MASTER

PROGRESS REPORT

SUBMITTED UNDER CONTRACT NO. EY-76-[illegible]-2968

MASTER

BETWEEN THE

DEPARTMENT OF ENERGY

AND

THE UNIVERSITY OF TENNESSEE

PERIOD

SEPTEMBER 15, 1977 TO SEPTEMBER 15, 1978

Title of Project

RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY

Principal Investigator

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A. Personnel

(1) T. Ffrancon Williams: Professor of Chemistry and Alumni Distinguished Service Professor.

(2) Hisao Murai: Postdoctoral Research Associate. Dr. Murai completed his appointment on May 31, 1978 after 20 months with the project. He is now at the Department of Chemistry, University of Alberta, Edmonton, Canada.

(3) Moon Bin Yim: Postdoctoral Research Associate. Dr. Yim completed his appointment on July 31, 1978 after 18 months with the project.

(4) Jih Tzong Wang: Postdoctoral Research Associate. Dr. Wang joined the project on May 1, 1978.

(5) Robert I. McNeil: Graduate Teaching Assistant and Research Assistant. Dr. McNeil received the Ph.D. degree in Chemistry from the University of Tennessee in March, 1978 and now holds a postdoctoral appointment at the Radiation Laboratory, University of Notre Dame.

(6) Reggie L. Hudson: Graduate Teaching Assistant and Research Assistant. Dr. Hudson received the Ph.D. degree in Chemistry from the University of Tennessee in August 1978, and is now an Assistant Professor of Chemistry at Eckerd College, St. Petersburg, Florida.

(7) Ashok M. Adur: Graduate Teaching Assistant. Mr. Adur is a candidate for the Ph.D. degree in Chemistry (with a major in Polymer Chemistry) at the University of Tennessee.

B. Employment

Dr. Williams devoted 25% of his time during the 1977-78 academic year to this research project, this being a University contribution to this Contract. He was also employed full time for three months during the summer of 1978. The postdoctoral research associates were employed full time during their specified appointment periods (see above). Other employees under the Contract were Dr. R. I. McNeil as a research assistant for the month of January, 1978 and Dr. R. L. Hudson as a research assistant from January 1, 1978 to August 31, 1978. From September 1 to December 31, 1977, Dr. McNeil and Dr. Hudson were supported by graduate teaching assistantships in the Department of Chemistry. Mr. Adur held a graduate teaching assistantship in the Department of Chemistry during the entire 1977-78 academic year, and was supported by funds from the University of Tennessee Polymer Consortium during the summer of 1978.

C. Facilities and Equipment

No serious problems were encountered during the past year in the operation of our major equipment consisting of an EPR spectrometer system, a cobalt-60 γ irradiation source (Gammacell 200), and a liquid helium transfer refrigerator system. These items have been described in earlier progress reports (ORO-2968-78, -81, -90, and -99). The basic EPR spectrometer (Varian V-4502-15) was acquired in 1966. The Gammacell 200 was installed in 1963 and reloaded in 1971.

The only equipment failure during the past year concerned the plug-in transfer oscillator (ACTO-Model 1255A) which is used in the frequency counter (Systron Donner Model 1037) to measure the X-band microwave frequency. This unit had to be returned to the manufacturers for repair on two occasions over a period of several months, and we were unable to locate a spare in the interim. Since we normally obtain the g-factors of radicals from direct measurements of magnetic field and microwave frequency, the absence of this unit was somewhat inconvenient. This experience points up our dependence on instrumentation and illustrates the need for adequate funding to maintain our equipment in good operational condition.

No significant equipment acquisitions were made during the past year.

