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RADIATION DEGRADATION OF POLYMETHACRYLAMIDE

City University of New York PH.D. 1984

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RADIATION DEGRADATION OF POLYMETHACRYLAMIDE

by

DANIEL O'CONNOR

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fullfillment
of the requirements for the degree of Doctor
of Philosophy, The City University of New York.

1984

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

5/8/84
date

Chairman of Examining Committee

5\8\84
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Abstract

RADIATION DEGRADATION OF POLYMETHACRYLAMIDE

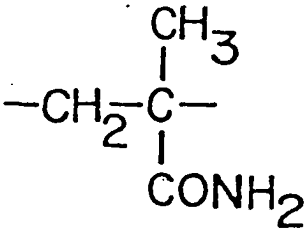
by

Daniel O'Connor

Advisers: Professors Nan-Loh Yang and Arthur Woodward

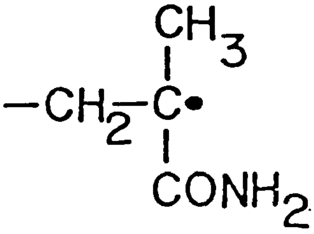
The effects of radiation on polymers have been studied for many years. When polymers are subjected to ultraviolet light or ionizing radiation, chain scission and crosslinking are possible.

In the present work the radiation degradations of several methacrylate type polymers were investigated. The primary polymer studied was polymethacrylamide (PMAAm) with the structure shown below:



$$-\mathrm{CH_2}-\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C}\\ |\\ \mathrm{CONH_2}\end{array}-$$

Ultraviolet irradiated PMAAm yielded a five line ESR spectrum with 22 gauss splitting which is believed to arise from a polymeric radical ending with a methacrylamide unit:



$$-\mathrm{CH_2}-\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{C}\bullet\\ |\\ \mathrm{CONH_2}\end{array}$$

An ESR spin trapping study of irradiated PMAAm with nitroso-t-butane suggested that the polymeric methacrylamide radical and the amide free radical are generated upon irradiation. A mechanism of degradation of PMAAm was proposed. The amide group is cleaved from the polymer backbone in a primary process. The polymer radical produced undergoes beta scission to yield the polymeric methacrylamide radical.

The degradations after exposure to gamma irradiation for PMAAm, a copolymer of methacrylamide (MAAm) with methyl methacrylate (MMA) and poly(isobornyl methacrylate) were also investigated. Molecular weight measurements were used to determine radiation G values in events per 100 eV. The G values found are listed below:

1. PMAAm $G_s-G_x=2.05$
2. Copolymer (MAAm - MMA) $G_s=0.92$ $G_x=0.09$
3. Poly(isobornyl methacrylate) $G_s-G_x=2.10$

The results obtained indicate that polymethacrylamide is a polymer which undergoes main chain cleavage upon irradiation. As such this polymer may have potential applicability as a positive resist for fabrication of microelectronic devices.

ACKNOWLEDGEMENT

The author wishes to express his deepest gratitude to Professors N.-L. Yang and A.E. Woodward for their expert advice and assistance during this project. He also thanks the Engineering and Chemistry Departments at the College of Staten Island, the Graduate School and University Center and PSC grants for financial support during this work.

LIST OF ABBREVIATIONS

1. PMAAm - Polymethacrylamide
2. PMMA - Poly(methyl methacrylate)
3. MAAm - Methacrylamide
4. MMA - Methyl methacrylate
5. ESR - Electron Spin Resonance
6. NMR - Nuclear Magnetic Resonance
7. GPC - Gel Permeation Chromatography
8. DMF - Dimethyl formamide
9. THF - Tetrahydrofuran
10. NtB - Nitrosotertiary butane

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I. Historical Background

A. Introduction and Objectives

The broad objective of this research was to elucidate the fundamental processes involved during the radiation degradation of several methacrylate type polymers. Specific polymers investigated were poly(methacrylamide), a copolymer containing methacrylamide with methyl methacrylate and poly(isobornyl methacrylate).

First an introduction to the effects of radiation on polymers is given. Sections which follow discuss electron beam lithography, electron spin resonance and spin trapping. A literature survey of ESR studies on methacrylamide and related compounds is also presented.

Approaches taken in this study may be outlined as follows. First Carbon-13 NMR spectroscopy was used to characterize the tacticity of the polymers produced. Next, molecular weight measurements utilizing gel permeation chromatography, membrane osmometry and automatic viscosity served to define the relations between gamma radiation dosage and molecular weights. Radiation G values for chain scission and crosslinking were determined. Chain scission seems to be the predominant process since the molecular weights of the polymers decrease as the radiation dosage increases. It is desirable to produce polymers with high values of G(scission) in order to maximize the sensitivity to ultraviolet light or ionizing radiation. Finally ESR spectroscopy and the ESR spin trapping technique were used to detect and identify the free radical intermediates produced upon ultraviolet irradiation of the polymers. The free radicals identified suggest that chain scission occurs for these polymers.

This investigation should contribute not only to the understanding of the fundamental processes during the irradiation degradation of polymers but also to modern electronic technology. Methacrylate type polymers are widely used as positive type resists for electron beam or photolithography. Poly(methyl methacrylate) has been widely used for this purpose. However it is desirable to develop new materials with enhanced performance characteristics such as sensitivity and resolution. An efficient resist would be a contributing factor to the next breakthrough in computer technology.

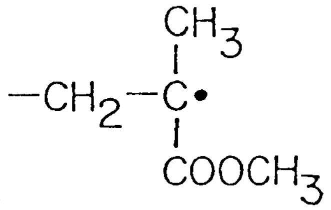
B. The Effects of Radiation on Polymers

Radiation chemistry of high polymers has been a subject of much interest since it was found that radiation may profoundly affect the behavior of many important commercial polymers (1)(2)(3).

Many studies have been performed on the changes in chemical structure of irradiated polymers as well as the resulting changes in their physical properties. Types of radiation involved include gamma rays, X-rays, high energy electrons and ultraviolet light.

There are two main groups of polymers. Polymers which crosslink upon irradiation undergo increases in molecular weight due to the fact that branched and network structures are being formed. Polymers that tend to degrade by chain scission yield monomeric units and smaller chain fragments.

Poly(methyl methacrylate) (PMMA) is a material that is known to degrade by chain scission. Gamma irradiation of PMMA in vacuo leads to the formation of several gaseous products including methane, hydrogen, carbon monoxide and carbon dioxide. Subsequent thermal treatment of irradiated PMMA resulted in the formation of monomer. A chain depolymerization process may be initiated at elevated temperatures by radicals trapped in the irradiated polymer. ESR spectra indicate that a free radical with the structure shown below may be obtained from irradiation of PMMA (4).



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\bullet$$

The ESR spectrum of PMMA after gamma irradiation at 300°K is shown in Figure 1.

Figure 1. ESR spectrum of irradiated PMMA at 300°K.

A total of nine lines are seen. It was explained that the aforementioned free radical was in two different structural conformations, giving rise to a quintet and a quartet.

