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Radiation Tolerant Polymeric Materials through the Incorporation of Small Molecule Dopants

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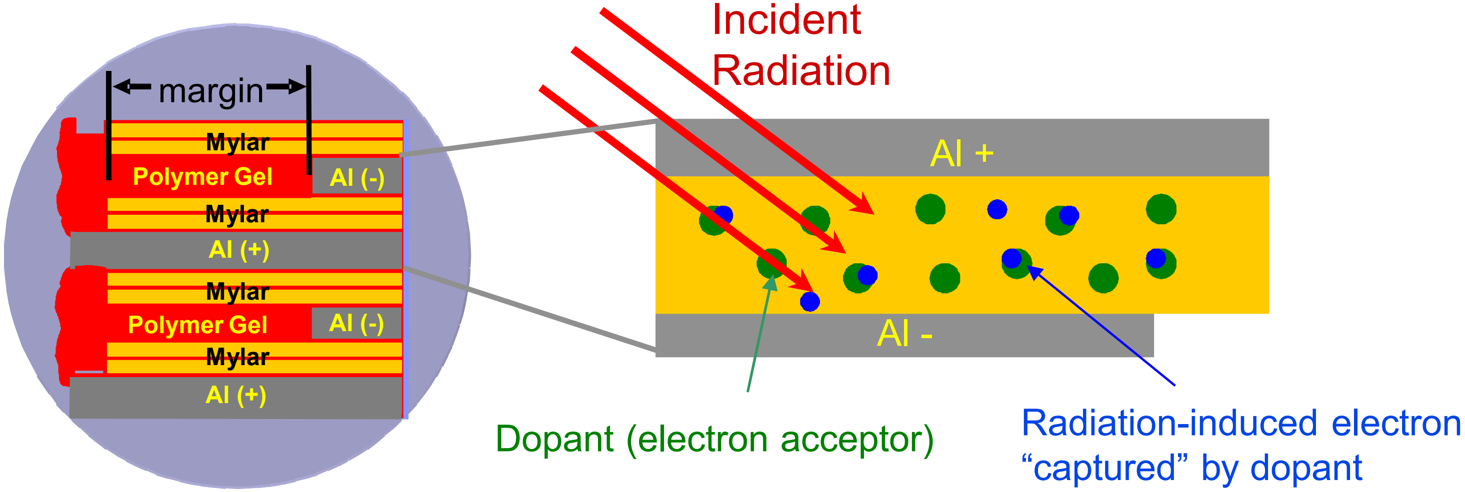
Sandia National Laboratories NM
[1]Organic Materials (1821)
[2]Organic Materials (2453)
[3]NNSA Satellite Programs (5732)

PolyMAC 2007,Kansas City, Missouri

Why is TNF-doped Mylar critical?



- Electron-hole pairs generated in radiation environment; electrons highly mobile
- Dopant scavenges electrons induced by the incident radiation
- TNF or an alternative electron trap is required to make the Mylar radiation tolerant

Historical developments

- Edwards (SNL)
  - Surveyed poly(vinylidene fluoride) (PVDF), poly(ethylene terephthalate) (PET, Mylar), and polysulfone for radiation resistant capacitors (late 1970's)[1]
- Kurtz, Arnold, and Hughes (SNL)
  - Continued work on PVDF and PET for radiation tolerance[2]
  - Found PET to be less inherently rad-hard, but after doping with TNF from benzyl alcohol, RIC reduced 99 % (early 1980's)[3]
  - Poor understanding of doping physics and RIC dependence on dopant and polymer

[1]L.R. Edwards, *Sandia Report* 1981 SAND-81-0667C
[2]S.R. Kurtz, R.C. Hughes, *JAP* 1983 54 p229-237
[3]S.R. Kurtz, C. Arnold, R.C. Hughes, *IEEE Trans Nucl Sci* 1983 30 4077-4080

Historical developments

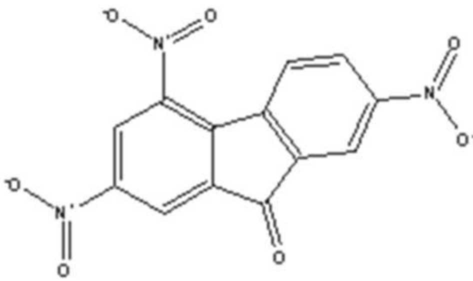
- Courtalds Perfomance Films (Virginia)
  - Produced doped TNF-mylar in 50,000 sq. ft. batches (late 1980’s)[1]
  - Last manufactured in 1993
  - TNF classified as an explosive in late 1990’s and external vendors will no longer use
  - Ethylene glycol selected as solvent without clear understanding

[1]G.C. Bischoff, L.R. Edwards, *Sandia Report* 1990 SAND-90-2362C

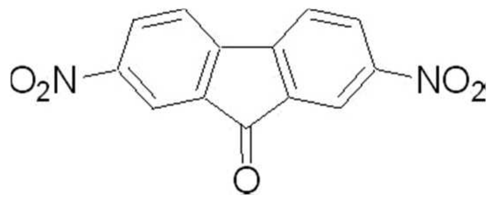
Insights from recent research

- Several different dopants provide > 95 % RIC reduction in mylar
  - Dopants with conjugated rings and electron-withdrawing constituents work well
  - E.g., tetracyanoquinodimethane (TCQM), nitroacenaphthene (NAN), and dinitrofluorenone (DNF)
- Ethylene glycol best solvent for most dopants
  - Whole range of solvents attempted (e.g., toluene, BEHS, MEK, DBP, DMSO, DMF)
  - Solubility parameter not a factor in doping effectiveness
  - Role of EG still not completely understood

