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REPORT DOCUMENTATION PAGE

AD-A223 409

	1b. RESTRICTIVE MARKINGS: None
	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release. Distribution unlimited.
4. PERFORMING ORGANIZATION REPORT NUMBER(S): TECHNICAL REPORT #10	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: University of Massachusetts; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code): Department of Chemistry, Lederle Graduate Research Tower, Amherst, MA 01003	7b. ADDRESS (City, State, and ZIP Code): 800 N. Quincy Street, Arlington VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research; 8b. OFFICE SYMBOL (If applicable): ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code): 800 N. Quincy Street, Arlington VA 22217-5000	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. N00014-87; PROJECT NO. K-0464; TASK NO.; WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification) (UNCLASSIFIED)

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS

12. PERSONAL AUTHOR(S): P.M.Lahti

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Annual Report	FROM 11-1-88 TO 10-1-89	6 Mar 1990	

16. SUPPLEMENTARY NOTATION

Presented at Fall, 1989 ONR Contractor's Meeting : Summary of slide presentation.

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Organic radicals; organic polyradicals; theoretical and computational chemistry; unimolecular radical synthesis . JES

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Progress in theoretical and synthetic investigations of organic magnetic species is outlined by slides presented at the Office of Naval Research contractors' meeting of Fall, 1989. Overall, progress was made in synthesis of appropriate groups to allow photochemical and thermal generation of phenoxyl radicals in the solid phase. Thermal stability of a variety of substituted phenoxyl systems generated by these methods in PPMA matrices was investigated.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ■ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: Non-classified	
22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. Kenneth Wynne / Dr. JoAnn Milliken	22b. TELEPHONE (Include Area Code): 202-696-4410	22c. OFFICE SYMBOL: ONR

OFFICE OF NAVAL RESEARCH

Contract # N00014-87-K-0464

R&T Code 413c037

Technical Report #10

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS AND OLIGOMERS

by Paul M. Lahti

Presented at

Office of Naval Research Contractors' Meeting
Autumn, 1989

University of Massachusetts
Department of Chemistry
Amherst, MA 01003

Submitted 6 March 1990

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS AND OLIGOMERS

by Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

OBJECTIVE:

To investigate the possibilies of generating magnetic information storage materials from basically non-metallic organic precursors, in order to combine the technological usefulness of magnetism with the practical usefulness of organic polymeric materials.

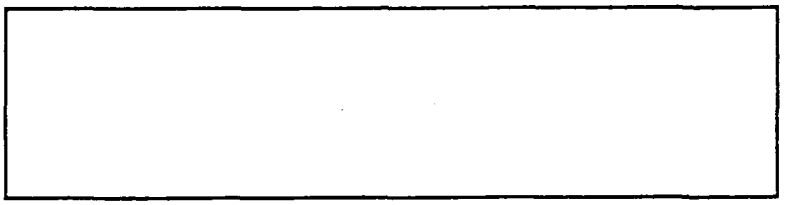
APPROACH:

Theoretical computations allow selection of polyradical polymer structures likely to yield high-spin magnetic properties. Experimentally we synthesize as model compounds small segments of a potential highly magnetic polymer, then test the predictions of theory by standard methods for investigating magnetic properties (electron spin resonance, magnetic susceptibility). Successful predictions for small models will imply that it is worth attempting synthesis of larger polymers predicted to have desirable magnetic properties.

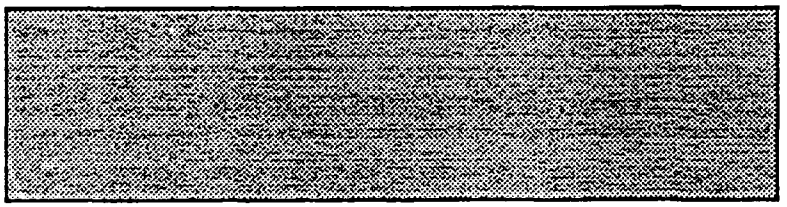
RESULT:

Theory does predict that linkage of several radical units into an oligomer will in many cases yield high-spin organic polyradicals. Experimental generation of such species will constitute the first step toward creating truly polymeric magnetically imaged organic materials.

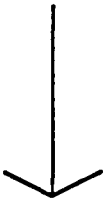
IDEALIZED USE OF POLYRADICAL MAGNETIC MATERIAL
PERMANENT READ-ONLY MEMORY

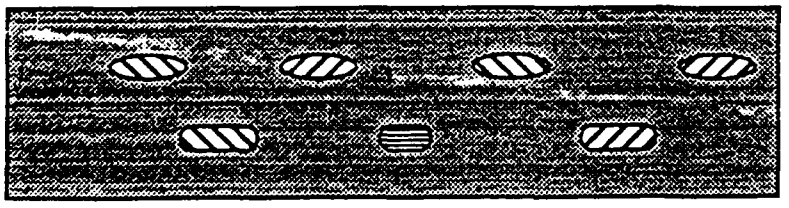


Inert Polymer Backbone
(Support Phase).



Latent Magnetic Precursor
Overlaid on Inert Polymer Base.





Information Encoded
By "Developing" Some
Portion of Precursor
To Become Magnetic.

INTEREST IN ORGANIC FERROMAGNETIC MATERIALS

J. S. Miller, A. J. Epstein, W. M. Reiff — *Chem. Rev.* **88**, 201(1988), *Accts. Chem. Res.*, **21**, 114(1988).

R. Breslow, et al. — *Pure Appl. Chem.*, **54**, 927(1982), *J. Am. Chem. Soc.*, **109**, 6412(1987), *J. Am. Chem. Soc.*, **110**, 3970(1988)

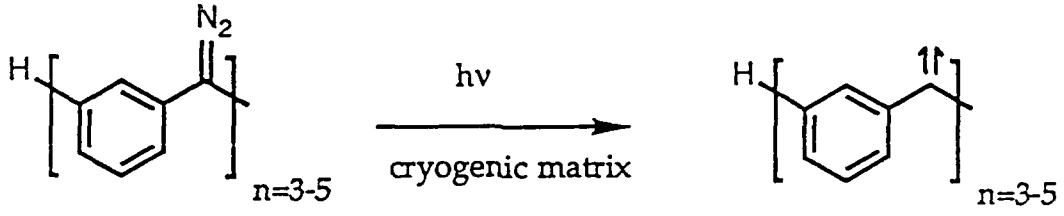
Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, V. N. Spector — *Nature*, **126**, 370(1987)

J. B. Torrance, S. Oostra, A. Nazzal — *Synth. Metals*, **19**, 709(1987).

Experimental Work Toward Synthesis of High Spin Polyradicals

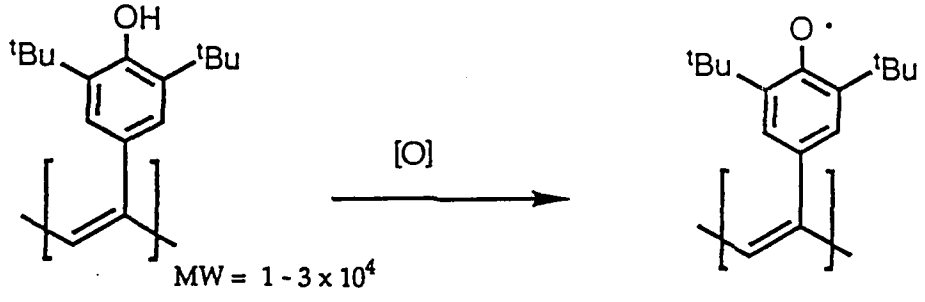
Examples include:

Cf. T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, K. Itoh, *J. Am. Chem. Soc.* 1984, *106*, 6449; 1986, *108*, 368 and references therein.