The reciprocal weight average molecular weight of PMMA increased linearly with the radiation dosage in the range of one to eleven megarads with G(scission) = 1.65 and G(crosslink) = 0. Crosslinking is believed to be negligible in the process. Other polymers that undergo chain scission are polyisobutylene and poly(α-methyl styrene).

In some polymers a controlled degree of crosslinking may prove beneficial to the physical properties of the materials. However too much radiation may cause some polymers to become brittle and degrade with subsequent loss of their valuable properties.

C. Electron Beam Lithography

Electron beam lithography has become an important technique in the fabrication of microelectronic devices such as integrated circuits (5). Polymer coatings are used as resists in lithography. A resist which becomes more soluble after irradiation is said to be a positive resist. The polymer used here must be of the degrading type. A resist which becomes less soluble after irradiation is called a negative resist. The polymer used in this case must be of the crosslinking type. Both positive and negative resists have been designed to maximize performance characteristics such as resolution, line width and sensitivity.

The lithographic process can be described as follows. A thin film of polymer is coated onto a substrate. The film thickness is usually not greater than five micrometers. After the sample is dried the exposure process is carried out. A mask is applied to the regions of the resist that are not to be irradiated. The exposed areas are irradiated with ultraviolet light or the electron beam. Figures 2 and 3 describe the processes occurring for positive and negative resists.

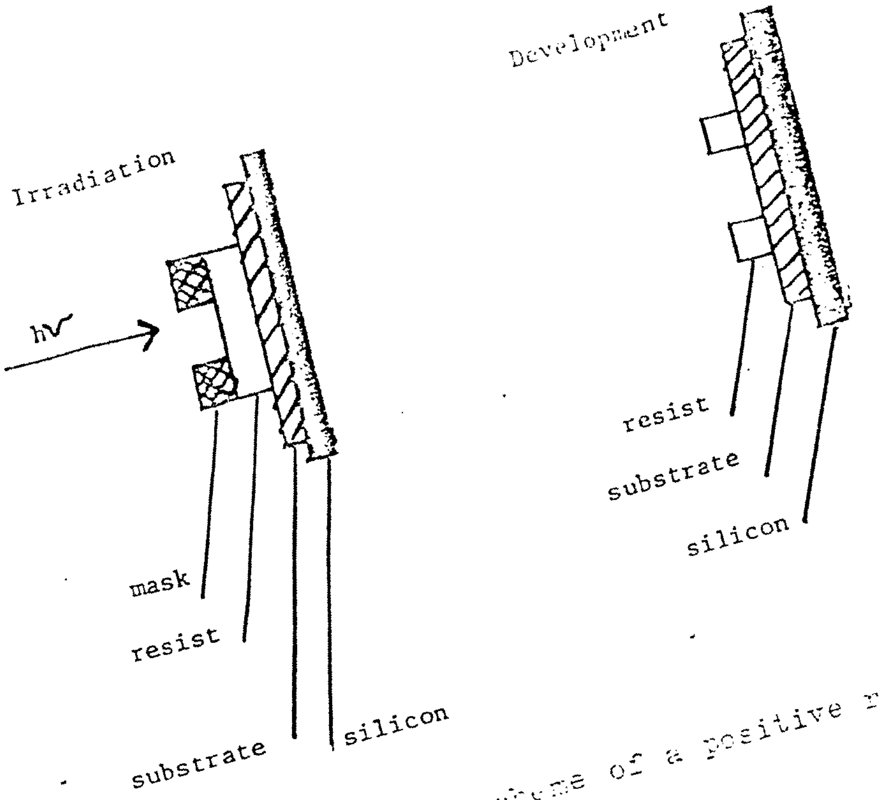


Figure 2. The scheme of a positive resist.

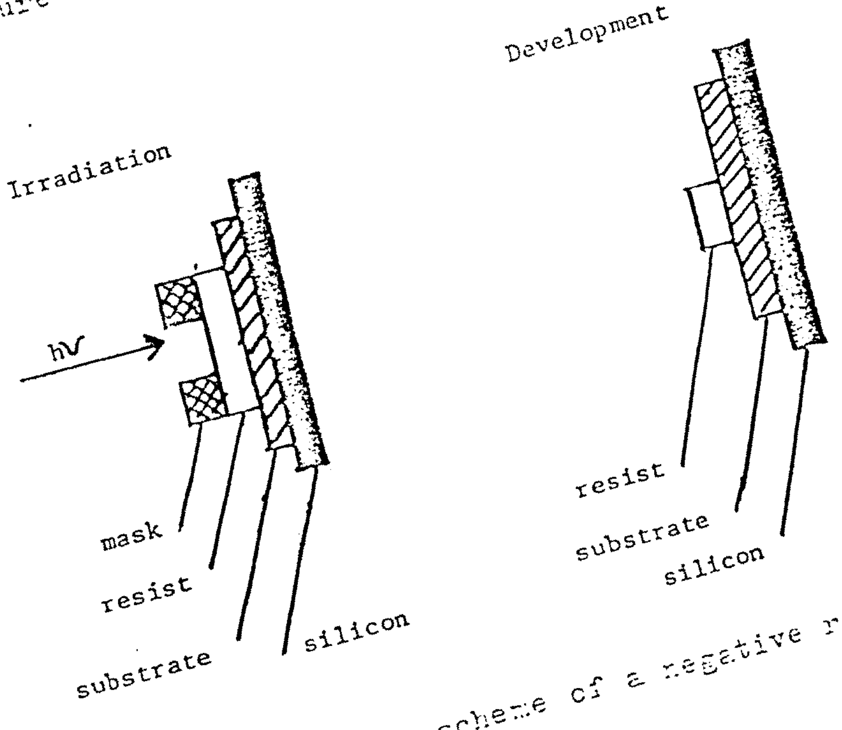


Figure 3. The scheme of a negative resist.

After irradiation the film is developed, leaving only certain areas of the resist. The exposed areas of the substrate may be etched and then the resist is removed. The desired pattern of the circuit remains.

PMMA has been widely used as a positive resist for electron beam exposure (6)(7). This polymer has a high resolution but its sensitivity is not as high as that of some negative resists. It is therefore desirable to develop new materials with both high resolution and good sensitivity for electron beam lithography.

In the present study poly(methacrylamide) (PMAAm) and its copolymers with methyl methacrylate were investigated as to their behavior upon irradiation with ultraviolet light and gamma rays. Experiments performed here suggest that the aforementioned materials undergo main chain degradation when irradiated.

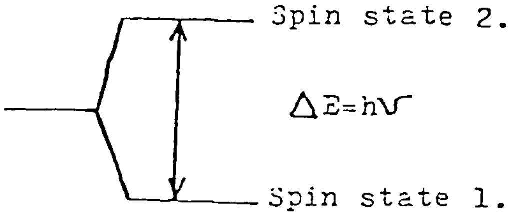
The use of a thermally treated PMAAm as a positive electron beam resist has been reported (8). This thermally treated polymer has both intramolecular and intermolecular imide bridges. The material was found to be highly sensitive when irradiated under the electron beam. The resist sensitivity increased as the accelerating voltage of the electron beam increased. Hole depths of nearly 4000 angstroms could be obtained.

