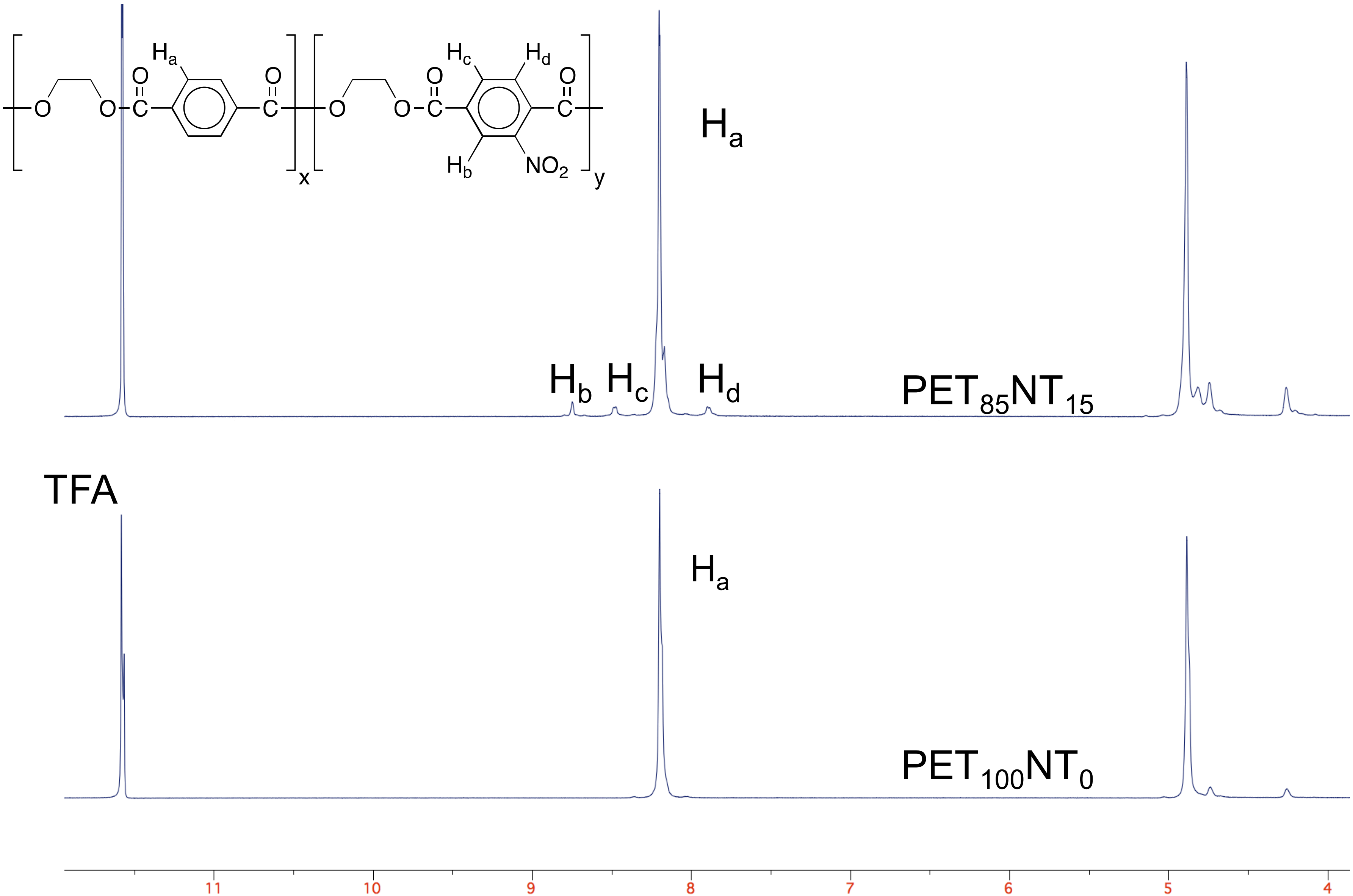
- Nitro pendant groups can disrupt crystallinity
  - Processing advantages
  - Improve on certain material properties (solubility, pilling, brittleness, etc.)