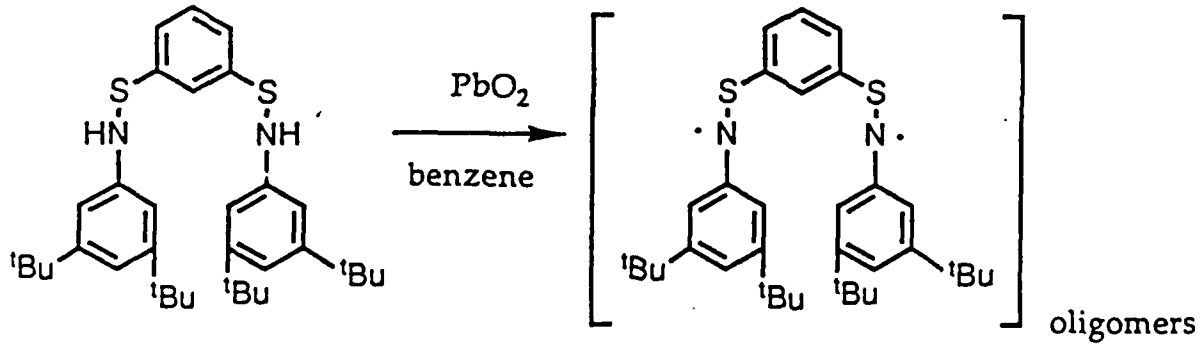
high spin state
polycarbenes
observed, characterized

H. Nishide, N. Yoshioka, K. Inagaki, E. Tsuchida, *Macromolecules*, 1988, *21*, 3120.



Stable, with about
1 free spin / 10 monomers
by ESR spin counting.

Y. Miura, T. Ohana, *J. Org. Chem.*, 1988, *53*, 5770.



oligomers

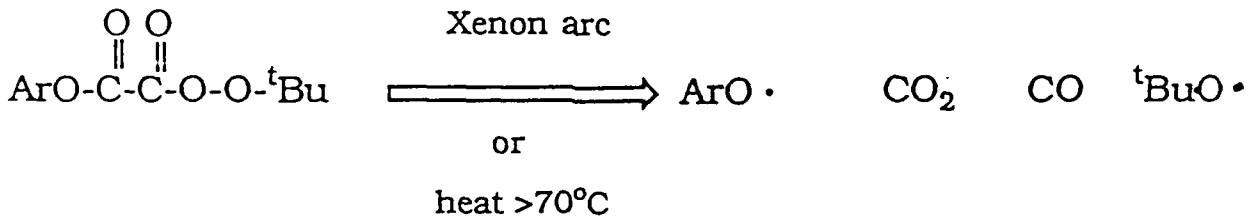
DESIRED: A unimolecular strategy to generate phenoxyl radicals in solution OR in solid state.

STRATEGY

diamagnetic labile precursor

paramagnetic phenoxyl radical

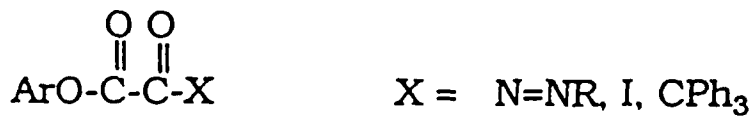
OUR PRESENT METHOD



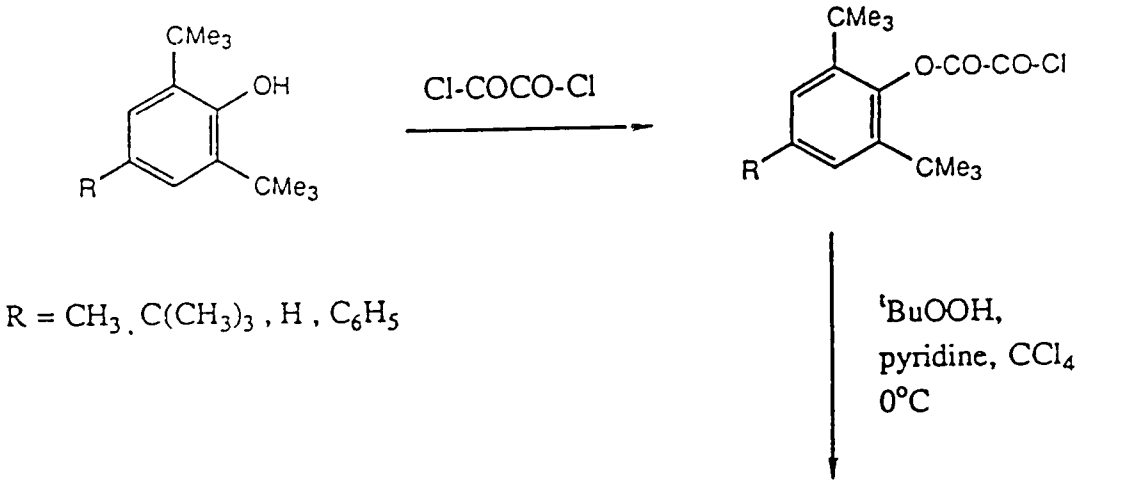
ADVANTAGES

1. Easy and cheap to make
2. Fairly easy to store for some time, soluble in common solvents
3. Some photolability, easy thermal decomposition at > 70°C.

