On the Novel Use of Nitroxides and α-Tocopherol as Radiolytically-Produced Free Radical Scavengers in UHMWPE

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Electron vs. Hydrogen Transfer Mechanisms

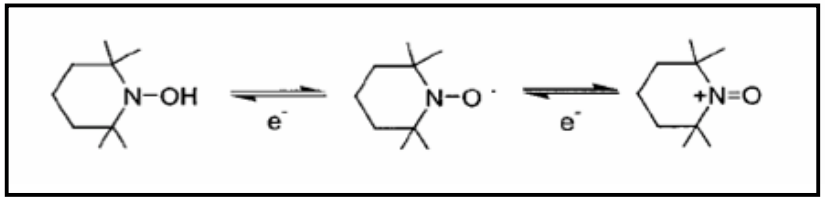
- Electron: nitroxide (TEMPO) vs.
  Hydrogen: phenol (α-tocopherol)

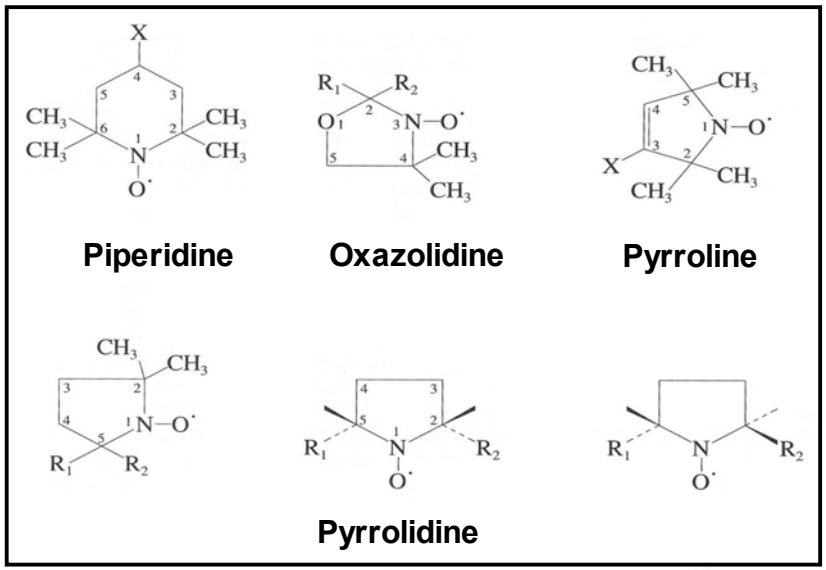
- Mechanisms
  - Overall interaction with UHMWPE free radicals
    - Carbon-centered
    - Peroxyl
    - Alkoxyl
  - Reaction rate constants → competing reactions

- Importance
  - Be able to explain results with mechanisms
  - Understand mechanisms for better design

Nitroxides, a class of antioxidants

- Electron transfer mechanism
- Long radical lifetime, stable
- MRI contrast agent
- Spin labeling reagents, ESR probes
- Radioprotectants *in vivo*
  - Reactive oxygen species: O_2^-, H_2O_2
  - C-centered radical trapping
  - Lipid peroxidation prevention
- Polymerization
  - Nitroxide Mediated Radical Polymerization (NMRP)





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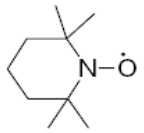


2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)

Proposed Mechanism of Oxidative Degradation Protection

Free Radicals Produced in UHMWPE

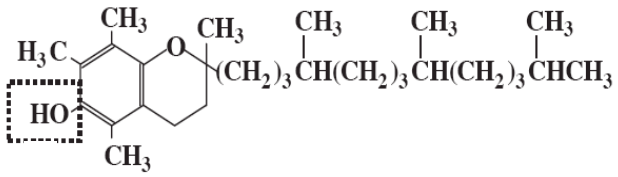
⇝ $-CH_2-CH_2-$ $R\cdot$ Alkyl

$-RH=RH-\dot{R}H$ Allyl

$RO\cdot + O_2 \rightarrow RO_2\cdot$ Peroxyl

$RO\cdot$ Alkoxyl

Vitamin E (α-tocopherol)