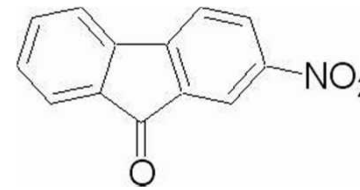
Materials



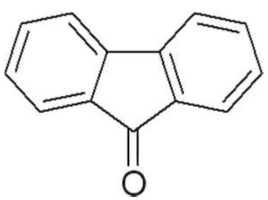
2,7,9-trinitro-9-fluorenone
(TNF)



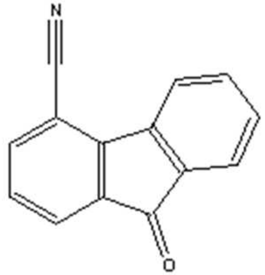
2,7-dinitro-9-fluorenone
(DNF)



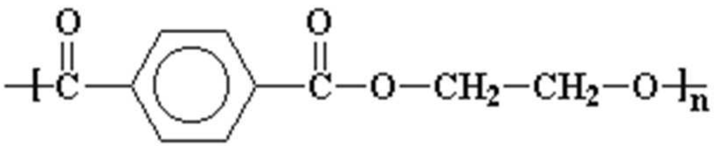
2-nitro-9-fluorenone
(NF)



9-Fluorenone
(F)



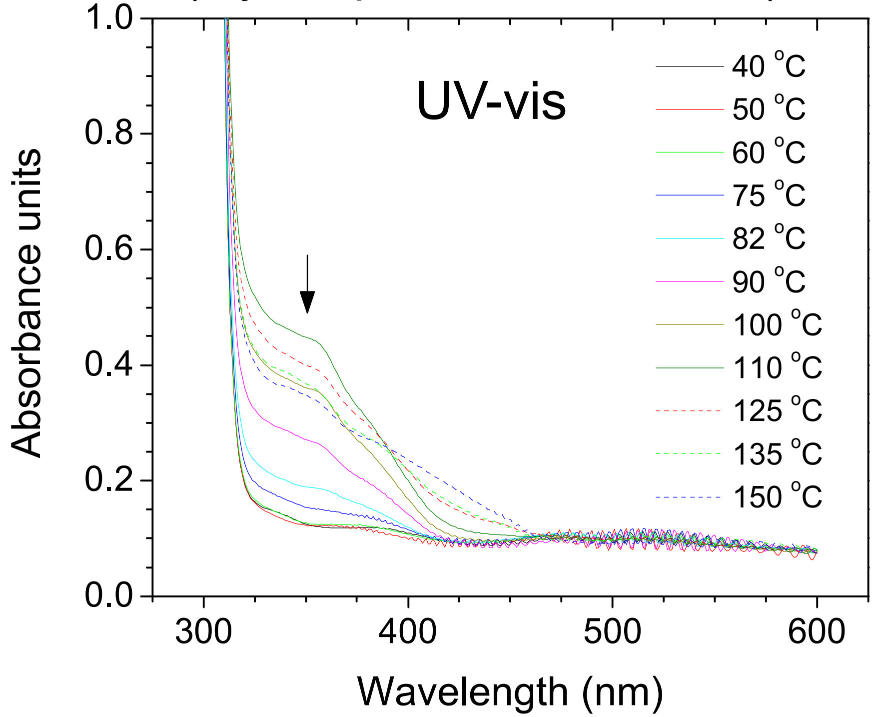
Cyanofluorenone
(CF)

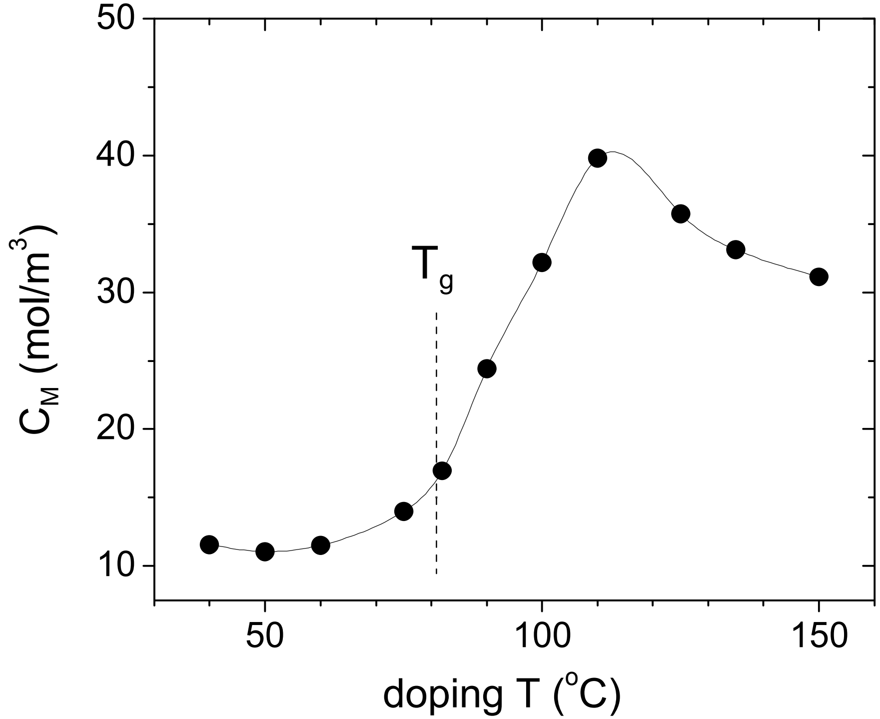


Poly(ethylene terephthalate)
(PET)