POSSIBLE FUTURE APPROACHES



Synthesis of Peroxyoxalate Precursors for Phenoxy Systems



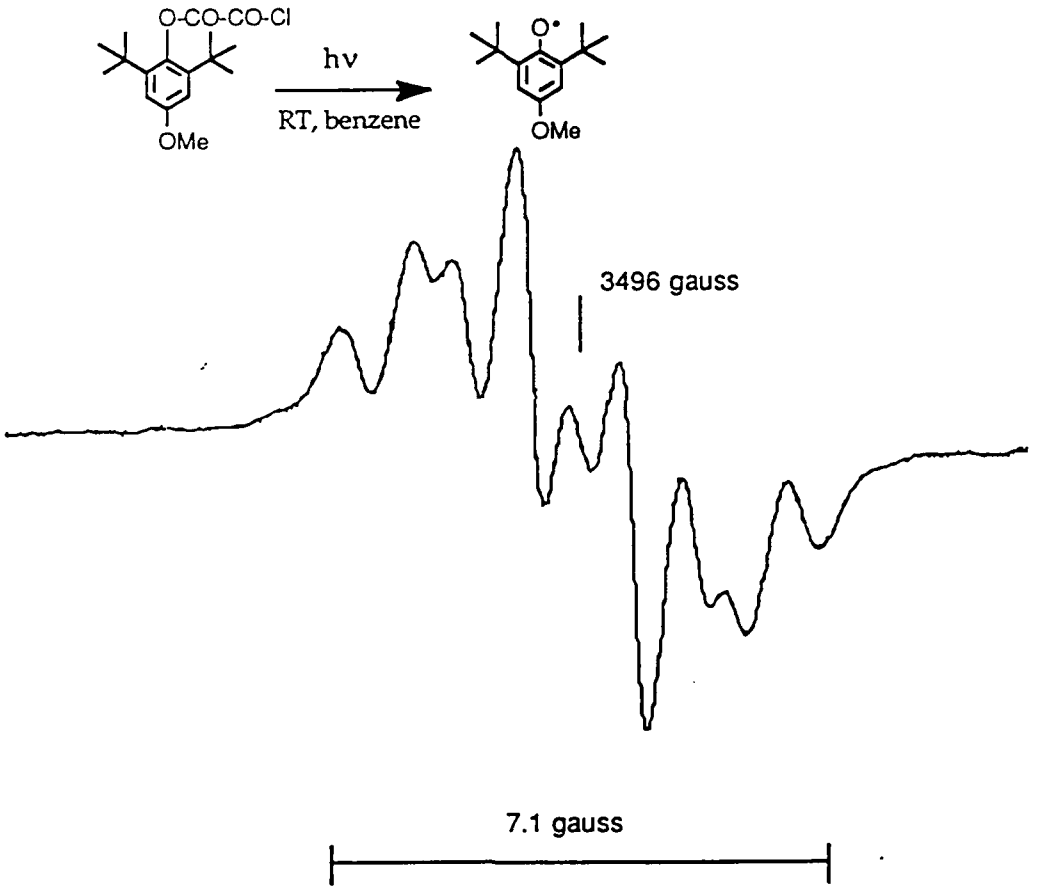
$R = CH_3, C(CH_3)_3, H, C_6H_5$

stable for several days at 25°C in benzene

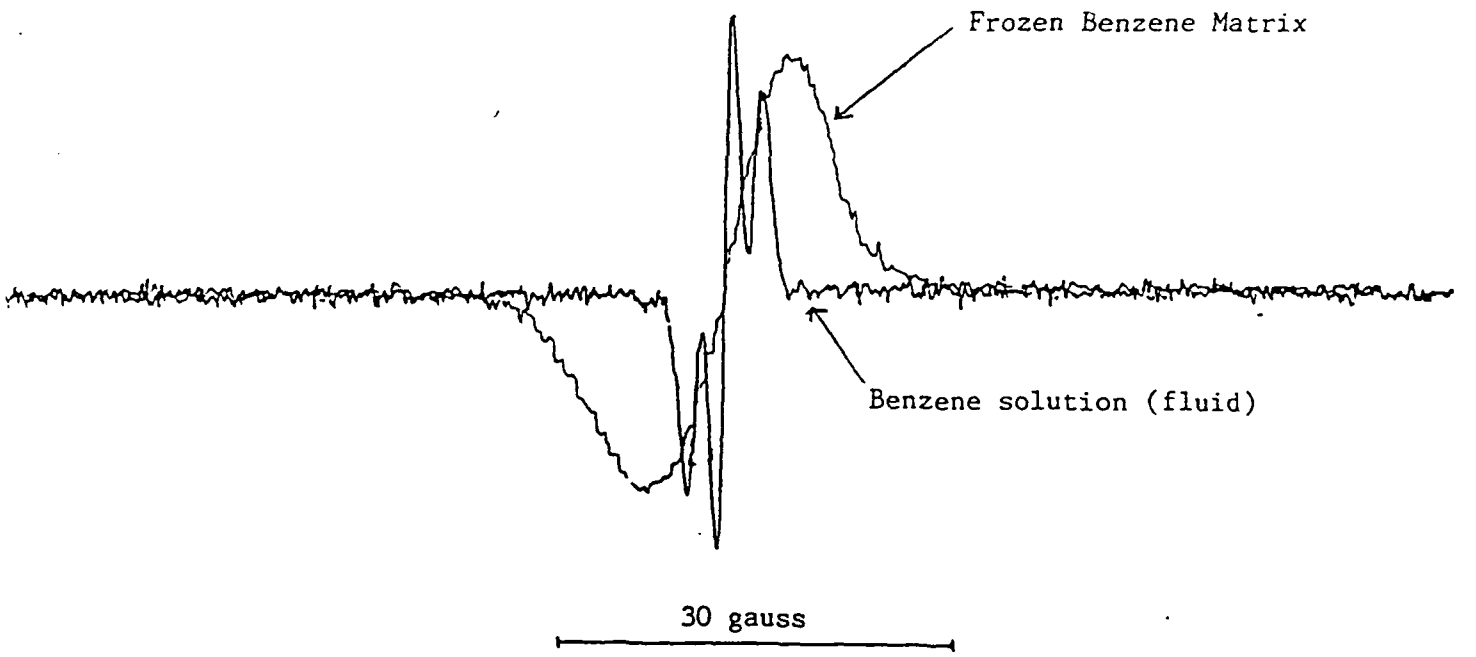
ESR

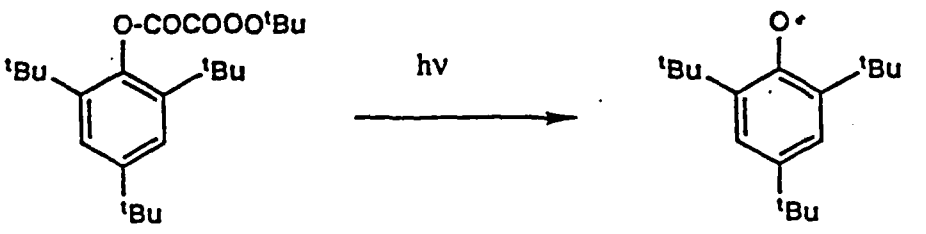
pentane recryst. at -78°C
good room temperature stability