D. P. R. Kint, et al. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3761- 3770.

Synthesis


x $H_3CO-C(=O)-C_6H_4-C(=O)-OCH_3$ + y $H_3CO-C(=O)-C_6H_3(NO_2)-C(=O)-OCH_3$ + HO OH
DMT
DMNT
EG
TBT = Titanium(IV) *t*-butoxide
1. Transesterification: TBT, 190 °C
2. Polycondensation: 220 °C - 270 °C
H_a
H_c
H_d
H_b
NO_2
PET/NT copolyester

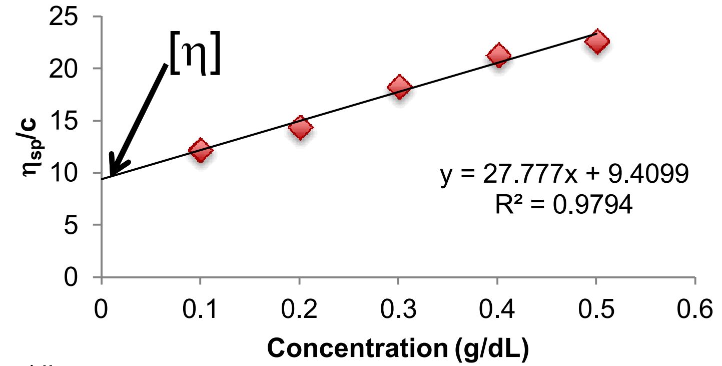