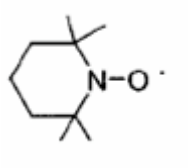
Hydrogen Transfer Mechanism reference

$RO_2\cdot + \alpha\text{-T} \rightarrow ROOH + \alpha\text{-T}\cdot$ [14, 15, 16,17]

$\alpha\text{-T}\cdot + \alpha\text{-T}\cdot \rightarrow$ stable dimer [14, 15, 16]

Nitroxide- TEMPO

(2,2,6,6-Tetramethylpiperidine-1-oxyl)



$= >NO\cdot$

Electron Transfer Mechanism reference

$R\cdot + >NO\cdot \rightarrow >NOR$ [3, 9, 11, 12]

$RO_2\cdot + >NO\cdot \leftrightarrow >NOOOR \rightarrow >N^+=O + RO_2^-$ [10]

$>NO\cdot + e^- \rightarrow >NOH$ [3, 13]

$R\cdot + >NOH \rightarrow >NO\cdot + RH$ [9, 10]

$RO\cdot + >NOH \rightarrow >NO\cdot + ROH$ [9]

Infiltration & Stability-FTIR

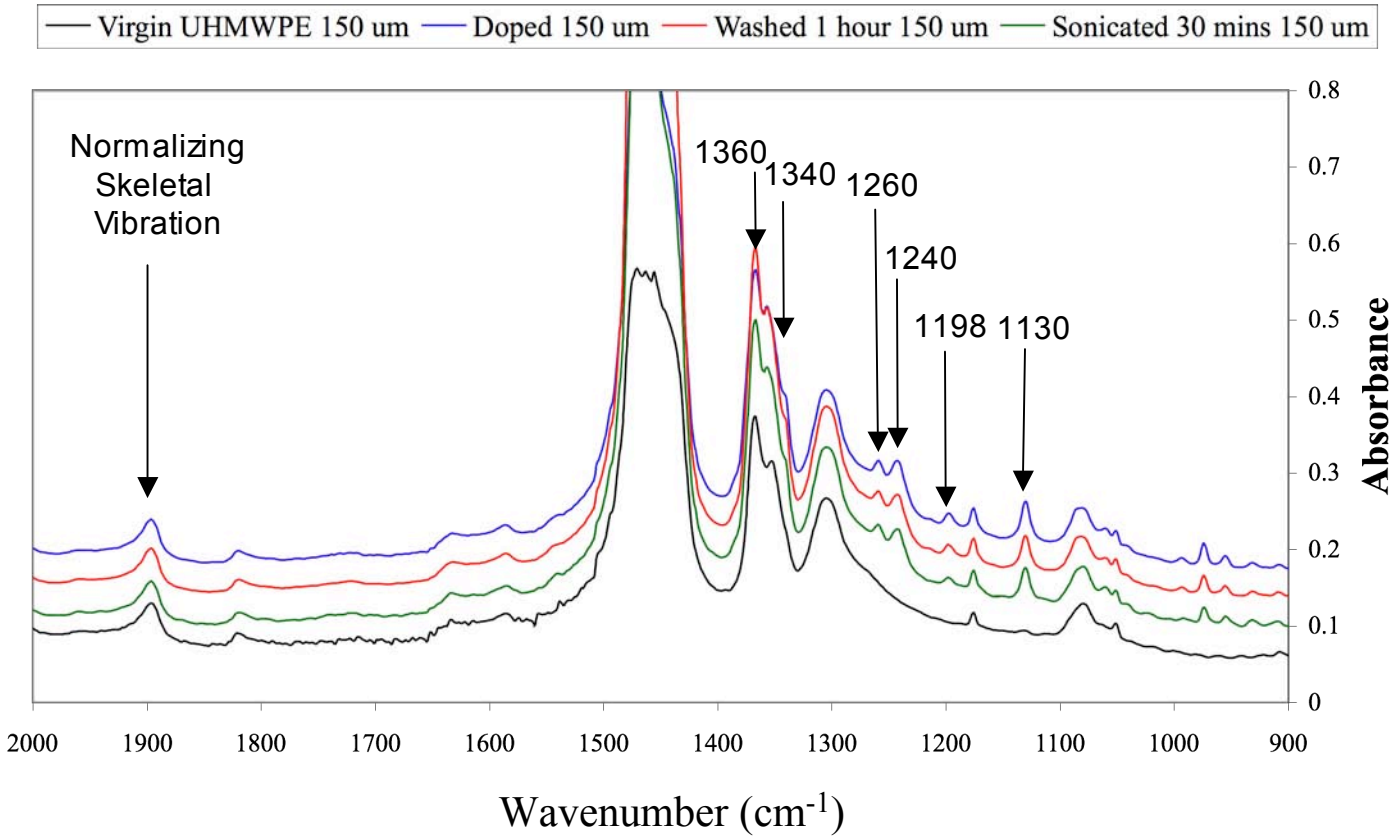
- Aim: Prove stability of TEMPO molecule in UHMWPE matrix
- Thin films doped
  - 100 μm
  - 150 μm
  - 200 μm
- Short term stability:
  - Washed- Hot bath 1 hours
  - Sonicated- 30 minutes
- Normalized for thickness
- Index taken of
  - $\frac{\textit{Height at TEMPO charact.}\upsilon\textit{ doped sample}}{\textit{Height of undoped sample at same }\upsilon}$