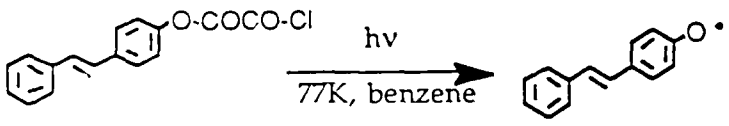
^{1}HNMR, IR

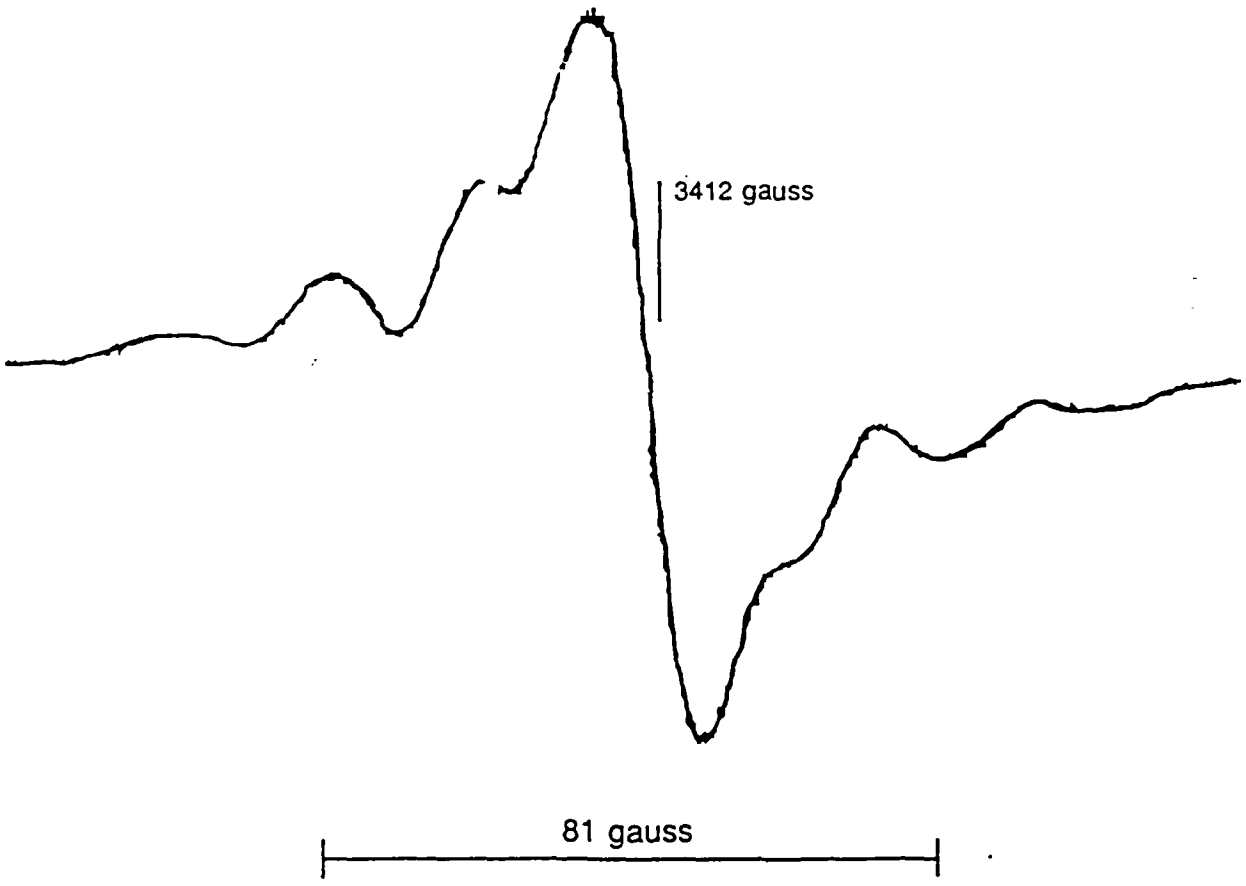

O-CO-CO-Cl
OMe
hν
RT, benzene
O•
OMe
3496 gauss
7.1 gauss

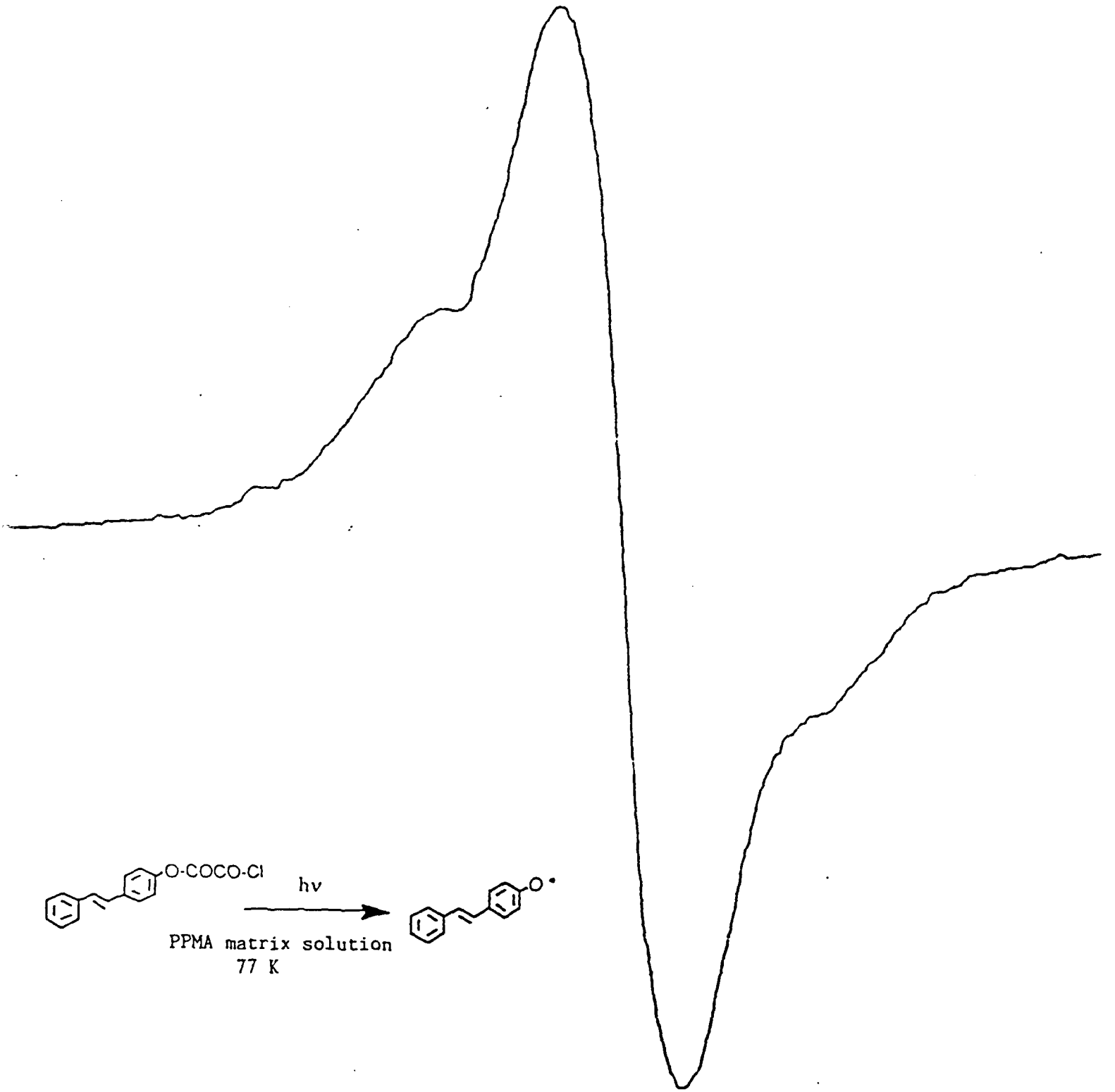
ESR Spectra in rigid matrix are much broader than in solution