However there are no reports in the literature concerning the radiation degradation of PMAAm. The following study was undertaken in order to determine the changes in structure of PMAAm after irradiation and to elucidate its mechanism of degradation.

D. Electron Spin Resonance and Spin Trapping

ESR measurements may be carried out on paramagnetic substances, i.e., materials that have one or more unpaired electrons. An unpaired electron has a magnetic moment μ. When the electronic moments are placed in a magnetic field (H_0), the moments split up into two spin states separated by a certain energy ΔE as described in Figure 4.

Moment in absence of H_0. Moment and H_0.



Energy levels of μ in H_0.

Figure 4. Electronic moment and magnetic field.

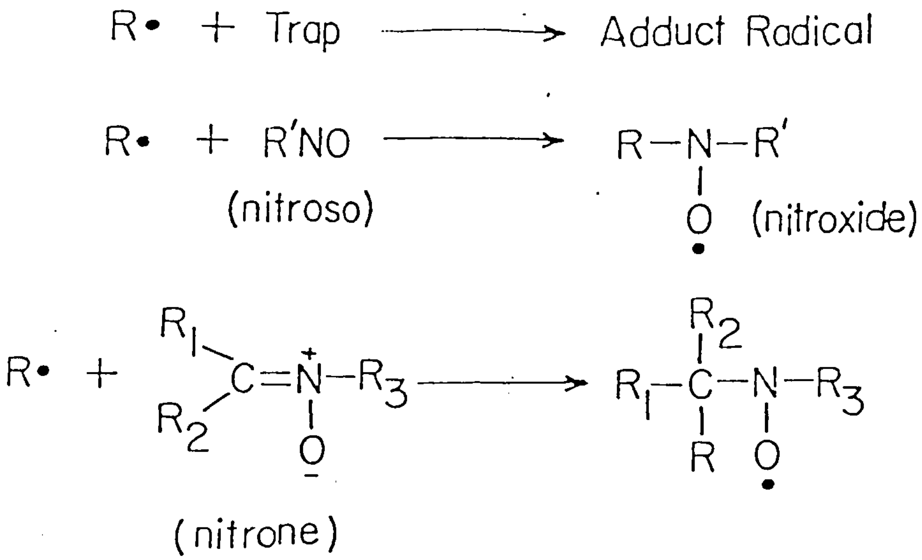
The moments precess around the applied magnetic field as shown. Microwave radiation ($h\nu$) is now introduced to the sample. When the magnetic field and frequency are just right, the moment absorbs energy and flips to the other spin state. It is the absorption of energy which produces the ESR signal. Normally ESR spectra are recorded as the first derivative curves.

The magnetic moment of a nucleus near to the unpaired electron may interact with the electronic moment. This type of interaction is called a hyperfine coupling. The ESR signal may be split into a multiplet as a result of this coupling. The total number of lines in a multiplet depend on two factors namely the number of nuclei that interact with the unpaired electron and the spin quantum numbers of those nuclei.

The expected number of lines in a multiplet is $2nI+1$ where n equivalent nuclei of spin quantum number I interact with the unpaired electron. For example the methyl radical has a four line spectrum due to coupling with three equivalent protons ($I=\frac{1}{2}$). The ditertiary-butyl nitroxide free radical has a three line spectrum due to coupling with the nitrogen 14 nucleus ($I=1$).

Since free radicals are usually generated upon ultraviolet irradiation of polymers, ESR spectroscopy is the method of choice for the study of free radical intermediates during the irradiation of polymers.

Spin trapping studies have proved useful for the investigation of free radicals by ESR spectroscopy (9)(10). In a spin trap experiment a short lived, reactive free radical (R•) reacts with a trapping agent to yield a relatively stable adduct free radical which may be studied. The adduct radical may then yield information about the radical which was initially trapped. Trapping compounds fall into two categories, nitroso compounds and nitrones. Equations which describe the trapping process are shown below:

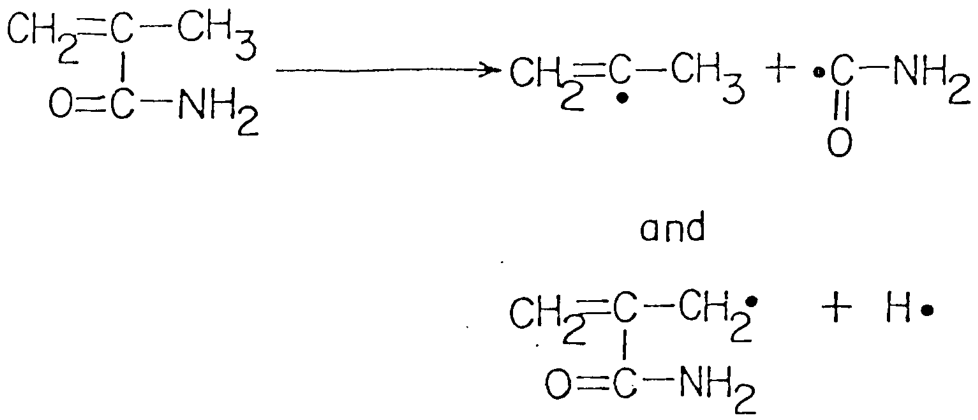


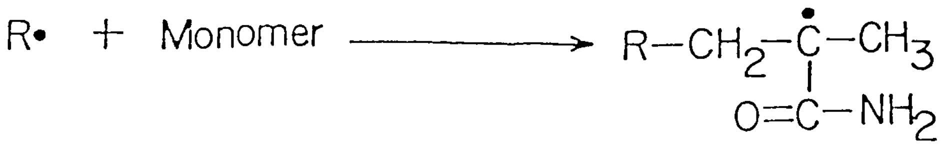
Nitroso compounds have an advantage over nitrones. The former materials can provide a fingerprint of the initial radical. However the nitroso compounds do have disadvantages. Nitroso compounds tend to exist in a dimeric state which is inactive as a trapping agent. Ultraviolet light must be used to dissociate the dimer. Also the UV radiation may cause side reactions of nitroso compounds with the formation of undesired radicals. The most common compound for trapping studies is nitroso-tertiary butane, which was used for studies performed in this work.

E. Literature Survey for ESR Spectroscopy

1. ESR Studies of Methacrylamide Polymerization

Before proceeding to the study of polymethacrylamide perhaps it would be instructive to discuss results of ESR experiments obtained from the polymerization of the monomer methacrylamide. Ueda (11) prepared single crystals of methacrylamide. Subsequently these crystals were irradiated with gamma rays at 288°K. The reactions believed to occur upon irradiation of methacrylamide are shown below:





"Radical I"

One possibility is to have cleavage of the carbon - carbon bond at the amide group. It may also be possible for hydrogen abstraction from the methyl group. A free radical may react with monomer to initiate polymerization. "Radical 1" would be obtained. An ESR spectrum was recorded for the sample of irradiated methacrylamide and is shown in Figure 5.