NMR Verification of Nitration



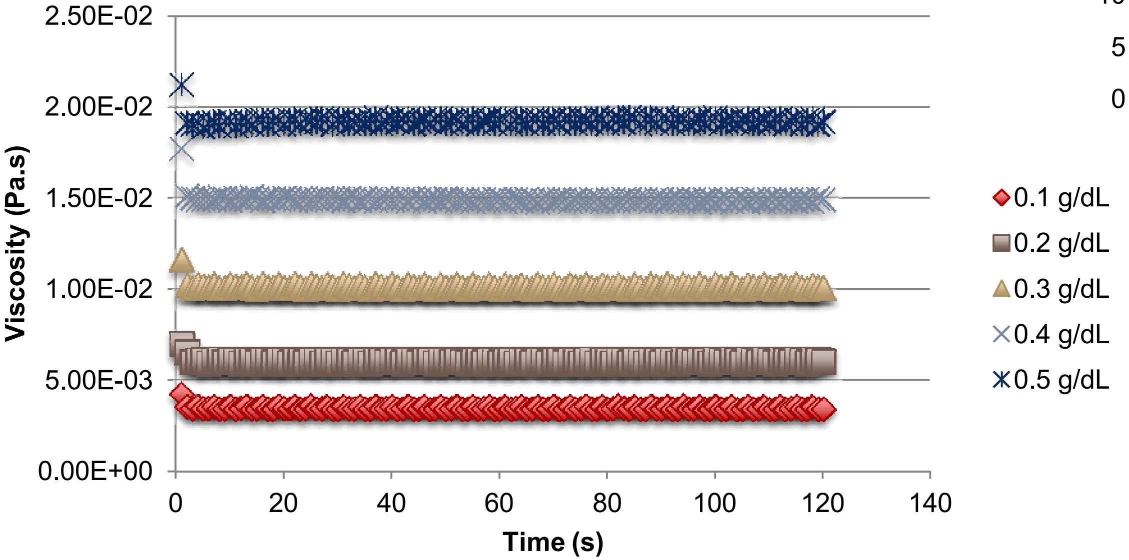
Molecular Weight Determination

- Polymer solubility prevented GPC
- Dilute solution viscosity employed

Mark-Houwink Plot



PET/NT 90/10
M_v=29,000



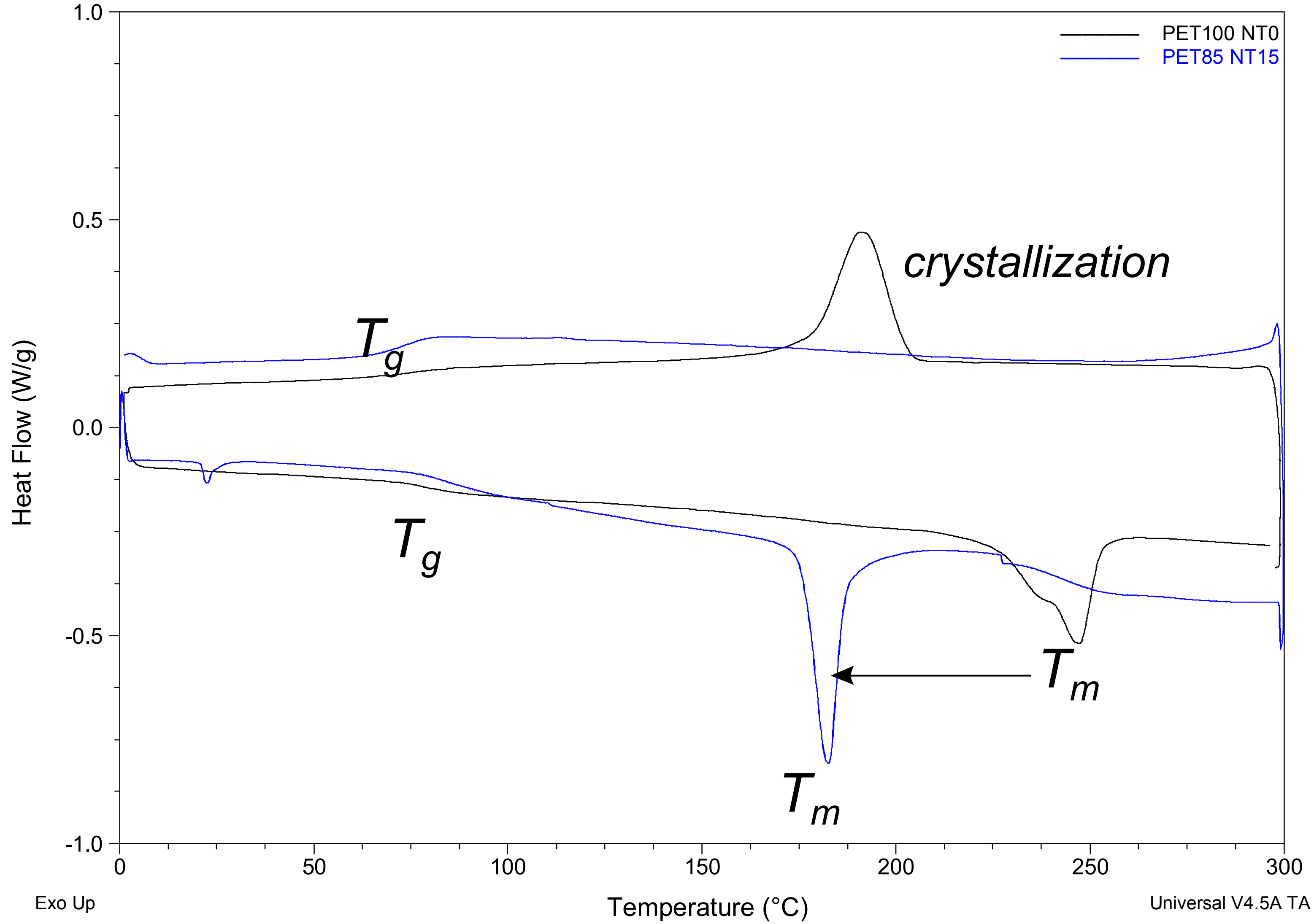
$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$$\eta_{sp} = \eta_{rel} - 1$$