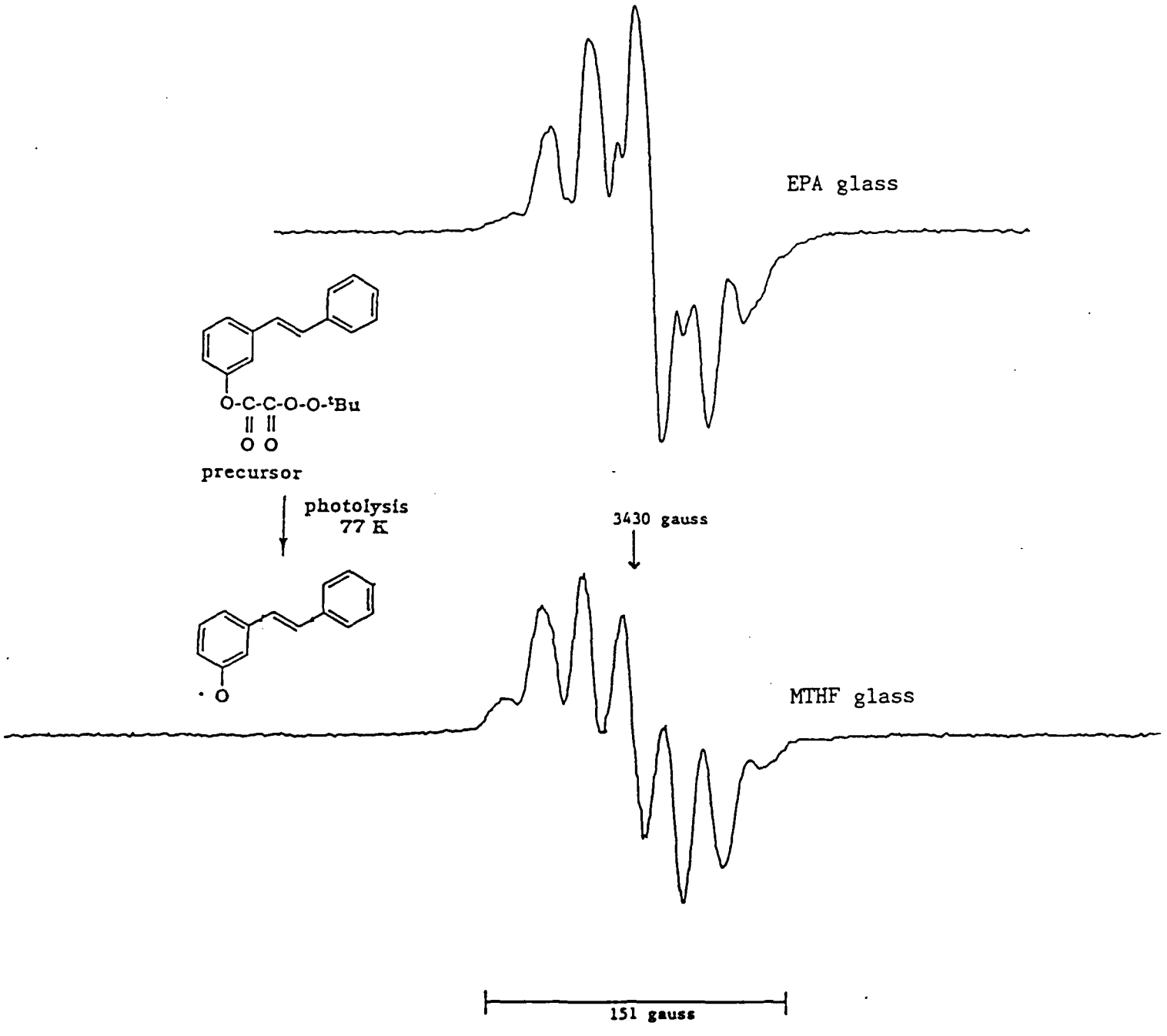



O-COCO-Cl
hν
77K, benzene
O•

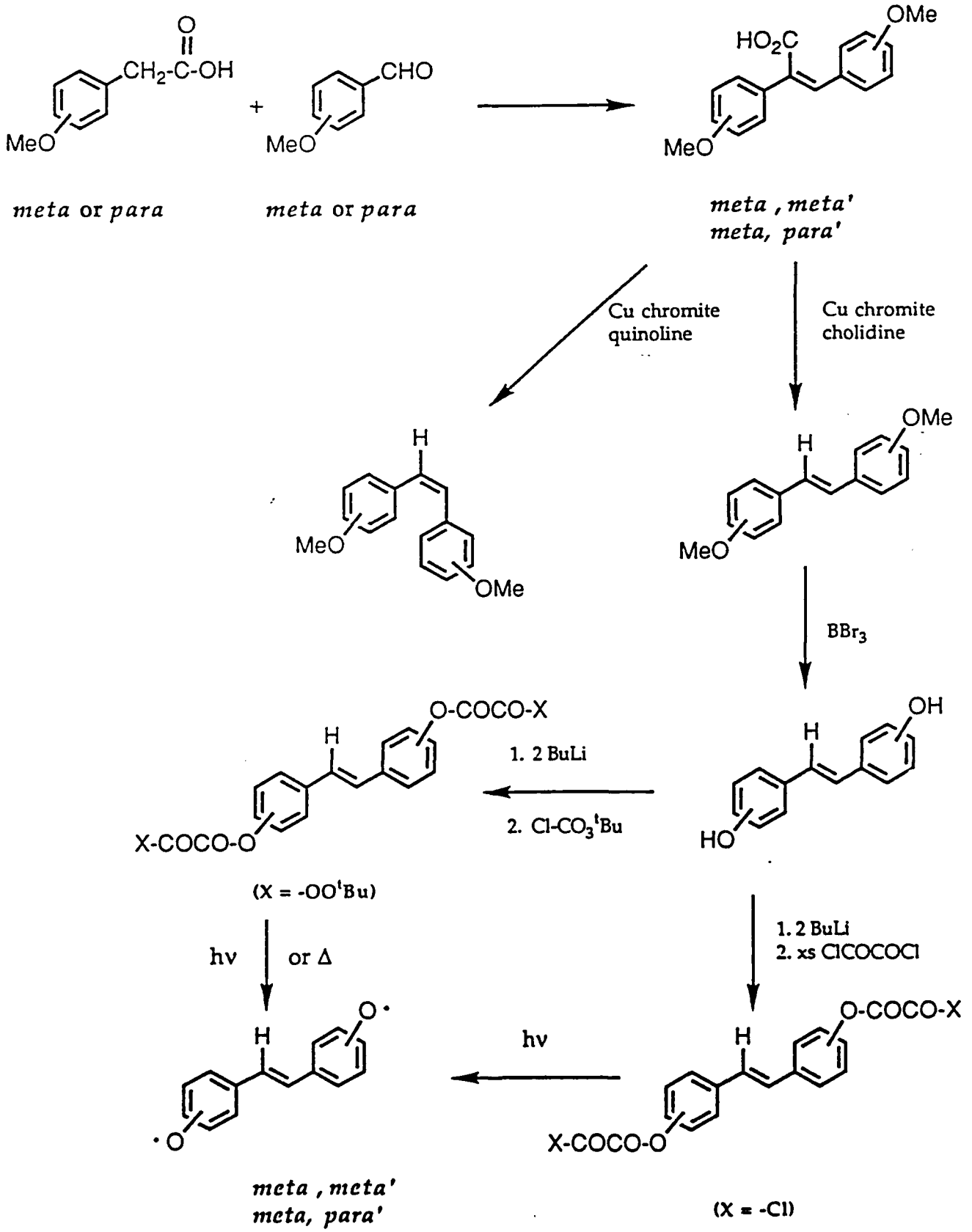

3412 gauss
81 gauss

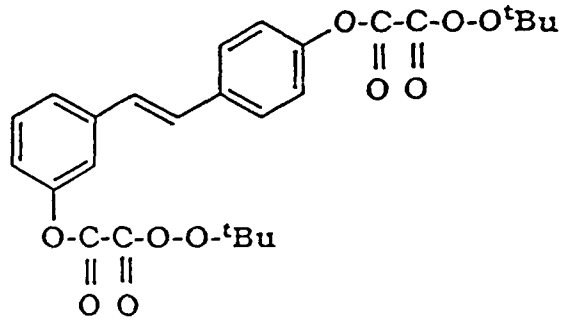


(SIMILAR LOSS OF FINE STRUCTURE IS OBSERVED IN NEAT SAMPLE IRRADIATION)


EPA glass
O-C-C-O-O-tBu
O O
precursor
photolysis
77 K
3430 gauss
MTHF glass
151 gauss