Doping temperature dependence

TNF-doped mylar spectra
(mylar spectrum subtracted)





- C_M rapidly increases above T_g, then decreases above ~ 115 ^{o}C

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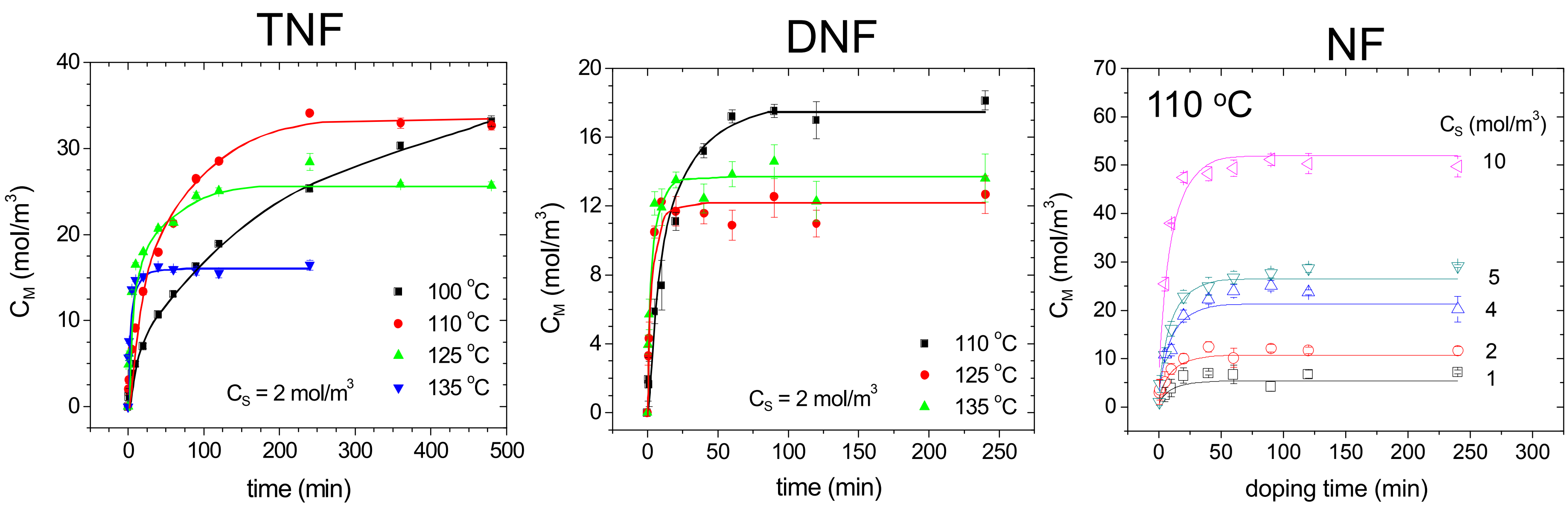
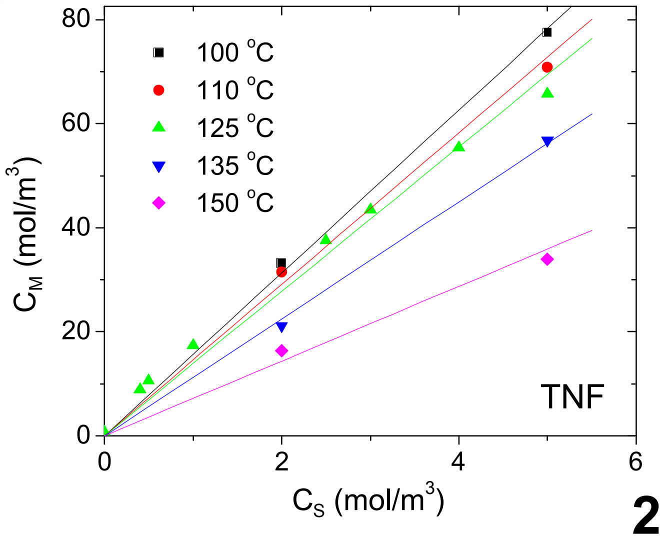
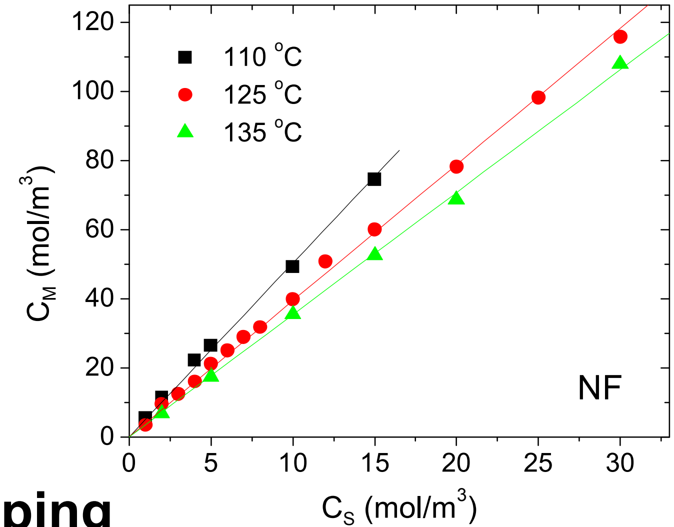
Short-time doping behavior