D. Outline of Progress and Publications

Apart from the results reported in our publications and conference presentations as listed below, a noteworthy practical achievement during the past year was the development of cryogenic techniques to allow samples to be γ irradiated at 4 K and then transferred to the EPR spectrometer for subsequent observations at 10-15 K and above. By this means we were able to detect the adduct methyl radical in γ-irradiated dimethyl sulfoxide-$\underset{\sim}{h}_6$ (DMSO-$\underset{\sim}{h}_6$). Previous work confined to 77 K (Y. J. Chung, K. Nishikida, and F. Williams, J. Phys. Chem., 78, 1882 (1974)) had shown that the $CD_3\cdot$ adduct radical was produced by the irradiation of DMSO-$\underset{\sim}{d}_6$ but the corresponding $CH_3\cdot$ adduct was not detected in DMSO-$\underset{\sim}{h}_6$ under exactly the same conditions. This is an example of an "all-or-nothing isotope effect" (J. T. Wang and F. Williams, J. Am. Chem. Soc., 94, 2930 (1972)). When DMSO-$\underset{\sim}{h}_6$ is irradiated at 4 K and observed at temperatures below 50 K, the $CH_3\cdot$ adduct radical is in fact detected. Moreover, the ^1H coupling constant for the $CH_3\cdot$ adduct is 18.94 G as compared to the value of 23.04 G for the free $CH_3\cdot$ radical. This is about the same percentage reduction in hyperfine coupling that was found for the $CD_3\cdot$ adduct radical from DMSO-$\underset{\sim}{d}_6$, the corresponding values being 2.99 G for the adduct and 3.58 G for the free $CD_3\cdot$ radical. At temperatures higher than 50 K, the $CH_3\cdot$ adduct radical in DMSO-$\underset{\sim}{h}_6$ is found to decay at a fairly rapid rate which explains why this species is not observed when the experiments are carried out at 77 K. Detailed work on the decay of the $CH_3\cdot$ adduct indicates that the mechanism is one of intramolecular hydrogen atom transfer from the CH_3 group in the CH_3SO^- moiety. Thus, the very large isotope effect is similar to that found in our earlier studies of hydrogen atom abstraction (E. D. Sprague and F. Williams, J. Am.

Chem. Soc., **93**, 787 (1971)).

We have also completed a study of D-atom abstraction by trapped H and D atoms in 3-methylpentane-$\underline{d}_{14}$ at temperatures below 50 K (H. Murai and F. Williams, unpublished work). The hydrogen (or deuterium) atoms were generated by the photolysis of HI (or DI) with ultraviolet light. It has been found that the rate-determining step for the decay of the hydrogen atoms is not a de-trapping process but a deuterium abstraction reaction from the perdeuterated matrix. This reaction is characterized by a very low activation energy (36 cal at 25 K) and proceeds by means of quantum-mechanical tunneling. This work will be submitted for publication in the near future.

The other main thrust of our work at this time continues to be concerned with the discovery and characterization of fluorine-containing radicals. In addition to the work already reported on the radical anions of tetrafluoroethylene (*Chem. Phys. Letters*, **51**, 433, 438) and the halogenotrifluoroethylenes (ORO Document No. ORO-2968-113), we have initiated EPR studies on other fluoro-olefins and partially fluorinated hydrocarbons. In particular, very clear spectroscopic evidence has recently been obtained for the radical anion of 1,1-difluoroethylene (J. T. Wang and F. Williams, unpublished work). Since ethylene itself does not appear to form radical anions, it is significant that the substitution of the two hydrogens by fluorines at one of the carbon atoms appears to increase the electron affinity of the molecule.

During the year two Ph.D. theses (by Robert I. McNeil and Reggie L. Hudson) were completed under this project. The abstracts of these dissertations are included below.

SECTION 1 - CURRENT REPORTS

I. [ORO-2968-112] AN ESR STUDY OF THE PHOTOLYSIS OF TRAPPED RADICALS IN γ-IRRADIATED CARBOXYLIC ESTERS AT 77-87 K (Reggie L. Hudson and Ffrancon Williams, *J. Phys. Chem.*, **82**, 967 (1978)).

ABSTRACT: The photobleaching of trapped radicals in γ-irradiated carboxylic esters, RC(O)OR', has been studied by ESR spectroscopy. Two different reactions have been characterized. The radical anion $R\dot{C}(O^{-})OR'$ is photobleached by visible light to give the alkyl radical R'• by a process of β-scission. Bleaching by uv light causes the radical formed by hydrogen-atom loss from the ester group R' to give the acyl radical $R\dot{C}O$ which can undergo subsequent photolysis by visible light to form the alkyl radical R•. All previous work on the carboxylic esters is consistent with these reactions.

II. [ORO-2968-113] EPR SPECTRA AND STRUCTURE OF THE CHLOROTRIFLUOROETHYLENE AND BROMOTRIFLUOROETHYLENE RADICAL ANIONS (Robert I. McNeil, Ffrancon Williams, and Moon Bin Yim, DOE document no. ORO-2968-113, submitted for publication).