Important absorbances:

- 1360 cm^{-1} — CH_3 groups[1,8]
- 1340 cm^{-1} — -NO moiety[1,6,7,8]
- 1260 cm^{-1}
- 1200 cm^{-1} — C-N stretch[8]
- 1130 cm^{-1}

TEMPO Infiltration and Stability

FTIR Spectra of 150 μm TEMPO Doped Thin Films

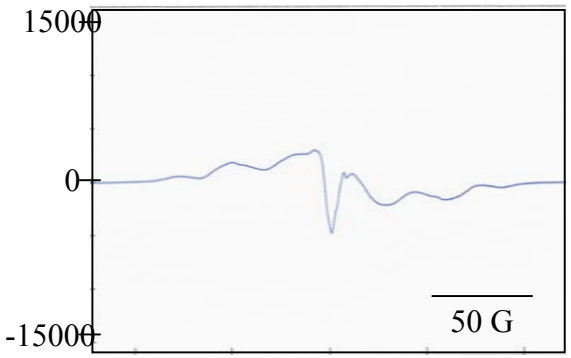


	1360 cm^{-1}	1340 cm^{-1}	1260 cm^{-1}	1199 cm^{-1}	1130 cm^{-1}
Doped	0.16	0.69	0.01	0.03	19.01
Washed	0.41	0.70	0.01	0.03	16.92
Sonicated	0.35	0.627	0.01	0.03	16.00