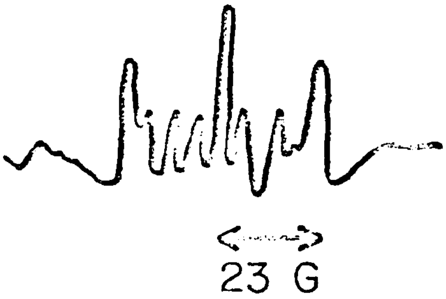
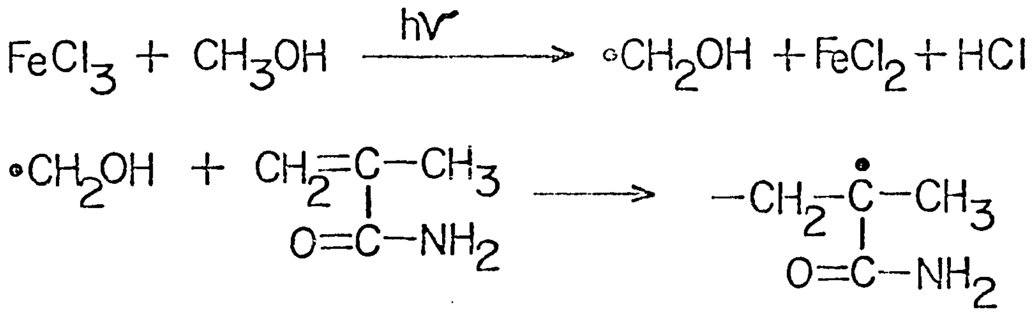


Figure 5. ESR spectrum of irradiated methacrylamide at 293°K.

The ESR spectrum of irradiated methacrylamide shows two sets of lines. First there is an anisotropic sextet which is believed to arise from a free radical with the unpaired electron on a nitrogen atom. Second there is an isotropic quintet with a hyperfine splitting of 23 Gauss. The quintet is believed to arise from radical 1. Here it was explained that the three methyl protons and one of the beta methylene protons from "radical 1" were interacting with the unpaired electron. This explanation would account for the five line spectrum with approximate binomial intensity distribution of 1:4:6:4:1.

More recently an ESR study was made on the free radical photoinitiated polymerization of methacrylamide in a rigid glass of methanol at low temperature (12). The reactions for photoinitiated polymerization are shown below:



$$\mathrm{FeCl_3} + \mathrm{CH_3OH} \xrightarrow{h\nu} \cdot\mathrm{CH_2OH} + \mathrm{FeCl_2} + \mathrm{HCl}$$

$$\cdot\mathrm{CH_2OH} + \mathrm{CH_2{=}}\underset{\mathrm{O{=}C-NH_2}}{\underset{|}{\mathrm{C}}}\mathrm{-CH_3} \longrightarrow \mathrm{-CH_2-}\underset{\mathrm{O{=}C-NH_2}}{\underset{|}{\dot{\mathrm{C}}}}\mathrm{-CH_3}$$

"Radical 1"

Radical 1 would be obtained during polymerization. The sample was held at -140°C for several minutes and then the temperature was lowered to -160°C. The ESR spectrum recorded for this sample is depicted in Figure 6.

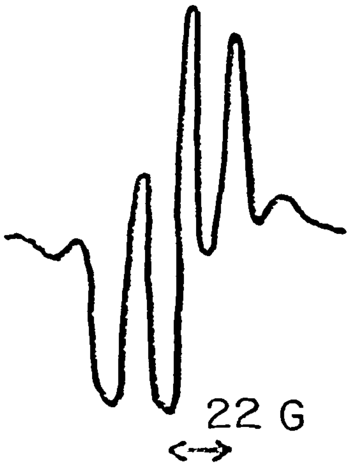


Figure 6. ESR spectrum obtained during the polymerization of methacrylamide.

A five line spectrum with a hyperfine coupling of 22 Gauss was obtained. The intensities ratio of the lines is approximately 1:4:6:4:1. This spectrum is believed to arise from "radical 1." The basis for this assignment was that four equivalent protons were interacting with the unpaired electron. Three of these protons were from the methyl group and one proton from the beta methylene group. There was no measurable interaction of the second beta methylene proton with the unpaired electron.

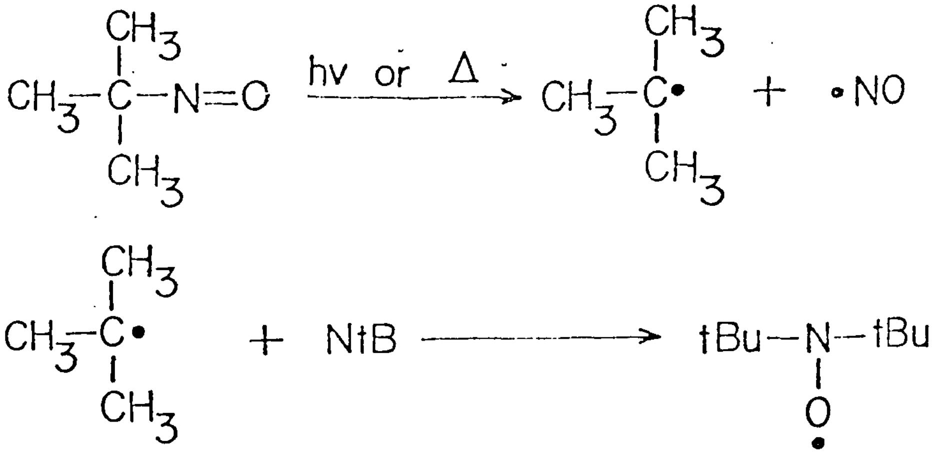
2. Nitroso Compounds as Spin Trapping Agents

Nitroso compounds and nitrones have been employed as trapping agents. Radical intermediates may react with nitroso compounds to form stable nitroxide radicals which may be studied by the ESR technique. Nitroso-tertiary butane (NtB) has been widely used as a trapping agent.

Nitrosoalkanes have been found to exist in a dimeric form which is in equilibrium with the monomeric form (13) (14).

$$\underset{\text{dimer}}{(\mathrm{RNO})_2} \rightleftharpoons \underset{\text{monomer}}{2\ \mathrm{RNO}}$$

NtB tends to exist in a dimeric form which is colorless. The monomer has a blue color. The dimer is inactive as a trapping agent. The monomeric form of the compound must be generated from the dimer by heat or photolysis. The monomeric form may then undergo free radical reactions. The monomer form of NtB has the disadvantage of being thermally and photochemically unstable. The side reactions that NtB may undergo are shown below:



NtB is broken down into a tertiary butyl free radical and nitrogen oxide. The t-butyl radical may be trapped by NtB to yield the ditertiarybutyl nitroxide radical. If one were to photolyze a sample in the presence of NtB a t-butyl radical will be generated in addition to whatever radicals are obtained from the sample. Since many different radicals may be trapped, complicated ESR spectra may result. However if an excess of sample over NtB is used then the formation of impurity nitroxides will be minimized. NtB was photolyzed with red light (wavelength = 680 nm.) and an ESR spectrum was obtained. This spectrum is shown in Figure 7.