Synthesis of Dioxy-Stilbenes

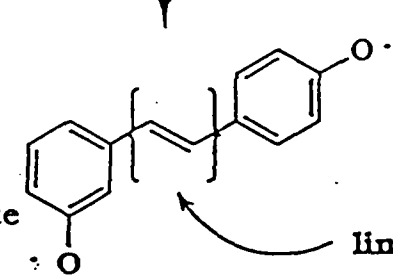




I

precursor

photolysis
77 K



if only one center generated, get a monoradical

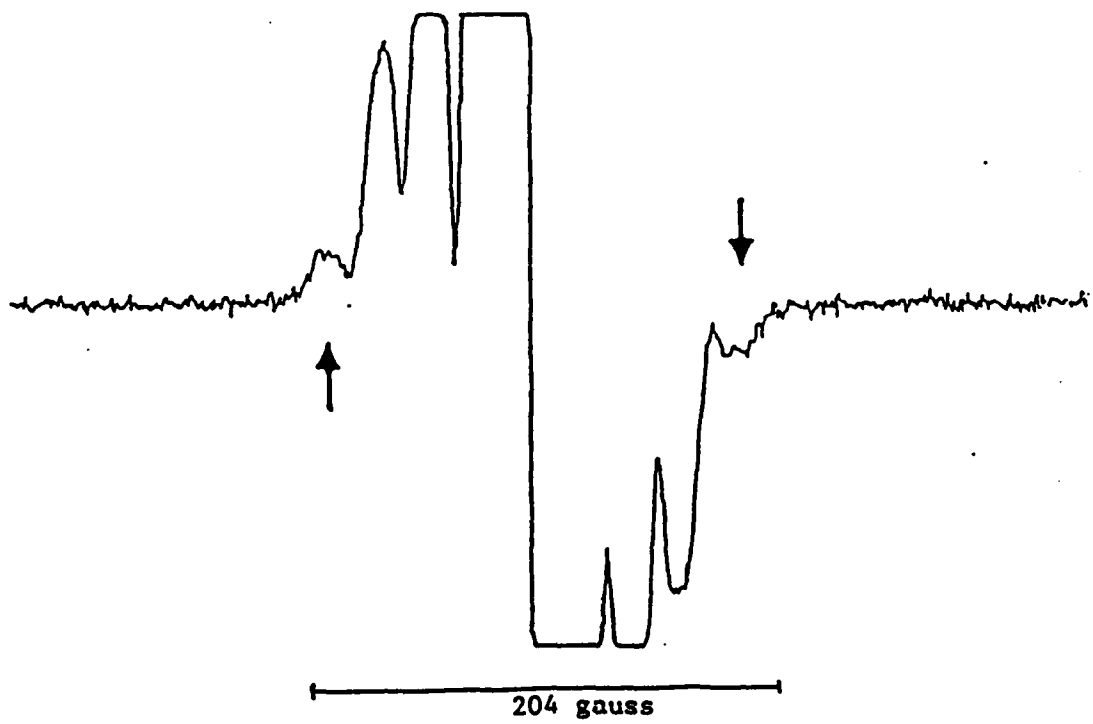
II

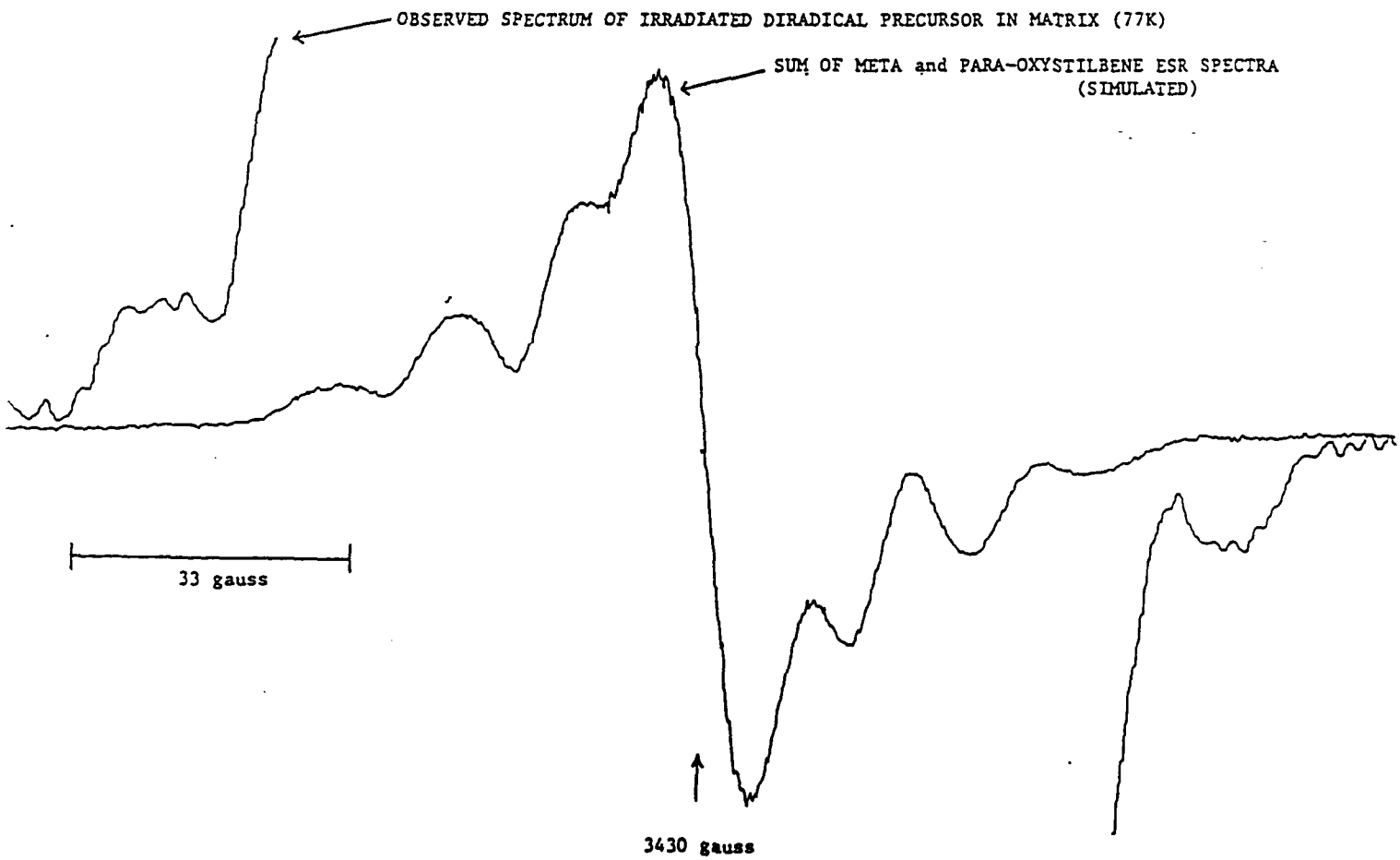
linking spacer "-X-"

Theory predicts a paramagnetic triplet ground state for this molecule.

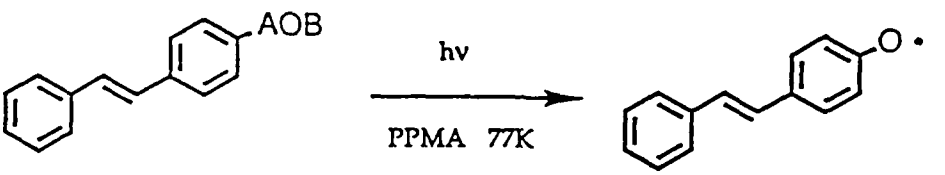
diradical is produced when both centers are generated

3430 gauss (half-field observed, 25 gauss wide)