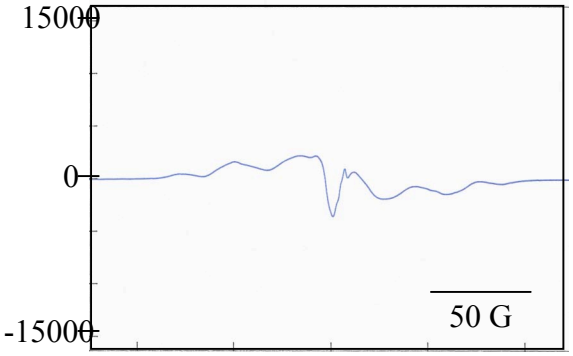
EPR: Low Temperature Spin Trapping

- Doped films, unirradiated
- Small pellets γ irradiated (25 kGy) in air at 77K (liquid N_2)
  - Virgin UHMWPE, α-t doped, TEMPO doped
  - Transferred to EPR cavity (115 K)
  - Slowly warmed to room temperature
    - 8 intervals of temperature analyzed:
      - 115 K, 150 K, 175 K, 200 K, 225 K, 275 K, 290 K
      - 297 K after 10 days
- Small pellets γ irradiated (25 kGy) in air at room temperature:
  - Virgin UHMWPE, α-t doped, TEMPO doped
- Dose rate: ~3 kGy/hr