ABSTRACT: EPR spectra attributable to the halogenotrifluoroethylene radical anions have been generated by electron attachment in solid solutions at low temperatures. From the orientation dependence and excellent line resolution of the $C_2F_3X^-$ spectra in tetramethylsilane solutions, it has been established that the hyperfine tensor for the heavy halogen X (X = Cl,Br,I) is markedly anisotropic, thereby demonstrating a large spin density in the p orbital of this halogen. The spin density distribution in these radicals strongly suggests that the unpaired electron occupies a σ* orbital, a conclusion which has been confirmed by CNDO/2 calculations. The EPR evidence for the radical anion assignment is consistent with gas-phase studies which indicate that electron attachment to chlorotrifluoroethylene proceeds by a non-dissociative

process at thermal electron energies.

III. EPR AND OPTICAL ABSORPTION STUDIES OF ELECTRON ATTACHMENT TO FLUORINE COMPOUNDS IN SOLID SOLUTIONS (Robert Irving McNeil, Ph.D. thesis, University of Tennessee, March 1978, 139 pp.).

ABSTRACT: The main contribution of this work is the preparation and spectroscopic characterization of radical anions derived from fluorine-containing compounds which were formed in condensed phases as a result of electron capture. These ions are of interest because they represent novel classes of negative ions. The ions, produced by gamma irradiation of frozen solutions of various fluorine-containing compounds in 2-methyltetrahydrofuran (MTHF) or tetramethylsilane (TMS), were characterized by EPR and then studied by optical spectroscopy. Photolysis of similar solutions containing N,N,N',N'-tetramethyl-p-phenylenediamine provided confirmation that the anions did result from electron capture. The distinctive feature of this work was the extensive use of TMS to obtain spectra which were nearly isotropic or which were completely anisotropic but showed orientation dependence.

The radical anion of tetrafluoroethylene, observed by EPR in a gamma-irradiated solution of tetrafluoroethylene in TMS-$\underline{d}_{12}$ at 120°K, exhibited hyperfine coupling to four equivalent fluorine nuclei, the values of the g factor and coupling constant of the isotropic spectrum being 2.0027 and 94.7 G. Analysis of the anisotropic spectrum, obtained from a gamma-irradiated solution of tetrafluoroethylene in MTHF at 87°K, revealed that the radical exhibited an axially symmetric hyperfine tensor, with parallel coupling $\underline{A}_{//}$ = 135.9 G and perpendicular coupling $\underline{A}_{\perp}$ = 74.4 G. Warming to 95°K a gamma-irradiated solution of tetrafluoroethylene in MTHF or 3-methylhexane resulted in the complete decay of the EPR spectrum of $C_2F_4^-$ and the growth of the anisotropic spectrum of $\underline{c}$-$C_4F_8^-$. The transformation was interpreted

as the cycloaddition of C_2F_4 to $C_2F_4^-$. A similar reaction was believed to occur in an irradiated solution of chlorotrifluoroethylene in MTHF. Evidence for the tetrafluoroethylene cycloaddition reaction was also obtained by optical spectroscopy. The optical spectrum of $C_2F_4^-$, obtained in MTHF or 3-methylhexane at 77°K, exhibited vibrational fine structure with a maximum at 508 nm. Warming the MTHF sample produced a decrease in the intensity of the $C_2F_4^-$ spectrum, a slight increase in absorption at 390 nm, the maximum in the optical spectrum of $\underline{c}$-$C_4F_8^-$, and a color change from red to gold.

Gamma irradiation of frozen solutions of chloro-, bromo-, and iodotrifluoroethylene in TMS-$\underline{d}_{12}$ yielded EPR spectra that were orientation dependent, so that rotation of the sample in the magnetic field enhanced one or another set of features. Each of the radicals exhibited an axially symmetric hyperfine tensor for the unique halogen. On the basis of the large spin densities in the highest p orbitals of the unique halogens, as calculated from the anisotropic coupling constants, the radicals were tentatively identified as CF_2CFCl^-, CF_2CFBr^-, and CF_2CFI^-. This work shows the usefulness of the EPR technique for the study of negative ions in the condensed phase.