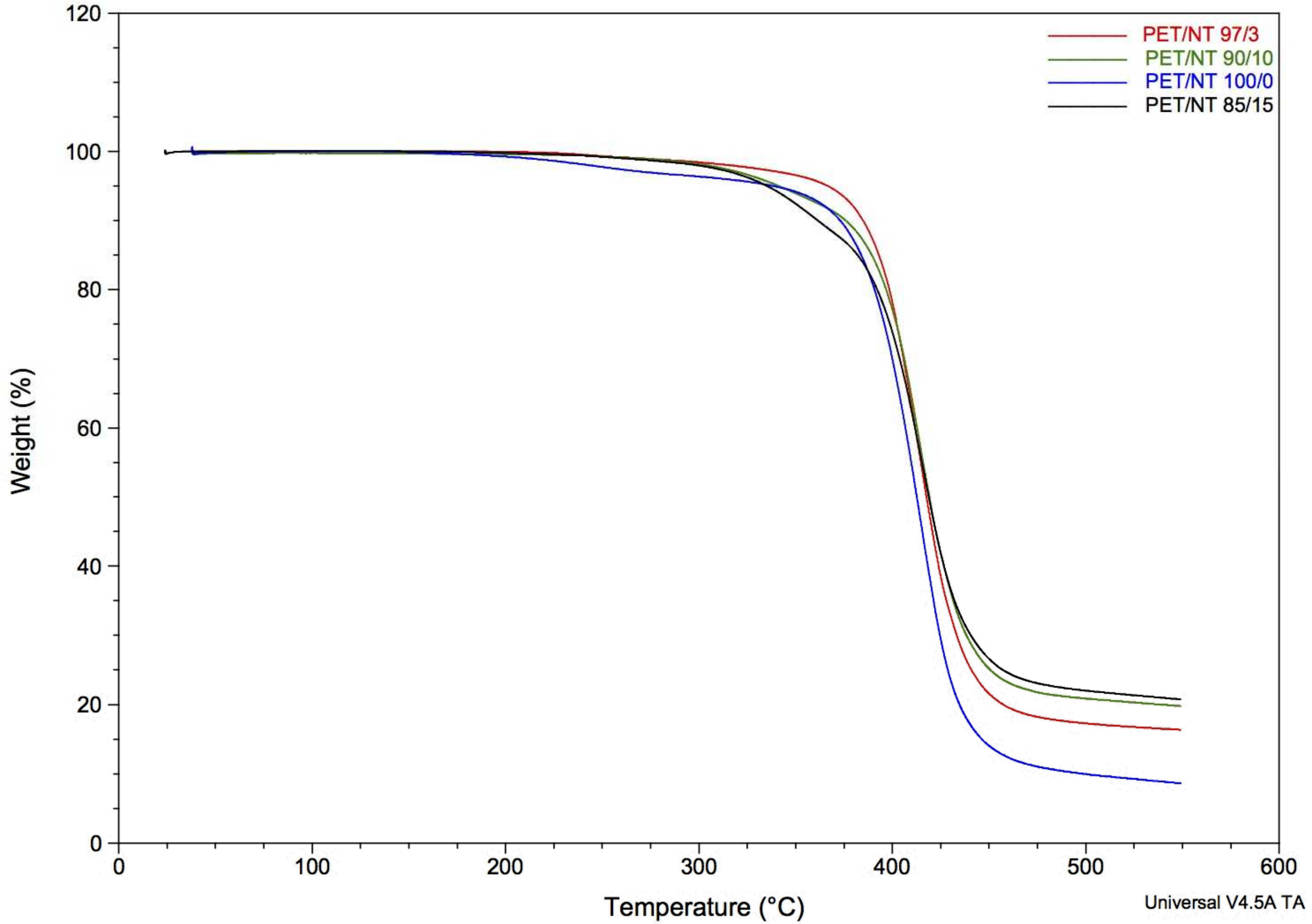
$$\eta_{red} = \frac{\eta_{sp}}{c}$$

$$[\eta] = KM^a$$

Thermal Characterization - DSC



Thermal Characterization - TGA



Characterization Overview

Composition	M_v	T_g (°C)	T_m (°C)	ΔH (J/g)	% Crystallinity
100/0	49,000	76	250	37	26.6
99.9/0.1	42,000	78	235	26	18.4
99.5/0.5	31,000	73	231	31	21.9
99.25/0.75	38,000	73	222	31	22.2
99/1	52,000	79	231	27	19.2
97/3	23,000	77	214	17	12.2
90/10	29,000	76	194	16	11.7
85/15	57,000	80	183	28	19.8

Film Preparation

- Solvent cast/drawn down using HFIP
- Rigorous drying schedule over temperature range up to 170 °C,
- Sputtering of electrodes for dielectric and breakdown characterization