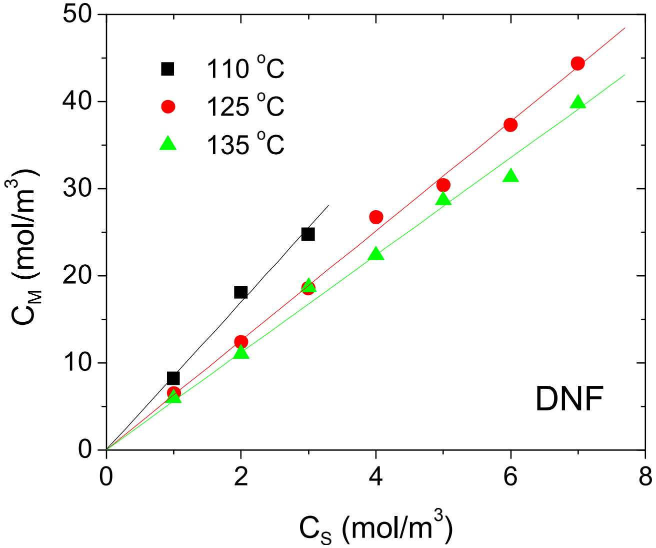
- Diffusion-limited behavior at short (kinetic-dominated) times

Long-term doping behavior



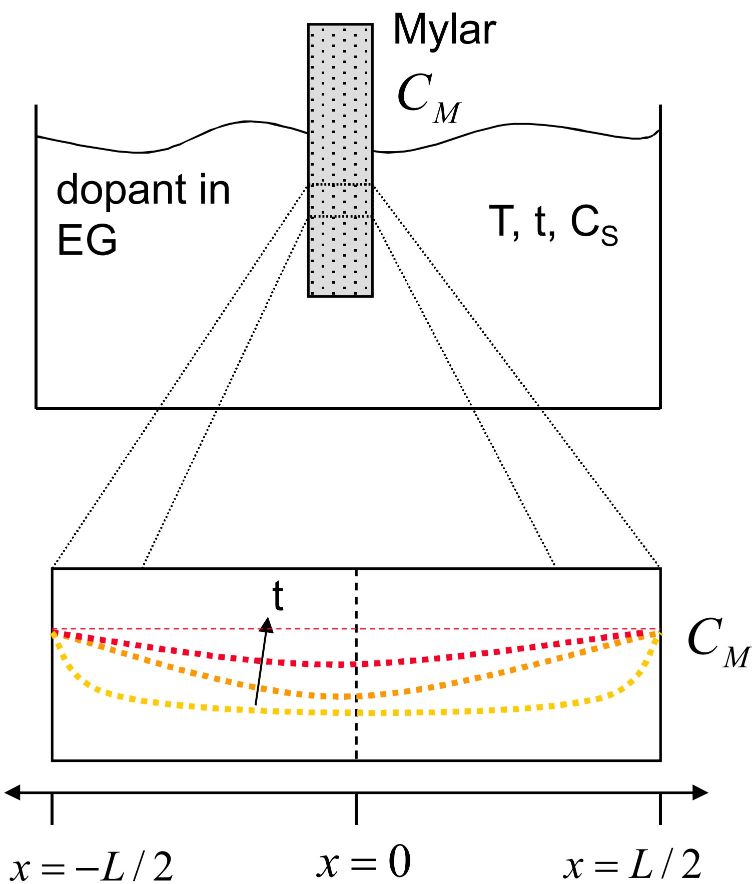


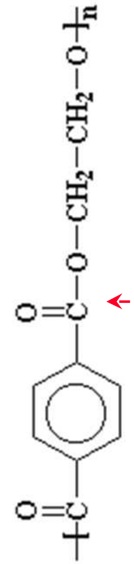
20 h doping



- Langmuir adsorption isotherm behavior at long (equilibrium) times

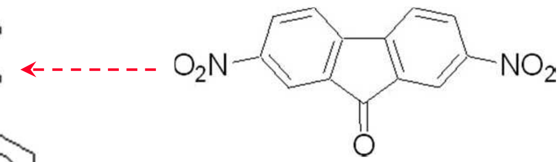
Adsorption-diffusion model





1) Adsorption[1]

$$d + M \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} d \cdot M$$



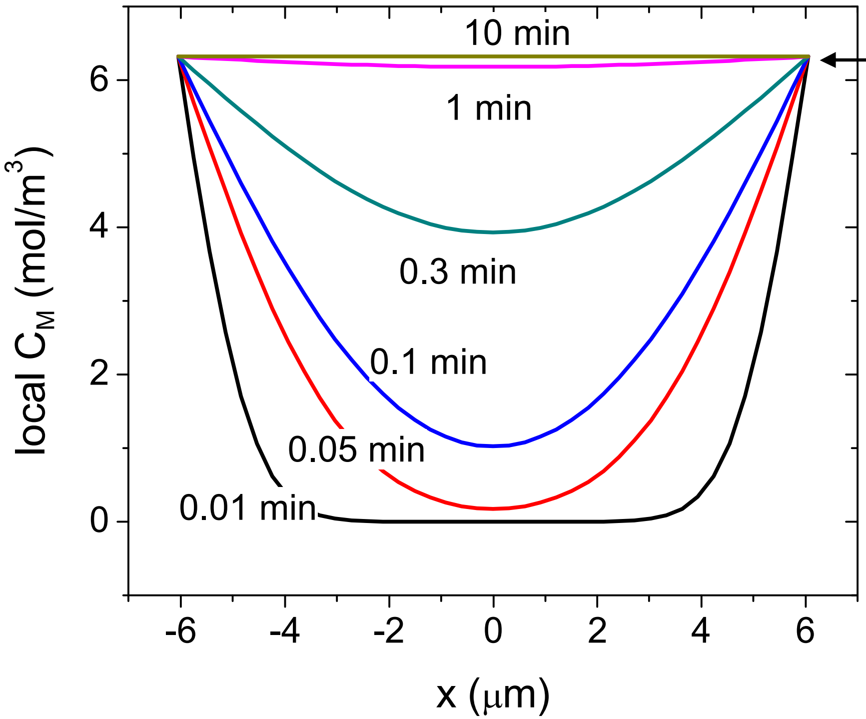
$$\frac{dC_{d \cdot M}}{dt} = k_A \left(C_S C_V - \frac{C_{d \cdot M}}{K_A} \right)$$