IV. INVESTIGATIONS OF STRUCTURE, BONDING, AND REACTIONS OF RADIATION-INDUCED FREE RADICALS IN THE SOLID STATE USING ELECTRON SPIN RESONANCE SPECTROSCOPY

(Reggie Lester Hudson, Ph.D. thesis, University of Tennessee, August 1978, 337 pp.).

ABSTRACT: Electron spin resonance spectroscopy (ESR) has been used to study the structure, bonding, and reactions of several types of free radicals produced by γ irradiation of solids at 77 K. Well-defined spectral patterns and the use of photolysis and annealing treatments assisted the analyses and interpretations. Many samples showed preferential orientation effects enabling characteristic anisotropic patterns to be obtained. In some cases

single crystals were used to check the analysis of powder spectra.

The radical anion BF_3^- was generated and identified unequivocally in a matrix of tetramethylsilane at 77 K. Both the ESR data and theoretical calculations support a pyramidal structure with a bond angle of about 110°. The previous assignment of a spectrum from irradiated $NaBF_4$ to BF_3^- was found to be in error as was the conclusion that BF_3^- is a planar radical. The present experiments showed that BF_3^- has ESR parameters consistent with those of the isoelectronic radicals CF_3, NF_3^+, and F_2NO. A matrix diagonalization calculation showed that the boron and fluorine hyperfine coupling constants of BF_3^- were of the same sign.

γ Irradiation of polycrystalline trimethyl borate at 77 K gave an ESR spectrum which was assigned to the dimer radical anion $[(MeO)_3B{\bullet}B(OMe)_3]^-$. Single crystal studies were used as a check on the analysis of the powder patterns. The spin distribution was accounted for by a D_{3d} structure with a one-electron bond between the two boron atoms.

Radical anions of dialkyl carbonates were observed for the first time and found to undergo a β-scission reaction to produce alkyl radicals. This free radical reaction is unusual in that it proceeds both thermally and photochemically. For the dimethyl carbonate radical anion, ^{13}C parameters were obtained from a ^{13}C enriched sample.

The photolysis of trapped radicals in γ irradiated carboxylic esters, RC(O)OR', was studied by ESR spectroscopy and two different reactions were characterized. The radical anion $R\dot{C}(O^-)OR'$ was photobleached by visible light to give the alkyl radical $\dot{R}'$ by a process of β-scission. Bleaching by uv light caused the radical formed by hydrogen-atom loss from the ester group R' to give the acyl radical $R\dot{C}O$ which underwent subsequent photolysis by visible light to form the alkyl radical R•. Nearly all the previous work on the carboxylic esters is consistent with these reactions.

Two hypervalent silicon radical anions were prepared and examined in $Si(OCH_3)_4$. Only two other radical anions of this type are known and, since the spectra were isotropic, no anisotropic coupling constants could be obtained from those experiments. The results of the present work thus represent the first complete sets of data on the silicon 3s and 3p spin densities for such species.

The first PL_3^- radical anion was prepared by the γ irradiation of crystalline trimethyl phosphite, and identified through its photolysis reactions and from the results of radiation chemical experiments. In both single crystal and polycrystalline samples, $P(OMe)_3^-$ was found to undergo geometric rearrangements of its ligands as the sample was annealed.

A published analysis of the ESR spectrum of $As_2Et_6^+$ was found to be in error by assuming the radical would have only a seven-line spectrum. This radical has been prepared from triethyl arsine and its spectrum reinterpreted as the full sixteen-line pattern expected from a second-order analysis.

Several other systems were examined in various types of experiments, the most significant results from these being the measurements of rate constants for methyl radical decay in methanol glasses from 100 to 15 K. The Arrhenius plot was nonlinear and the reaction rate constant appeared to reach a limiting value below 40 K. These results have been discussed in terms of simple models for quantum mechanical tunneling of hydrogen atoms in the solid state.

SECTION 2 - UPDATE OF PREVIOUS REPORTS

V. [ORO-2968-106] ELECTRON SPIN RESONANCE STUDIES OF ELECTRON ATTACHMENT TO FLUOROCARBONS AND RELATED COMPOUNDS (A. Hasegawa, M. Shiotani, and F. Williams, Faraday Discussions Chem. Soc., No. 63, 157 (1977)).