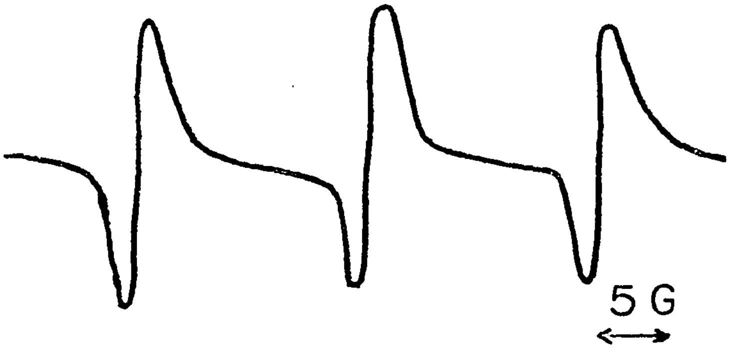


Figure 7. ESR spectrum of irradiated NtB at -25°C.

The three line spectrum is assigned to the di-t-butyl nitroxide free radical. The measured hyperfine splitting is 15.7 Gauss. When NtB was irradiated with gamma rays (16) di-t-butyl nitroxide was obtained. A three line spectrum with coupling of 17.2 was reported. The difference in the hyperfine splittings may be attributed to differences in temperature or solvent.

Other nitroso compounds have been employed as trapping agents such as nitroso benzene and 2,4,6-tri-t-butyl nitroso benzene. Since the samples studied in this work were water soluble, NtB was selected as the trapping agent because of its appreciable solubility in water.

3. Spin Trap Studies of Methacrylamide Polymerization

Otsu and coworkers (17) applied the spin trapping technique to the polymerization of some methacrylamide derivatives. Attempts were made on the polymerization of N-methyl methacrylamide and N,N-dimethyl methacrylamide. Ditertiarybutyl peroxyoxalate was used as a free radical initiator in a benzene solution of the monomer with NtB. Figure 8 depicts the ESR spectrum recorded for N-methyl methacrylamide.

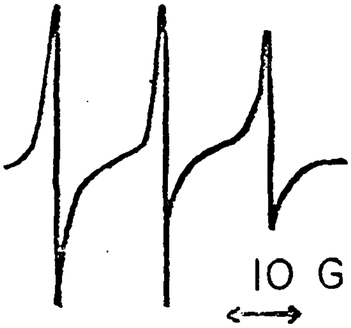
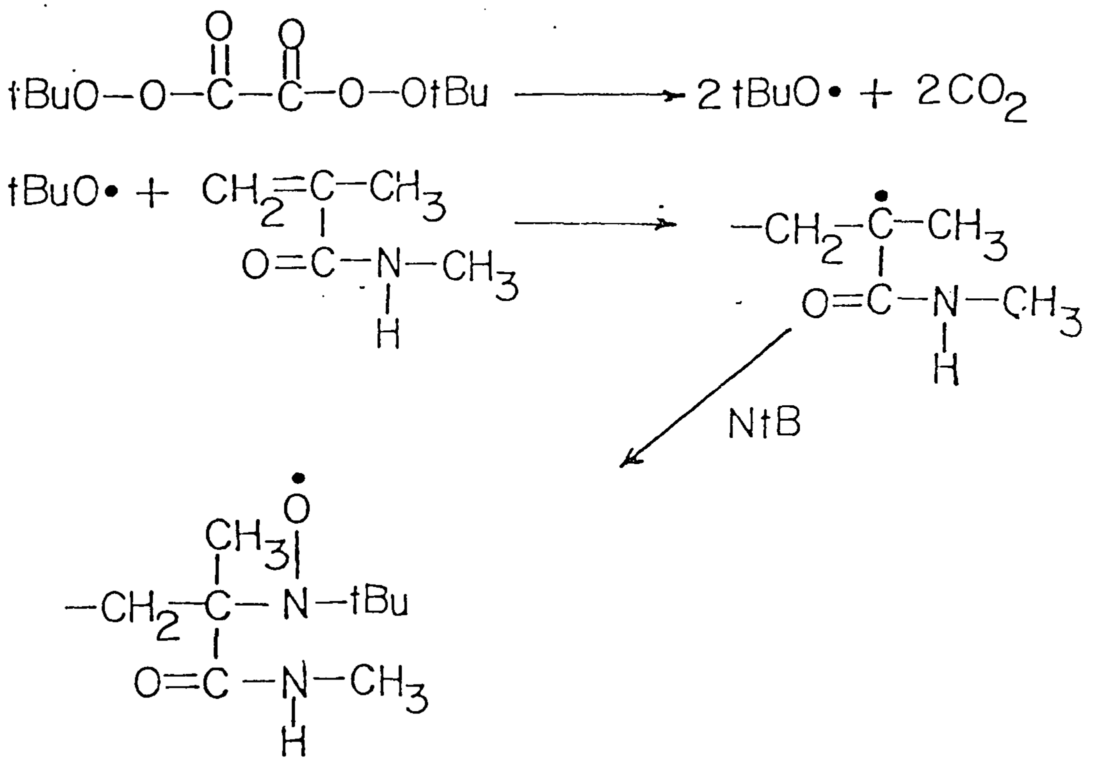


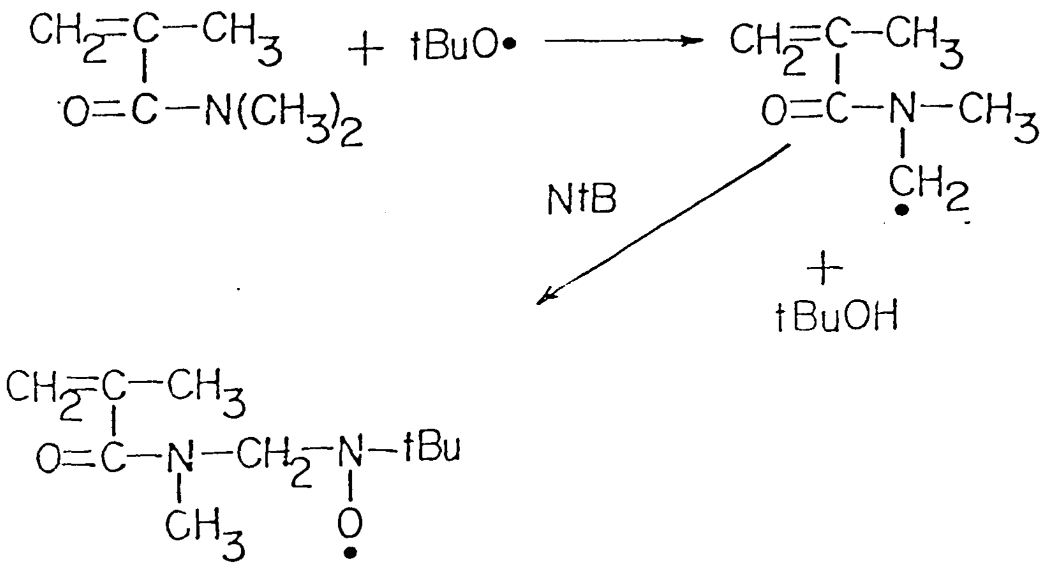
Figure 8. ESR spectrum for spin trapping during polymerization of N-methyl methacrylamide.