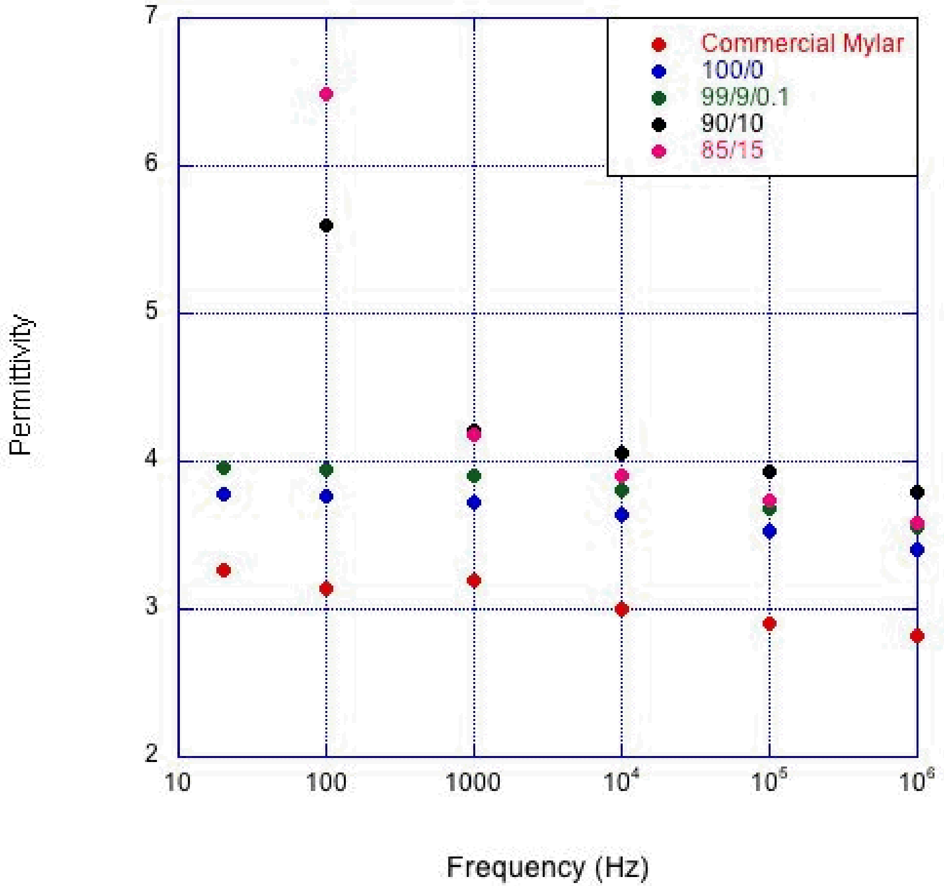
$PET_{100}NT_{0}$ $PET_{99}NT_{1}$

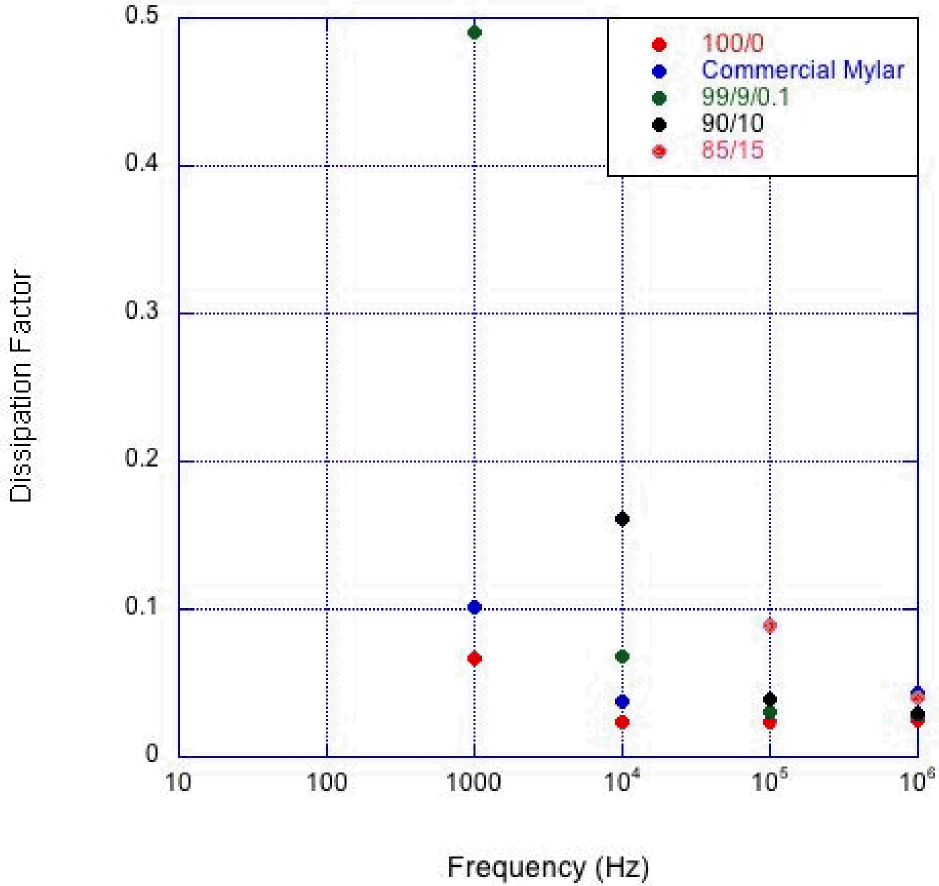
polymer

dried film

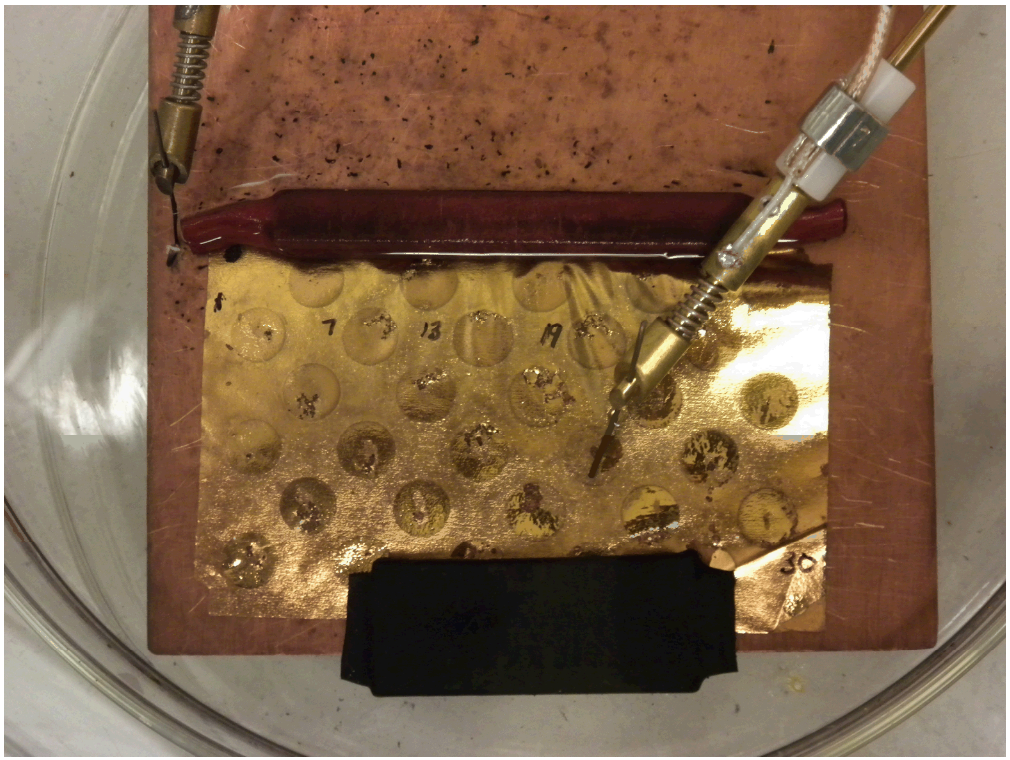