2) Diffusion[2,3]

$$\frac{\partial}{\partial x}\left(D \frac{\partial C_M}{\partial x} \right) = \frac{\partial C_M}{\partial t}$$

[1]S.H. Fogler, *Elements of Chemical Reaction Engineering* 1999
[2]R.B. Bird, W. E. Stewart, E. N. Lightfoot, *Transport Phenomena* 1960 p352-370
[3]R.M. Barrer *J Chem Soc* 1951 1874-1876

Modeled diffusion profiles



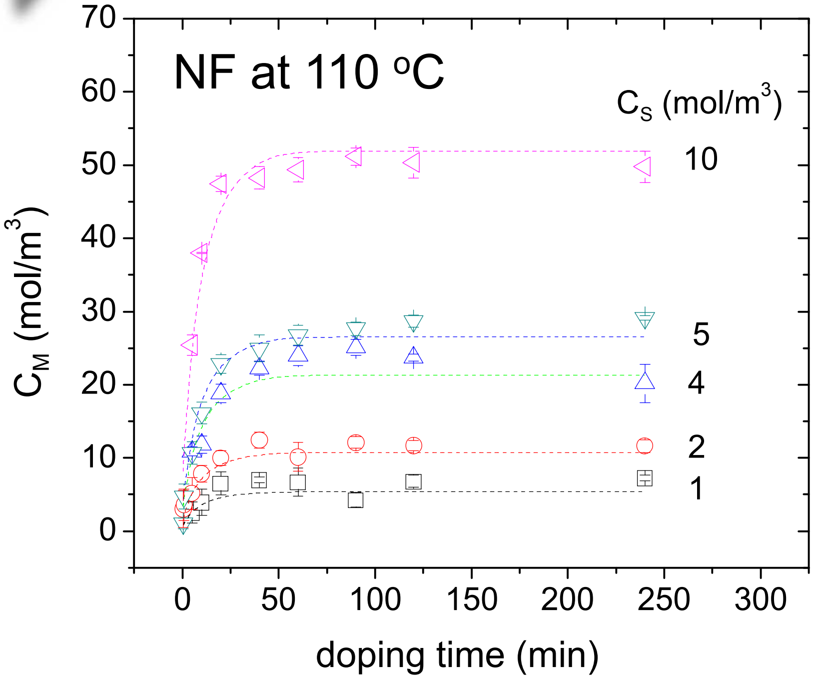
$C_{d \cdot M}$ constant over time

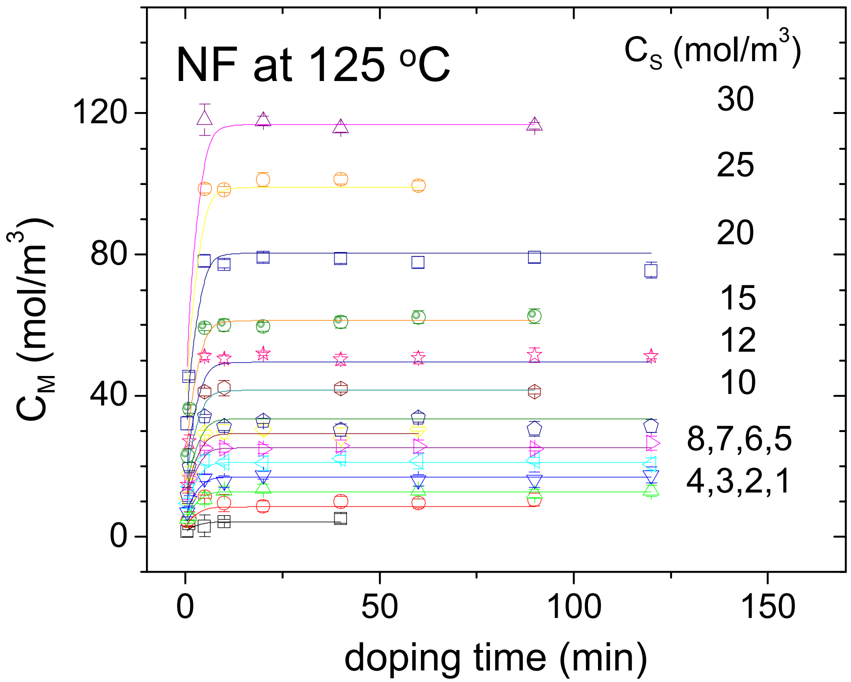
Films are annealed above T_g and UV-vis evaluates average concentration

$$C_{d \cdot M} = \frac{C_S C_t}{C_S + 1/K_A}$$

$$C_M(x,t) = C_{d \cdot M} \left\{ 1 - 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1/2)\pi} \exp\left[-(n+1/2)^2 \pi^2 \frac{Dt}{(L/2)^2} \right] \cos\left[(n+1/2)\pi \frac{x}{L/2} \right] \right\}$$