A three line spectrum with coupling of 15.5 Gauss is obtained. The reactions believed to occur for polymerization - spin trapping of N-methyl methacrylamide are shown below:



The t-butoxy radical initiates polymerization of N-methyl methacrylamide to yield a propagating free radical. The N-methyl methacrylamide radical is then trapped by NtB to give an adduct radical. The ESR spectrum of Figure 8 is assigned to the trapped propagating radical.

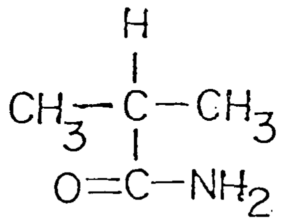
N,N-dimethyl methacrylamide was found to behave in a different way. When this monomer was allowed to react with the t-butoxy radical and NtB, hydrogen abstraction from one of the N-methyl groups occurred. The reaction scheme is shown below:



The structure of the adduct is shown. This result reflects the fact that radical homopolymerization of N,N-dimethyl methacrylamide is very difficult on the basis of steric problems.

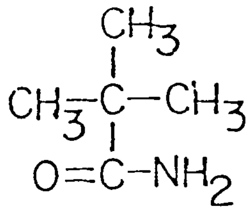
4. ESR Studies of Analog Compounds

Two low molecular weight analogs for polymethacrylamide are isobutyramide and pivalamide with the structures shown below:



$$\begin{array}{c} H \\ | \\ CH_3-C-CH_3 \\ | \\ O=C-NH_2 \end{array}$$

Isobutyramide

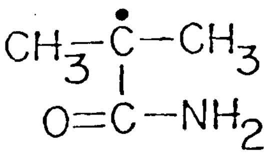


$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ O=C-NH_2 \end{array}$$

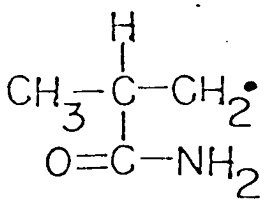
Pivalamide

Rustgi and Riesz (18)(19) made ESR spin trapping studies on many amide compounds including isobutyramide and pivalamide. Aqueous solutions of amide compounds were irradiated with ultraviolet light in the presence of hydrogen peroxide and NtB. Free radicals produced upon reaction of OH radicals with amide compounds were identified through the spin trapped adducts.

When isobutyramide was irradiated in the presence of H_2O_2 and NtB, the ESR spectrum of Figure 9 was obtained. The free radicals shown were obtained.



$$\begin{array}{c} \bullet \\ CH_3-C-CH_3 \\ | \\ O=C-NH_2 \end{array}$$



$$\begin{array}{c} H \\ | \\ CH_3-C-CH_2^{\bullet} \\ | \\ O=C-NH_2 \end{array}$$

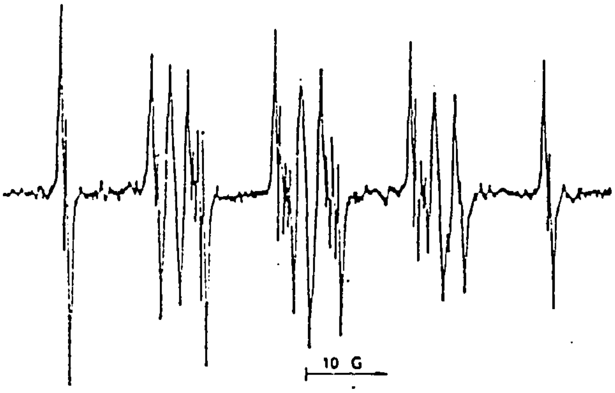


Figure 9. ESR spectrum of irradiated iso-butyramide with H_2O_2 and NtB in D_2O at room temperature.

When pivalamide was irradiated in the presence of H_2O_2 and NtB, the spectrum shown in Figure 10 was obtained. The structure of the radical that was trapped is also shown.

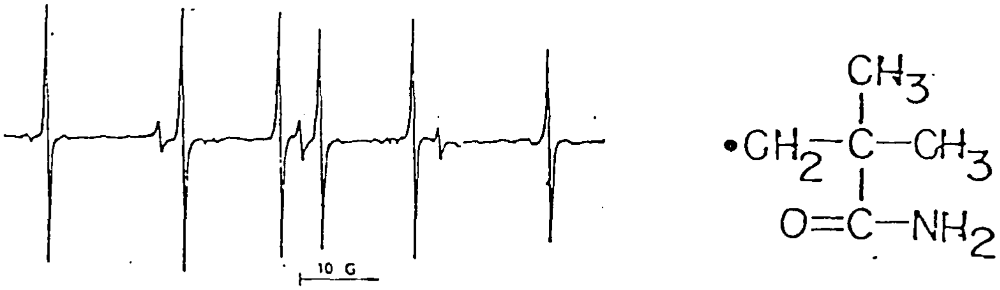


Figure 10. ESR spectrum of irradiated pivalamide with H_2O_2 and NtB in D_2O at room temperature.

The ultraviolet photolysis of formamide with NtB in aqueous solution was also performed. An ESR spectrum was obtained and is shown in Figure 11. The structure of the adduct radical is given.

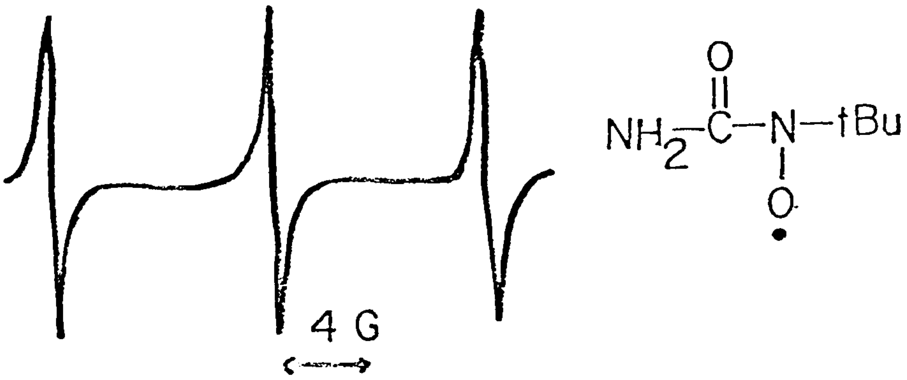


Figure 11. ESR spectrum of irradiated formamide with NtB in D_2O at room temperature.

This three line spectrum was assigned to the NtB adduct of the amide free radical. The hyperfine coupling of 10.45 Gauss is typical of trapped acyl free radicals.