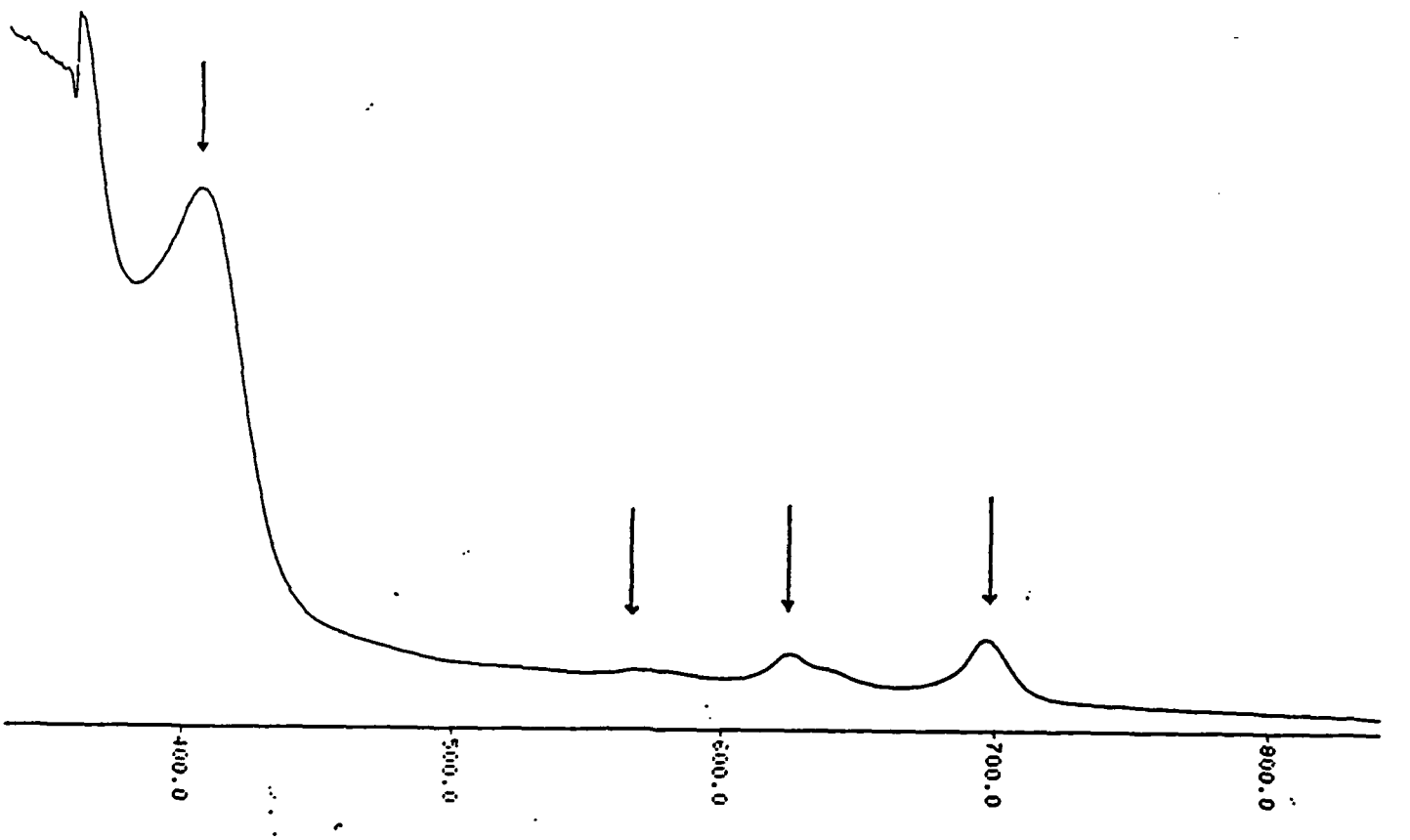



OBSERVED SPECTRUM OF IRRADIATED DIRADICAL PRECURSOR IN MATRIX (77K)
SUM OF META and PARA-OXYSTILBENE ESR SPECTRA
(SIMULATED)
33 gauss
3430 gauss

STABILITY OF UNHINDERED PHENOXYs IS EASILY MONITORED IN POLYMERIC MATRIX BY UV-vis SPECTROSCOPY.



AOB = -O-COCO-OO^{t}Bu

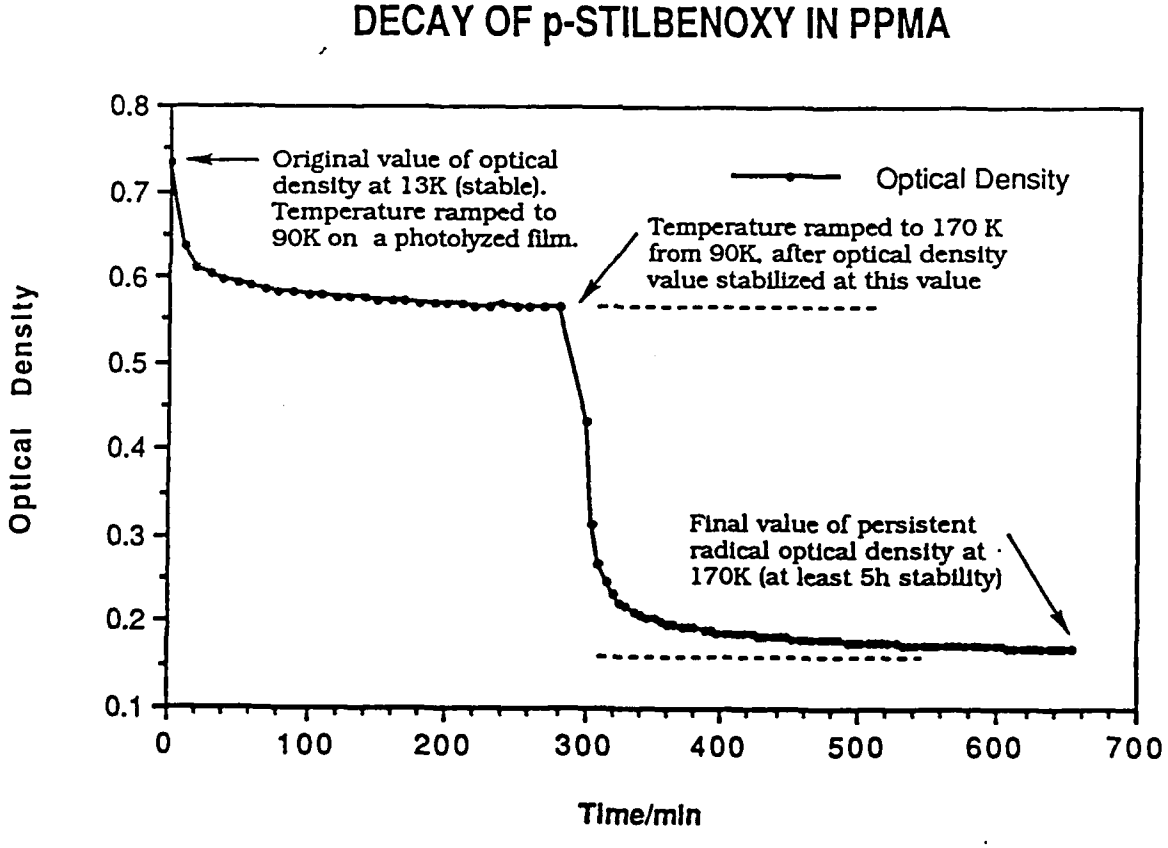


(Arrows indicate the *para*-stilbenoxy absorbances)

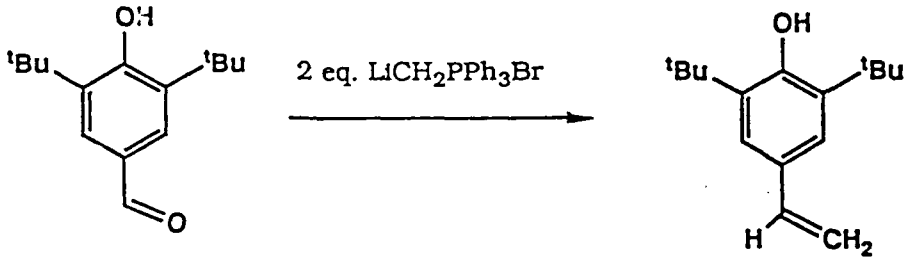
UNHINDERED RADICAL STABILITY IN MATRIX

Unhindered *para*-stilbenoxy appears indefinitely stable by UV-vis when generated in PPMA at 13K. When warmed swiftly (<4 min) to 90K, rapid absorbance decay occurs, which slows and leaves the absorbance (radical concentration) approaching an asymptotic value. Warming again to 170K results in the same behavior, with the final result being a much decreased (relative to the 13K value) but still finite amount of radical with stability for at least 5h at 170K. At room temperature, the radical appears to be completely quenched. Similar behavior occurs in polystyrene, but onset of decay behavior is faster. Some decay in both matrices has already occured by 77K with our typical 10% wt/wt radical-in-polymer mixes.