Doping over time

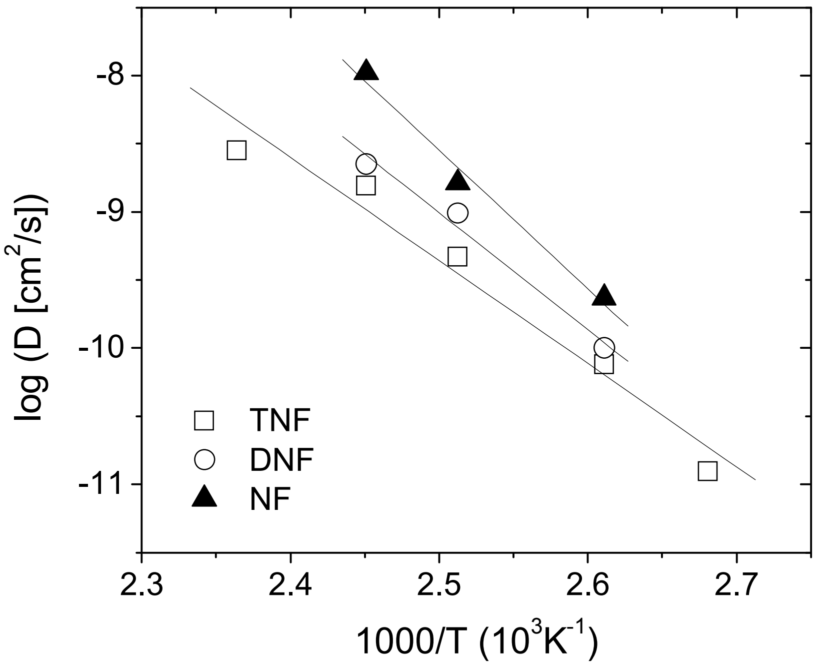




Data also modeled for

- NF (135 °C)
- DNF (110, 125, 135 °C)
- TNF (100, 110, 125, 135, 150 °C)
- CF and F in progress

Evaluated diffusivities

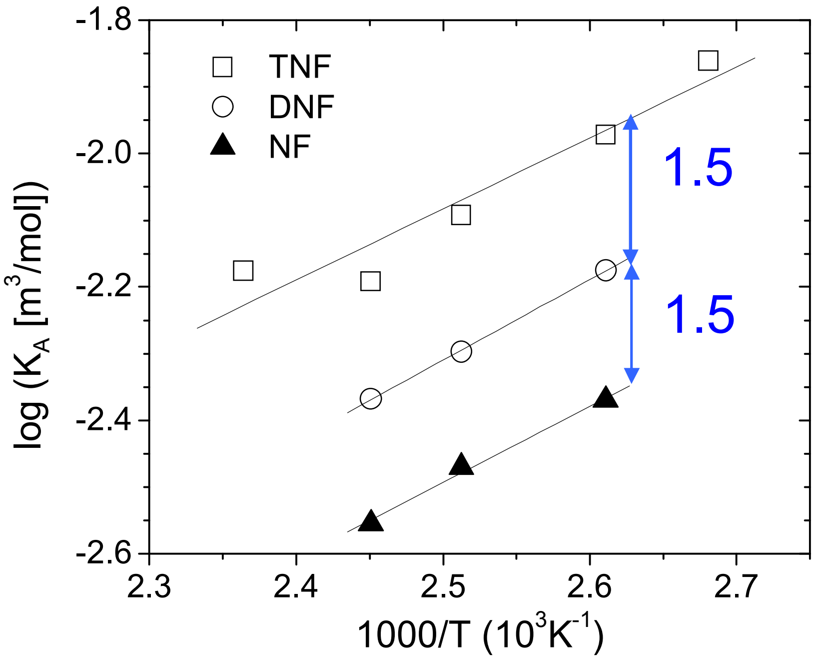


• Arrhenius T-dependence[1]
$D = D_0 \exp(E_a/RT)$

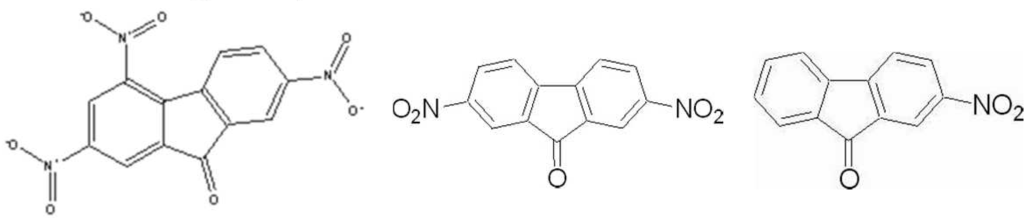
• Activation energy of diffusion dependent on molecular size, not functionality
→ Near-constant E_a physically meaningful

[1]D.D. Deppe, R. D. Miller, J. M. Torkelson, *J Poly Sci Poly Phys* 1996 34 2987-2997

Evaluated adsorption constants



- K_{A0} separated by equal increments because TNF has 3 interaction sites, DNF 2, and NF 1: reactivity increases by factor of 1.5 with each nitro group



$$K_A = k_A / k_{-A} \sim K_{A0} \exp(-E_a / RT)$$ [1]