II. Polymer Preparation and Characterization by C-13 NMR

The objective of this research was to study the degradation of a series of methacrylate type polymers by ultraviolet and gamma radiation. Methacrylate type polymers such as PMMA have a known tendency toward degradation with main chain scission and may be useful as positive type resists. The polymers selected in this work were the following:

1. Polymethacrylamide (high molecular weight)
2. Polymethacrylamide (low molecular weight)
3. Copolymers of methacrylamide with methyl methacrylate
4. Poly(isobornyl methacrylate)

The aforementioned polymers were prepared by free radical methods. High molecular weight PMAAm was prepared by redox polymerization of methacrylamide in aqueous solution at room temperature. PMAAm with molecular weight of 38,000 was prepared by benzoyl peroxide initiated polymerization in refluxing toluene. Low conversion copolymers with varying compositions of methacrylamide with methyl methacrylate were prepared in ethanol at 70°C with benzoyl peroxide as initiator. Poly(isobornyl methacrylate) was prepared by bulk polymerization of the monomer at 85°C.

Carbon-13 NMR is a powerful technique for the characterization of stereochemical configuration in vinyl polymers (20). In addition to the elimination of inherent problems of proton NMR, carbon-13 spectroscopy may be used to elucidate polymer tacticity and structural sequence in polymeric samples.

Pulse Fourier transform C-13 NMR spectroscopy has been used to study some common vinyl polymers including polystyrene, polypropylene and PMMA (21). For each polymer studied stereochemical fine structures were observed. Figure 12 illustrates an application of C-13 NMR to polymer structure (22).

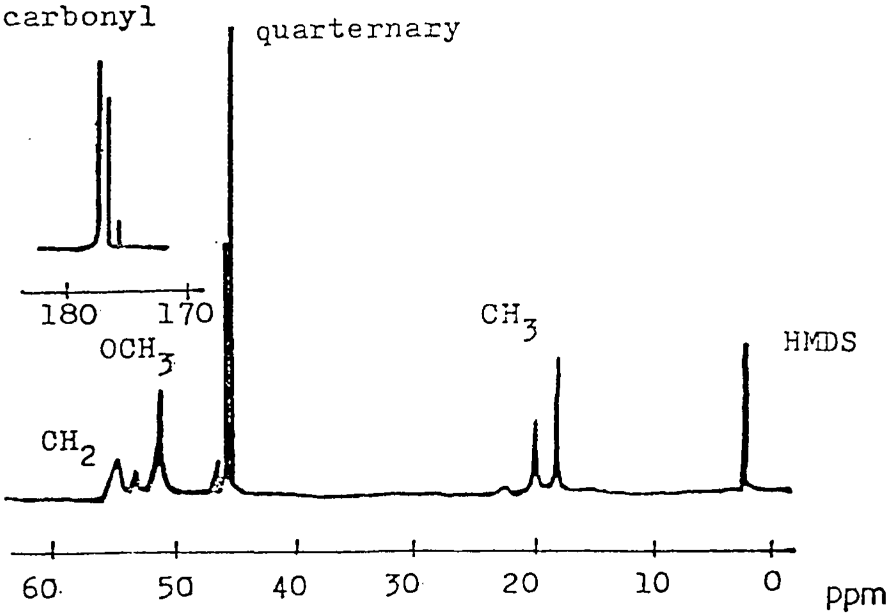


Figure 12. 25.2 MHz C-13 NMR spectrum of PMMA in trichlorobenzene at 120°C.

For PMMA the alpha methyl carbon, quarternary carbon and carbonyl carbon all show triad sensitivity (mm; the isotactic triad, rr; the syndiotactic triad and mr; the atactic triad). The methylene carbon shows diad sensitivity (meso and racemic). The spectrum indicates that the sample has a predominance of syndiotactic character.

Carbon-13 NMR may assist one to determine if polymerization follows Bernoullian statistics (i.e., that polymerization is stereospecifically random). With a single statistical parameter such as f_r (the fraction of racemic diads) one may predict the fractions of higher order sequences such as triads and tetrads. If Bernoullian statistics are obeyed at the triad level then the theoretical fractions of triad sequences are given by the following relations:

$$f(mm) = f_m^2$$
$$f(rr) = f_r^2$$
$$f(mr) = 2f_m f_r$$

In general vinyl polymers produced by free radical reactions at elevated temperatures follow Bernoullian statistics whereas polymers produced by ionic reagents generally do not. For ionic polymerization the growing chain end influences the placement of the incoming monomer unit.

The microtacticity of polymethacrylonitrile produced at 80°C by free radical polymerization was reported (23). The methyl region exhibited triad sensitivity with some further splitting to pentad structures. The methylene region showed partial resolution of tetrad structures. However the quarternary and nitrile carbons showed no fine structure. At the triad, tetrad and pentad levels polymethacrylonitrile closely followed Bernoullian statistics.

Poly(methacrylic acid) was synthesized in several stereoregular forms (24). Carbonyl and methyl carbon resonances were used to evaluate the proportions of triad fractions. Isotactic poly(methacrylic acid) was prepared by anionic polymerization of trimethylsilyl methacrylate followed by hydrolysis. The isotactic sample contained 93% mm triads. The syndiotactic sample was prepared by gamma irradiation in isopropanol at -78°C. The syndiotactic sample contained 85% rr triads. Atactic poly(methacrylic acid) was prepared at 60°C with AIBN as initiator. The latter polymer contained 44% mr triads and closely followed Bernoullian statistics.

Another polymer of interest that has been studied by C-13 NMR is polyacrylamide (PAM) (25). The methine region of PAM (42.4 to 43.2 ppm) showed triad sensitivity with further splitting to pentads. The methylene region (34.5 to 37.0 ppm) showed hexad resonances. The fraction of meso placement was 0.43. Based on this value the theoretical fractions for pentad and hexad sequences were calculated. Comparison with the observed intensities revealed that PAM closely followed Bernoullian statistics at the pentad and hexad levels.

Hatada and coworkers (26) studied a sample of PMAAm produced by a redox type polymerization. 50 MHz carbon spectra were reported for the polymer in d-6 ethylene glycol at 100°C. The polymer was predominantly syndiotactic in nature. The fraction of rr triads considering the alpha methyl resonance was 0.64. This result was in close agreement with $f_r = 0.83$ by assuming Bernoullian statistics. Pentad splittings were observed for the carbonyl carbon and the quarternary carbon exhibited triad sensitivity.

The polymer samples prepared in the present work were characterized by C-13 NMR to obtain information about their tacticities. Redox PMAAm and PMAAm made by benzoyl peroxide initiated polymerization were dissolved in D_2O - H_2O mixtures with urea. Dioxane was added for referencing with respect to TMS. The dioxane carbon shift appears at 67.4 ppm. Polymer concentration was in the range of 10% to 15% by weight. The NMR spectrum for PMAAm produced at high temperature appears in Figure 13. The spectral parameters and assignments are given in Table 1.