VI. [ORO-2968-107] HYDROGEN ATOM ABSTRACTION BY METHYL RADICALS IN METHANOL GLASSES AT 15-100 K: EVIDENCE FOR A LIMITING RATE CONSTANT BELOW 40 K BY QUANTUM-MECHANICAL TUNNELING (Reggie L. Hudson, Masaru Shiotani, and Ffrancon Williams, *Chem. Phys. Letters*, **48**, 193 (1977)).

VII. [ORO-2968-108] THE ISOTROPIC AND ANISOTROPIC EPR SPECTRA OF THE TETRAFLUOROETHYLENE RADICAL ANION (Robert I. McNeil, Masaru Shiotani, Ffrancon Williams, and Moon Bin Yim, *Chem. Phys. Letters*, **51**, 433 (1977)).

VIII. [ORO-2968-109] NOVEL CYCLOADDITION OF TETRAFLUOROETHYLENE TO THE TETRAFLUOROETHYLENE RADICAL ANION AT 95 K: DIRECT OBSERVATION BY EPR STUDIES (Robert I. McNeil, Masaru Shiotani, Ffrancon Williams, and Moon Bin Yim, *Chem. Phys. Letters*, **51**, 438 (1977)).

IX. [ORO-2968-110] ELECTRON SPIN RESONANCE SPECTRUM OF $[(MeO)_3B\cdot B(OMe)_3]^{-}$. A NOVEL σ-RADICAL WITH A ONE-ELECTRON BOND (Reggie L. Hudson and Ffrancon Williams, *J. Am. Chem. Soc.*, **99**, 7714 (1977)).

SECTION 3 - CONFERENCE PRESENTATIONS ETC.

Dr. Williams served as a discussion leader during sessions at the Gordon Conferences on Radical Ions (Brewster Academy, Wolfeboro, NH, June 19-23, 1978) and Radiation Chemistry (Holderness School, Plymouth, NH, July 17-21, 1978). He also presented departmental seminars by invitation during the 1977-78 academic year at the University of Cincinnati, University of Waterloo (Ontario, Canada), East Carolina University, Duke University, Appalachian State University, and Oak Ridge National Laboratory.

Three contributed papers were presented at the Ninth Southeastern Magnetic Resonance Conference held at Georgia State University, Atlanta, Ga. 30303, on October 6 & 7, 1977. The abstracts of these papers are given below.

Paper C8: Electron Spin Resonance Spectrum of $[(MeO)_3B{\cdot}B(OMe)_3]^-$. A Novel σ-Radical with a One-Electron Bond

Reggie L. Hudson and Ffrancon Williams

Following γ irradiation at 77 K, a sample of trimethyl borate, $B(OCH_3)_3$, gives a seven-line ESR spectrum. The polycrystalline sample shows the preferred orientation effect observed in this laboratory and others previously, so that by rotation of the sample in the spectrometer cavity new lines are found in the spectrum. The additional lines and the original seven make up a pattern of parallel and perpendicular hyperfine features indicative of coupling of an unpaired electron to two I=3/2 nuclei. The ESR spectrum is assigned to the interaction with the two ^{11}B nuclei (I=3/2, 80% natural abundance) in a trimethyl borate dimer radical anion, $[B(OCH_3)_3]_2^-$, with $A_{||}(^{11}B)=59.3G$, $A_{\perp}=39.8G$, $g_{||}=2.0020$, and $g_{\perp}=2.0043$. Inspection of the powder spectrum also shows the presence of both parallel and perpendicular lines for the ^{11}B-^{10}B dimer (for ^{10}B, I=3, 20% natural abundance) in the expected positions with the correct intensity relative to the ^{11}B-^{11}B lines. Exposure of the sample after γ irradiation to visible light removes all ^{11}B-^{11}B and ^{11}B-^{10}B lines, providing evidence that the dimer is an anion. Irradiated single crystals of $B(OCH_3)_3$ show clearly the expected features for the dimer radical anion ESR spectrum. Based on the derived spin densities, the radical is believed to possess a D_{3d} structure with the boron nuclei joined by a one electron bond. The results of INDO calculations on related radicals will be presented.