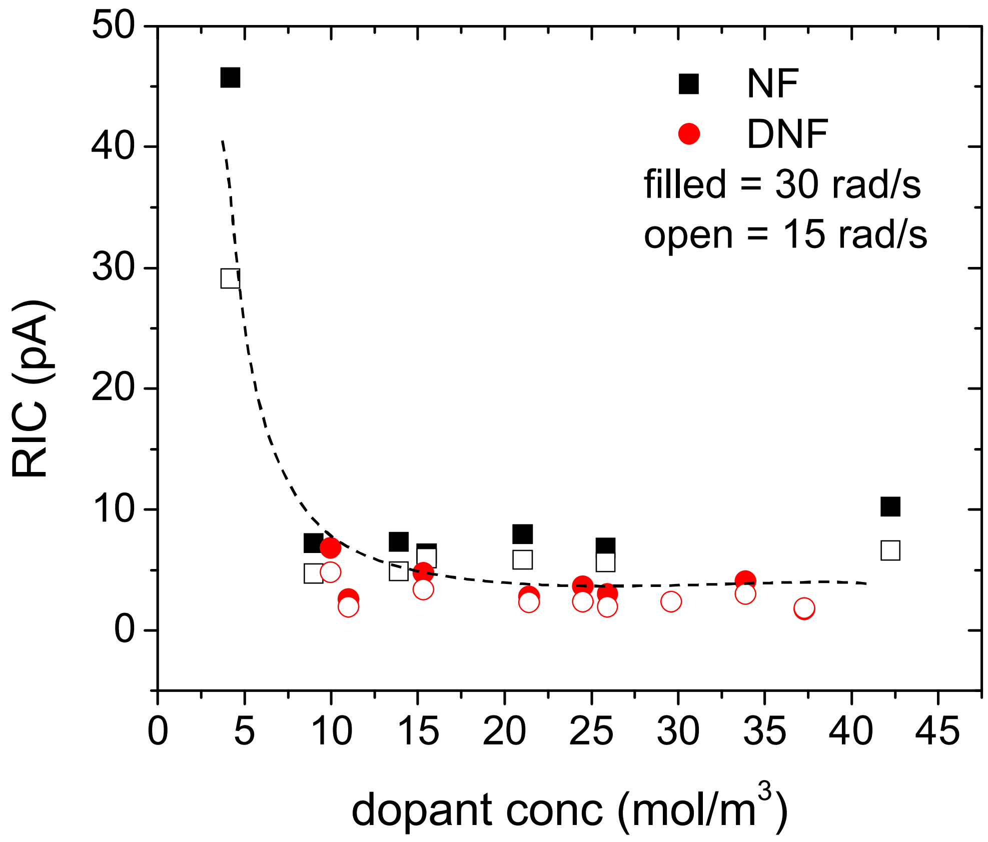
- Activation energies (slopes) of desorption constant
→ single adsorption physical bond between dopant and mylar

[1]S.H. Fogler, *Elements of Chemical Reaction Engineering* 1999

Summary of key points from modeled behavior

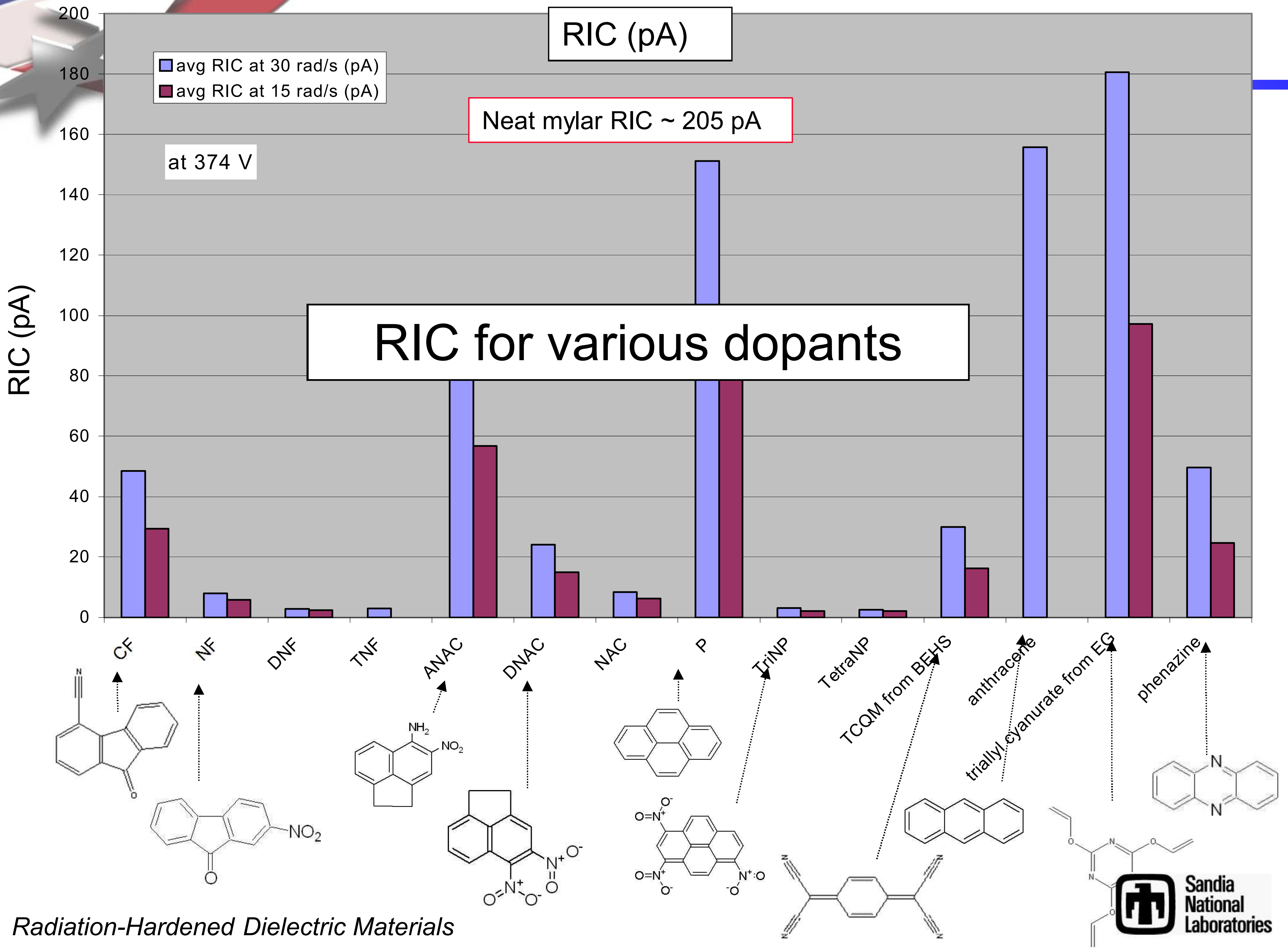
- C_M rapidly increases above T_g, then decreases above ~ 115 ^oC
- Diffusion-limited behavior at short (kinetics dominated) times
- Langmuir adsorption isotherm behavior at long (equilibrium) times
- Adsorption-diffusion model fits data very well for all systems examined
- Diffusivities and equilibrium adsorption constants match expectations and provide understanding of physical process
  - Diffusivity primarily dependent on molecular size
  - Forward adsorption increases with number of interaction sites
  - Reverse adsorption dependent only on single physical bond