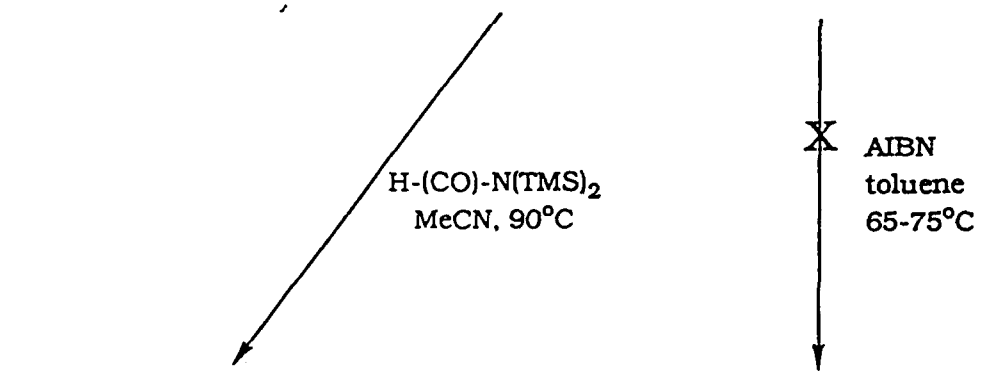
With some optimization, further increase in stabilization of unhindered radicals in polymer matrix may be possible.

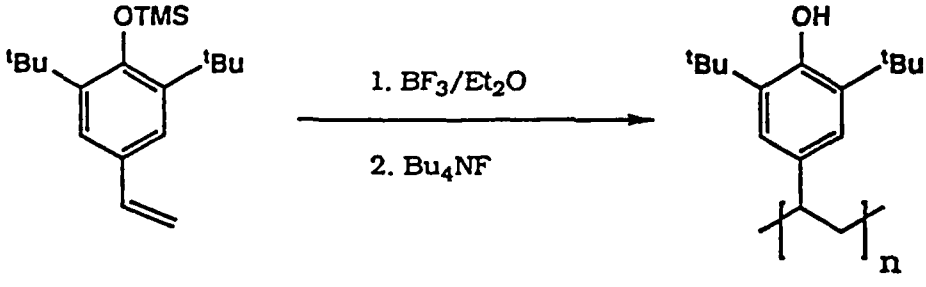


A NEW, EFFICIENT SYNTHESIS OF *para*-OLEFINIC 2,6-di-*tert*-Butylphenolic polymer precursors.



(previously reported in D. Braun, B. Meier, *Makromol Chem.*, 167, **119**(1973))

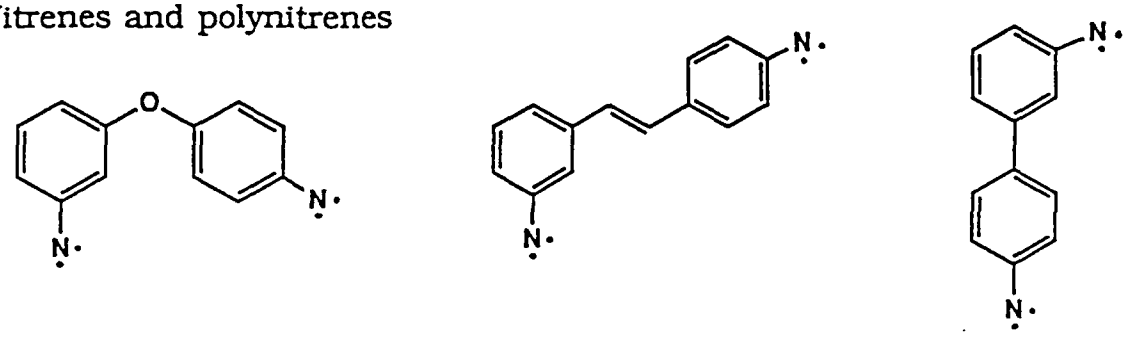




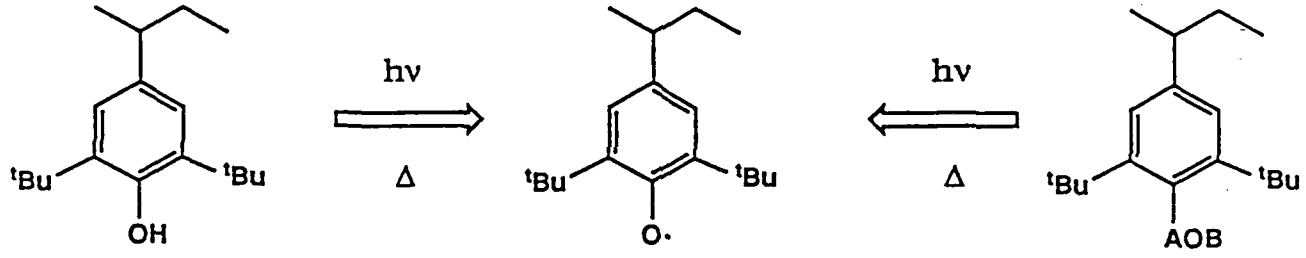
further functionalization of this polymer to the polyradical is desirable.

FUTURE WORK

1. Nitrenes and polynitrenes



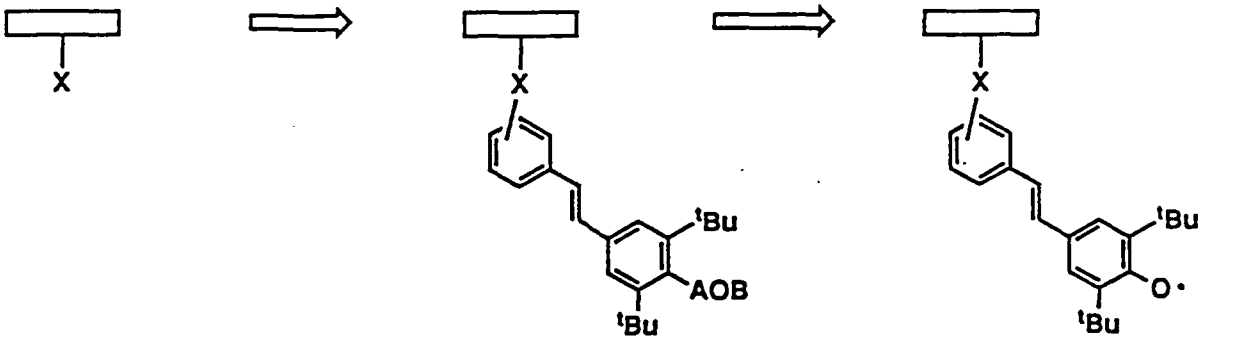
2. Poly(2,6-di-*tert*-butyl-4-oxy-styrene) derivatives and copolymers. Polymers with pendant hindered stilbenoxy groups.



+

$^{t}BuOO(CO)(CO)OO^{t}Bu$

highly paramagnetic?



highly paramagnetic?

3. Optimize radical production in polymer matrices

PPMA // ArO-X-Lv ⟹ PPMA // ArO· X Lv·

ACKNOWLEDGEMENTS

Group Members

David Modarelli	Organic Magnetic Materials
Frank Rossitto	Organic Magnetic Materials
Masaki Minato	Organic Magnetic Materials
Andrew Ichimura	Computational (Polyradicals)
Frank R. Denton III	Conducting Polymers
Ananda Sarker	Conducting Polymers
Mark Kearley	Pentamethylenepropanes

Support

Office of Naval Research (Magnetic Materials)
National Science Foundation (Departmental Computing)
Air Force Office of Scientific Research (Conducting Polymers)
Petroleum Research Fund (Pentamethylenepropanes)
Research Corporation (UV Spectroscopy)
Exxon Education Foundation
University of Massachusetts