Paper D4: EPR Studies of the Tetrafluoroethylene Radical Anion

Moon B. Yim, Robert I. McNeil, Masaru Shiotani, and Ffrancon Williams

The tetrafluoroethylene radical anion has been generated in solid solutions by electron addition to the parent molecule. Both its isotropic and anisotropic EPR spectra have been observed, including the isotropic ^{13}C satellite lines in natural abundance. The magnitude of the ^{19}F and ^{13}C hyperfine coupling constants are consistent with a planar ($\underline{D}_{2h}$) structure provided that the unpaired electron occupies the $5\underline{b}_{1u}$ (σ^*) rather than the $2\underline{b}_{1g}$ (π^*) molecular orbital which is predicted by *ab initio* calculations to be the LUMO of the parent molecule. By monitoring the spectral changes, in organic glasses at 80-95 K, the novel cycloaddition reaction $C_2F_4^- + C_2F_4 \rightarrow \underline{c}\text{-}C_4F_8^-$ has been discovered. According to the frontier orbital theory, the concerted reaction is symmetry allowed irrespective of whether the interaction is SOMO-LUMO or SOMO-HOMO, the SOMO of $C_2F_4^-$ being the $5\underline{b}_{1u}$ (σ^*) orbital suggested by EPR studies. The assignment of $C_2F_4^-$ as a σ radical also suggests that a concerted [2 + 2] suprafacial mechanism should be considered for the thermal cycloaddition reaction between two neutral C_2F_4 molecules.

Paper D5: ESR Studies of Hydrogen-atom Abstraction by Methyl Radicals: Further Evidence for Quantum Tunneling at Low Temperatures

Hisao Murai and Ffrancon Williams

The kinetics of methyl radical decay in ethanol glasses has been studied by ESR in the temperature range from 100 K down to 13 K. Although the reaction does not obey simple first-order kinetics, the decay curve at constant temperature is independent of the initial concentration of methyl radicals and shows a good correlation with the growth of CH_3CHOH radicals. Accordingly, the reaction is described as having composite first-order kinetics which probably results from spacial inhomogeneity between the reactants. The reaction rate constants have been determined from the initial slopes of the semi-logarithmic decay curves. The Arrhenius plot shows a positive curvature and the apparent activation energy is less than 1 kcal/mol at 75 K. As in a previous study in methanol glasses (<u>Chem</u>. <u>Phys</u>. <u>Letters</u>, **48**, 193 (1977)), the rate constant appears to reach a limiting value below 40 K. In deuterated ethanol (99 atom % D) at 77 K, the rate constant is at least a factor of 600 smaller than that observed in the protiated ethanol. Moreover, even this slow decay of methyl radicals in the C_2D_5OD glass is attributable to the selective abstraction of the remaining 1% hydrogens in the matrix. These results will be discussed and interpreted as evidence for H-atom abstraction by quantum-mechanical tunneling at low temperatures.

A paper was also presented at the Middle Atlantic Regional Meeting of the American Chemical Society at Hunt Valley, Maryland, April 5-7, 1978. The abstract is given below.

Characterization of Poly(β-Pinene) Prepared by Radiation-Induced Cationic Polymerization

Ashok M. Adur and Ffrancon Williams

The radiation-induced polymerization of dry β-pinene in bulk produces a crystalline polymer which has a low solubility in the monomer (F. Williams <u>et</u> <u>al</u>., <u>Nature</u>, <u>187</u>, 665 (1960); <u>J</u>. <u>Chem</u>. <u>Soc</u>., 1531 (1962)). The present study reports a fuller characterization of this polymer by various techniques. Both infra-red and ^{1}H NMR spectroscopy were used to establish the chemical repeat unit. The polymer was found to be birefringent and X-ray diffraction showed two distinct absorption peaks corresponding to lattice spacings of 4.04 and 4.96 Å. Since the chemical repeat distance of the extended chain is calculated to be 6.5 Å, these values indicate a triclinic unit cell. The polymer was found to be <u>ca</u>. 50% crystalline which is highly unusual for such a complex repeat unit. The degree of crystallinity of the polymer fractions showed a linear correlation with bulk density determined both by density gradient column and by flotation methods. Differential scanning calorimetry indicated a crystalline melting point of 206-208°C. Solubility and thermal characteristics will also be presented. The characterization data have been compared with results obtained for the polymer prepared by catalytic initiation using Lewis acids. It should also be noted that the polymer produced by radiation-induced polymerization undergoes extensive auto-oxidation on standing in the atmosphere and this reaction will be discussed.