sputter coated

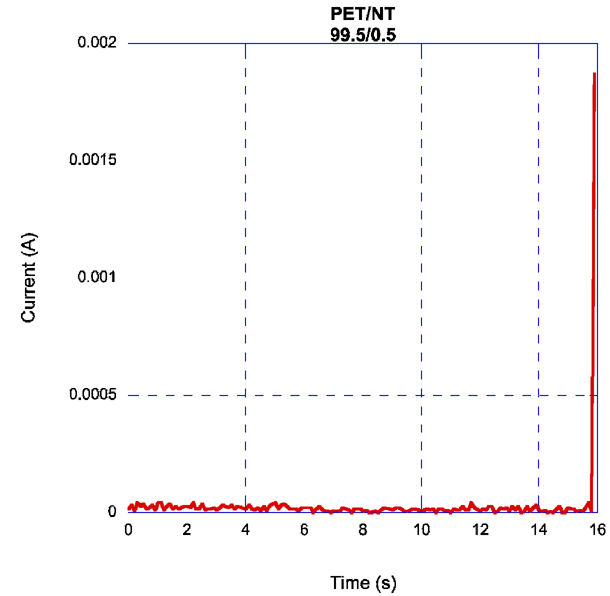
Dielectric Characterization

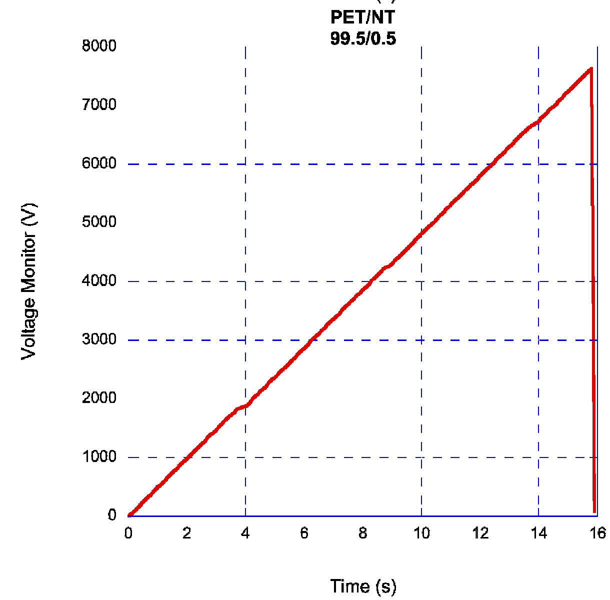




Breakdown Characterization







Breakdown Characterization