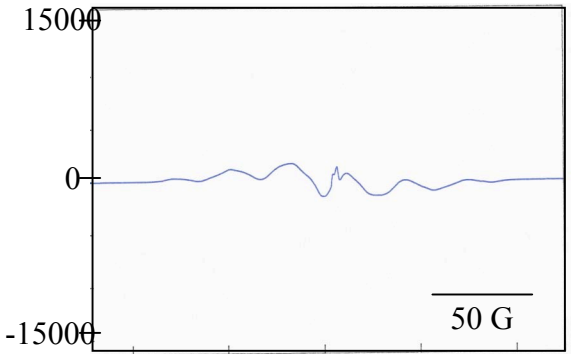
Spin Trapping- Virgin UHMWPE



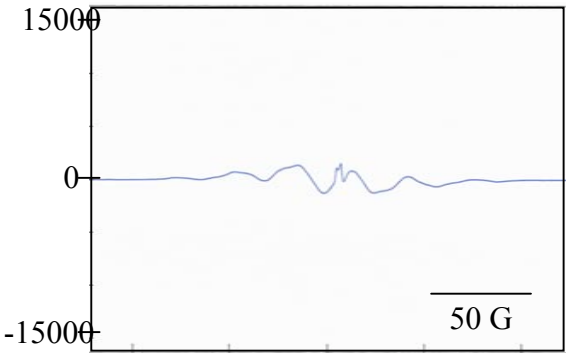
115 K



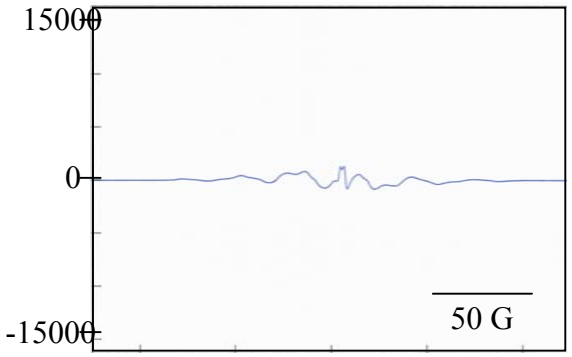
150 K



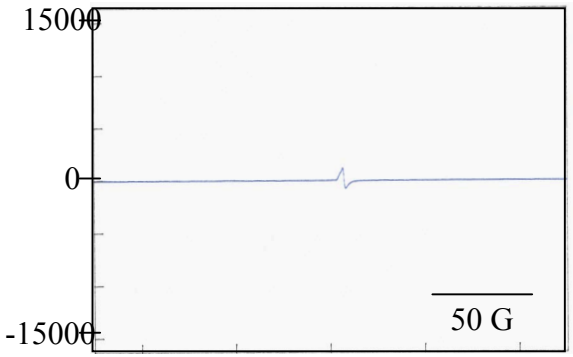
200 K



250 K

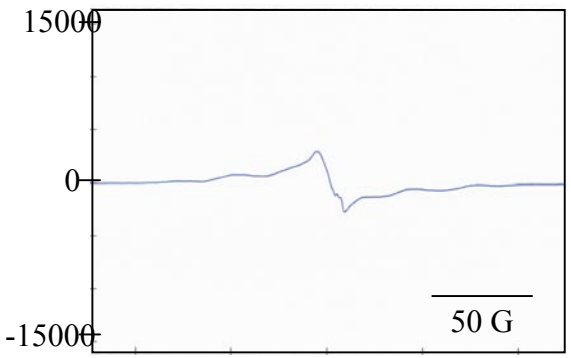


290 K

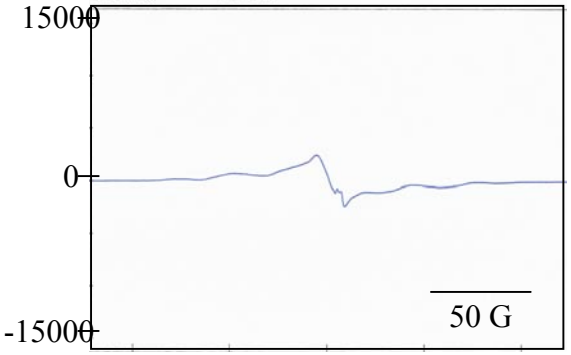


297 K
+ 10 days

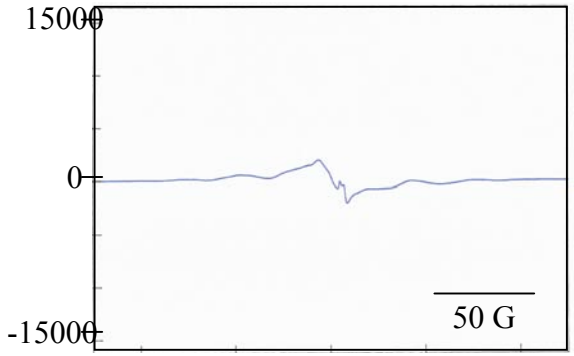
Spin Trapping- α-tocopherol doped UHMWPE