RIC as function of dopant concentration

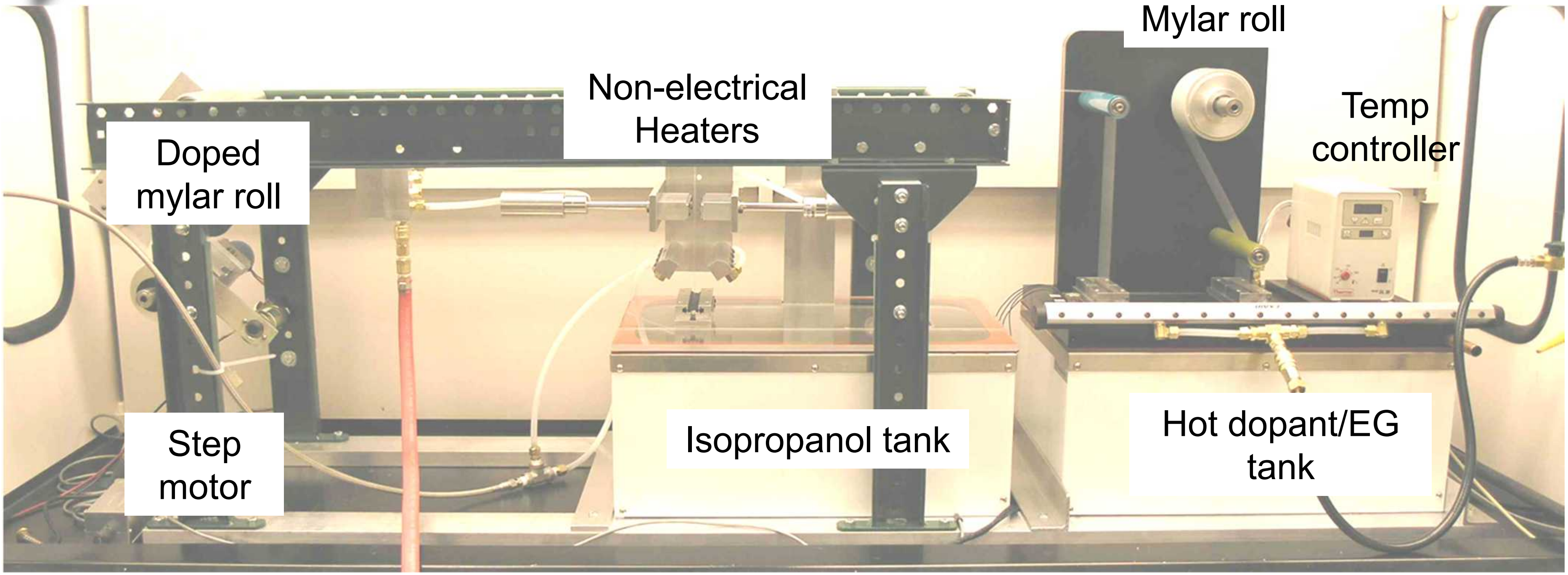


- 10 to 40 mol/m^3 provides 95 to 98 % reduction in RIC

RIC for various dopants



Automated pilot-plant for doping



- Winds at ~5 in/min = 17 in^2 / 12 hr
- Easily scalable to 4 ft wide mylar rolls
- Doping will proceed with NF, DNF, TNF, NAN, NP for radiation testing

* Designed and built by Joseph Lenhart, Phillip Cole, Lothar Bieg, John Schroeder, Don Green (SNL); Scott Burmeister (Burmeister Inc.)

Summary

1. Identified dopants to replace TNF
2. Developed adsorption-diffusion model to understand and control the physics
3. Developed pilot-scale process (scalable) to meet future weapons needs
4. Research enables gel-mylar technology for implementation in LEP and future weapons needs
5. Five papers in preparation or submitted (*Adv Mat*, *Langmuir*, *APL*, *JAP*) on doping and RIC physics

Acknowledgements

- Org. 1732 (Ginger de Marquis, Lothar Bieg, John McBrayer)

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