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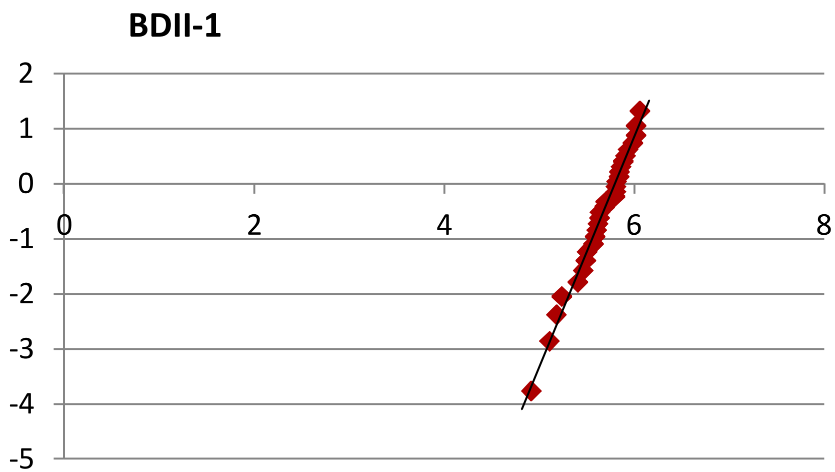
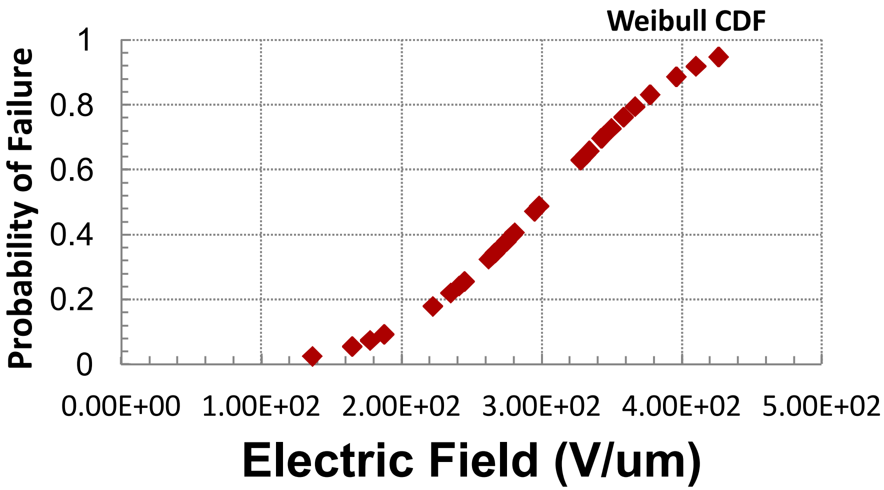
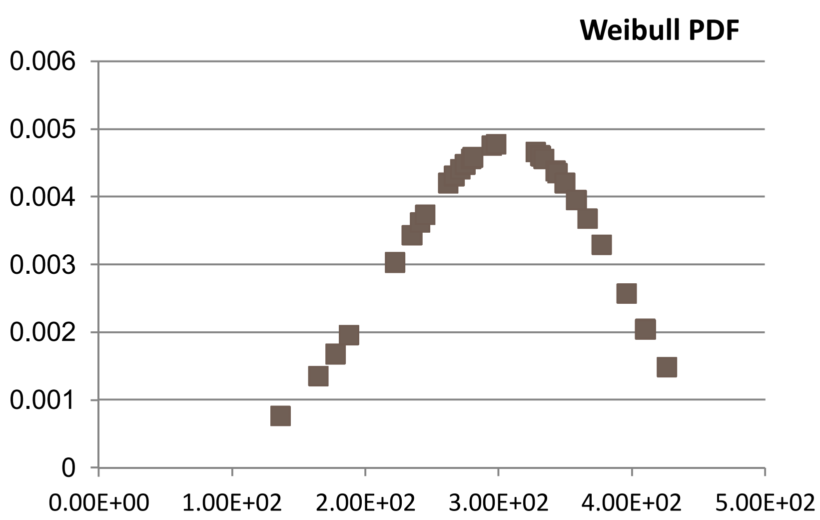