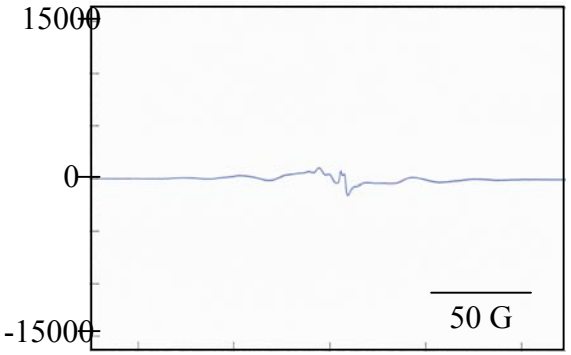
115 K



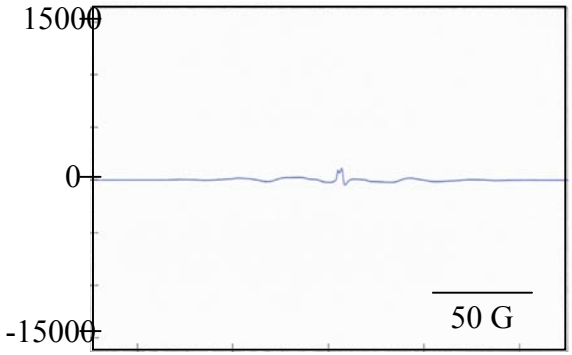
150 K



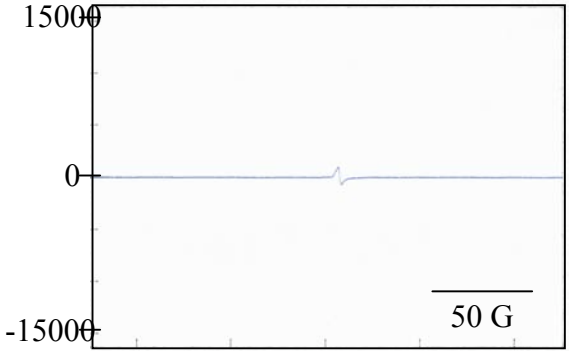
200 K



250 K

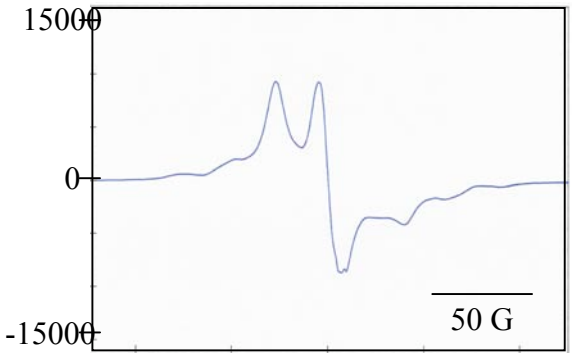


290 K

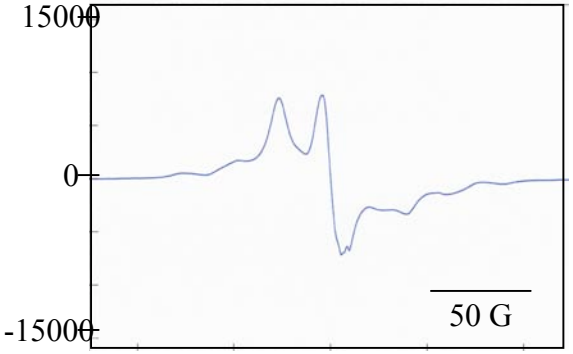


297 K
+ 10 days

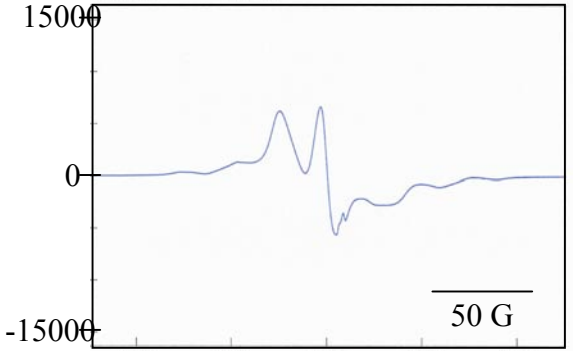
Spin Trapping-TEMPO Doped UHMWPE



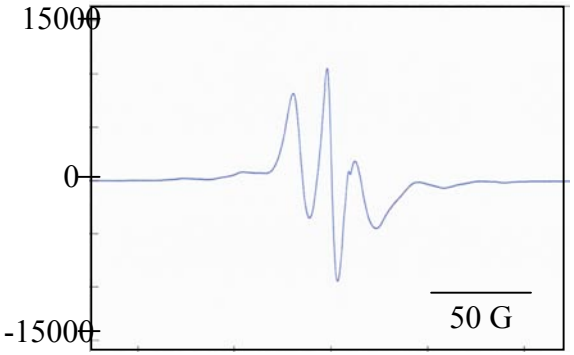
115 K



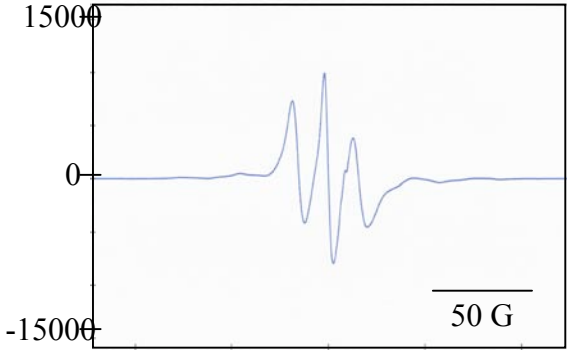
150 K



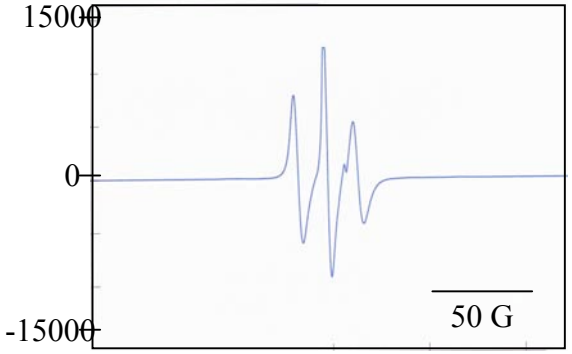
200 K



250 K

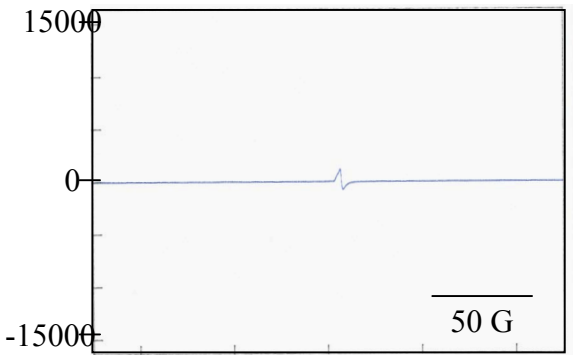


290 K

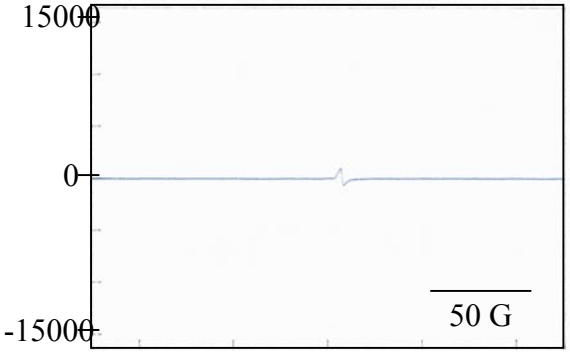


297 K
+ 10 days

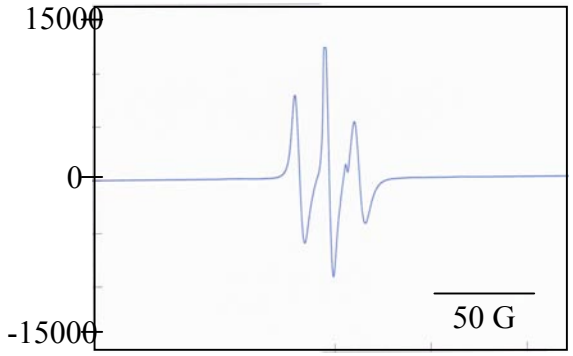
Liquid N_2 vs. Room Temperature Irradiation



Virgin- Irradiated 77 K



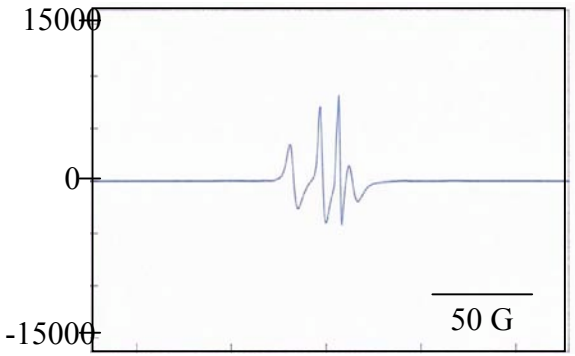
α-Tocopherol- Irradiated 77 K



TEMPO- Irradiated 77 K

Virgin- Irradiated Room Temp.

α-Tocopherol-Irradiated Room Temp.



TEMPO- Irradiated Room Temp.

Conclusions

- TEMPO is an efficient spin trap
- Nitroxides may possibly be efficient antioxidants in UHMWPE
- Elucidation of dominant mechanisms is necessary
- Accelerated aging/ mechanical testing is necessary
- Need to assess long term stability

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References

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