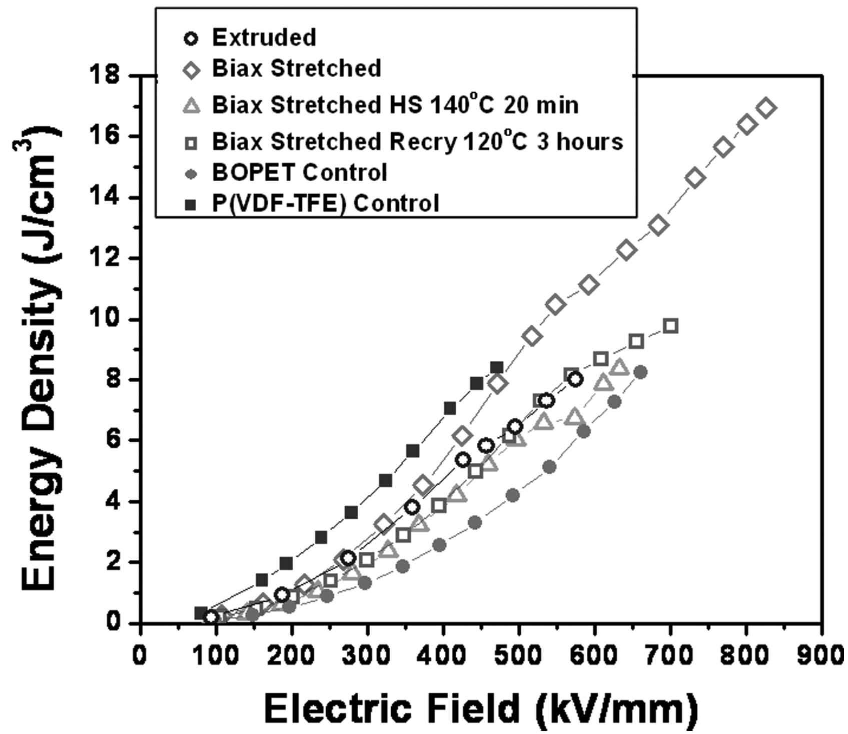




Composition	E_0 (V/μm)	beta	Energy Density (J/cm^3)
100/0	304.17	2.15	1.49
99.9/0.1	352.74	5.16	2.06
99.5/0.5	414.55	5.36	2.94
99.25/0.75	280.44	2.66	1.45
90/10	328.00	4.15	2.95
85/15	341.83	3.94	2.02

Nitrated vs. Virgin Mylar

- PET is extruded and quenched in an amorphous state and drawn to become biaxially oriented (BOPET)
- Subsequent heating allows for crystallization, which leads to high Young's modulus (~4 GPa)
- NPET for our studies is solvent cast
- Energy densities higher than similarly prepared PET, but not as high as BOPET (~5 J/cm^3)
- Processing similarly allows for more direct comparison



J. M. Carr, et al. *Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 882-896.

Conclusion

- A series of nitrated PET copolymers have been synthesized
- Incorporation of nitro-groups into the backbone have depressed the melting point of the polymers
- Increased permittivities and breakdown strengths are measured in these polymers
  - Nitro groups polarize the aryl pi-orbital electrons and serve as electron traps
- Biaxial orientation will be introduced to further enhance these properties

Acknowledgements

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