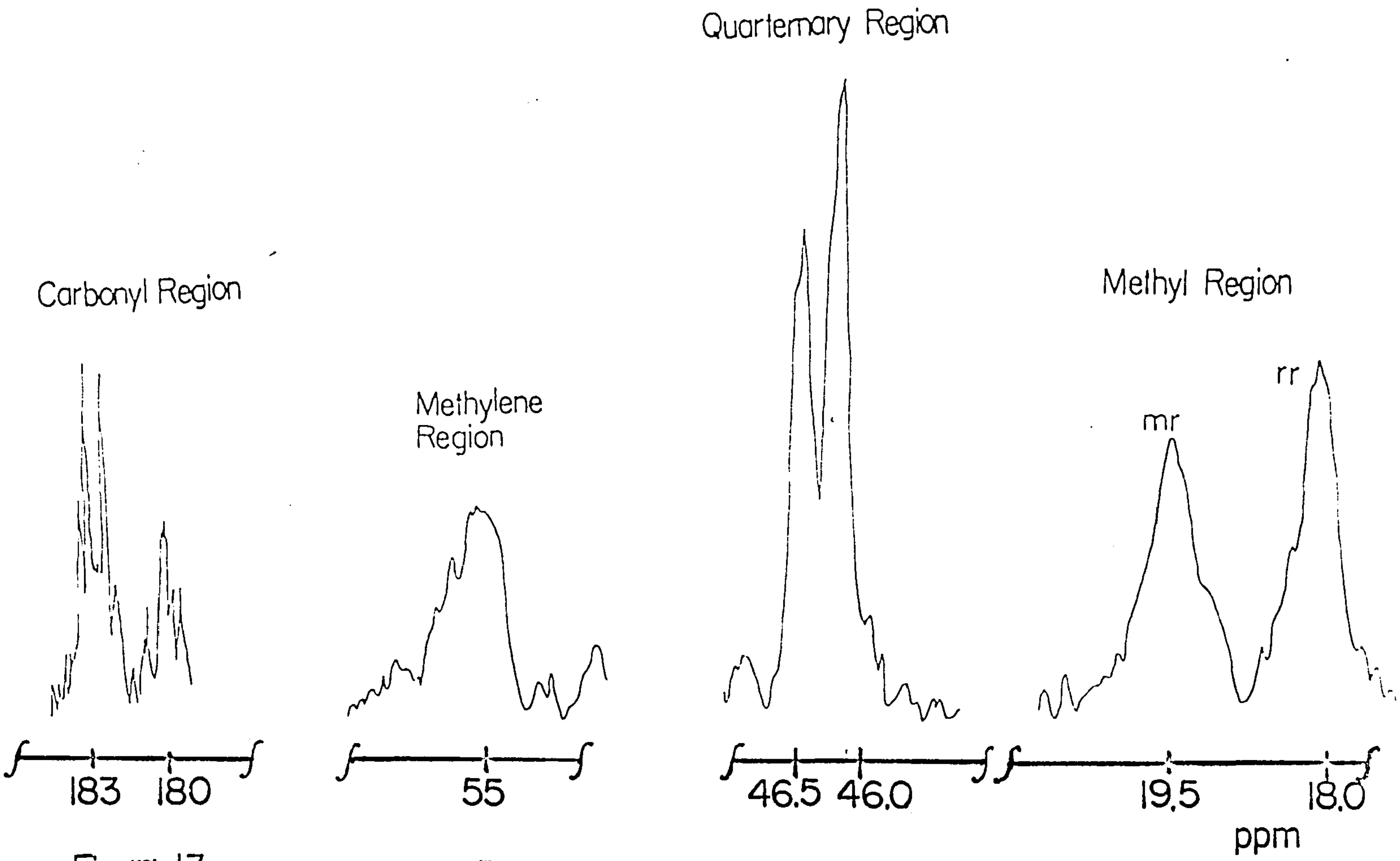


Figure 13. 20 MHz C-13 NMR spectrum for PMAAm produced at high temperature.

Table 1. Spectral data for PMAAm produced at high temperature.

Parameters:

Relaxation Delay: 1.0 second

Pulse Width: 60°

Line Broadening: 1 Hz

Number of Scans: 2,715

Temperature: 90°C

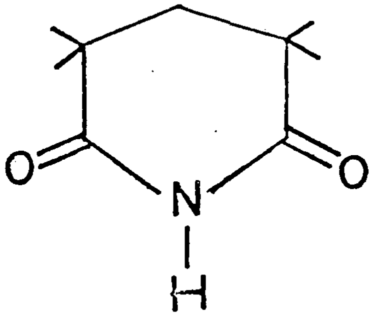
		Quantitative	
Assignment	Shift (ppm)	Detd.	Calc.
Methyl mm	———	0.00	0.07
" mr	19.5	0.47	0.40
" rr	18.1	0.53	0.53
Quarternary mm	47.1		
" mr	46.4		
" rr	46.1		
Methylene r	55.0		
Carbonyl mrrr	183.4		
" rrrr	183.1		
" rmrr	182.5		
" Imide	180.4		

$f_r = 0.73$

The alpha methyl region of the NMR spectrum was studied quantitatively for the evaluation of triad fractions. A relaxation delay of one second was used since this should be sufficient for quantitative accuracy.

Carbon-13 relaxation times have been reported for PMMA (27). For pyridine solutions of PMMA at 100°C the alpha methyl C-13 of syndiotactic PMMA had a T_1 value of 0.200 second. The same resonance in isotactic PMMA had a T_1 value of 0.377 second. Apparently tacticity has an influence on the T_1 value for carbons in a given polymer. The polymers studied here showed no measurable amounts of mm triads. It was then assumed that the relaxation time of the alpha methyl carbon in PMAAm was about 0.2 second. A relaxation delay of one second was then used. It was also assumed that the NOE factors for methyl carbons in different triads will all be about the same.

For PMAAm prepared at high temperature it appears that the rr triad is slightly favored over the mr triad. The calculated fraction of rr triads is 0.53. If a statistical parameter of $f_r = 0.73$ is assumed then a close fit with Bernoullian statistics is observed. The quarternary resonance was split into three peaks. In the methylene region only the racemic resonance could be observed. In the carbonyl region three pentad resonances were assigned; two of which were rr centered and one of which was mr centered. An additional resonance in the carbonyl region was also detected. This resonance may arise from a carbonyl carbon in an imide type structure:



The latter carbonyl resonance appeared at 180.4 ppm which seems to be out of the range of the resonances assigned to the stereotactic pentads. The compound 3,3-dimethyl glutarimide was investigated by C-13 NMR. The carbonyl resonance for this compound appeared at 176.9 ppm.

The shifts for PMAAm in aqueous urea solution are about one to two parts per million down field from the shifts obtained when d-6 ethylene glycol was used as solvent.

The C-13 NMR spectrum of PMAAm produced by the redox method is given in Figure 14. The spectral parameters and assignments are listed in Table 2.

Quantitative analysis of the methyl region of the aforementioned polymer revealed 18% mr triads and 82%

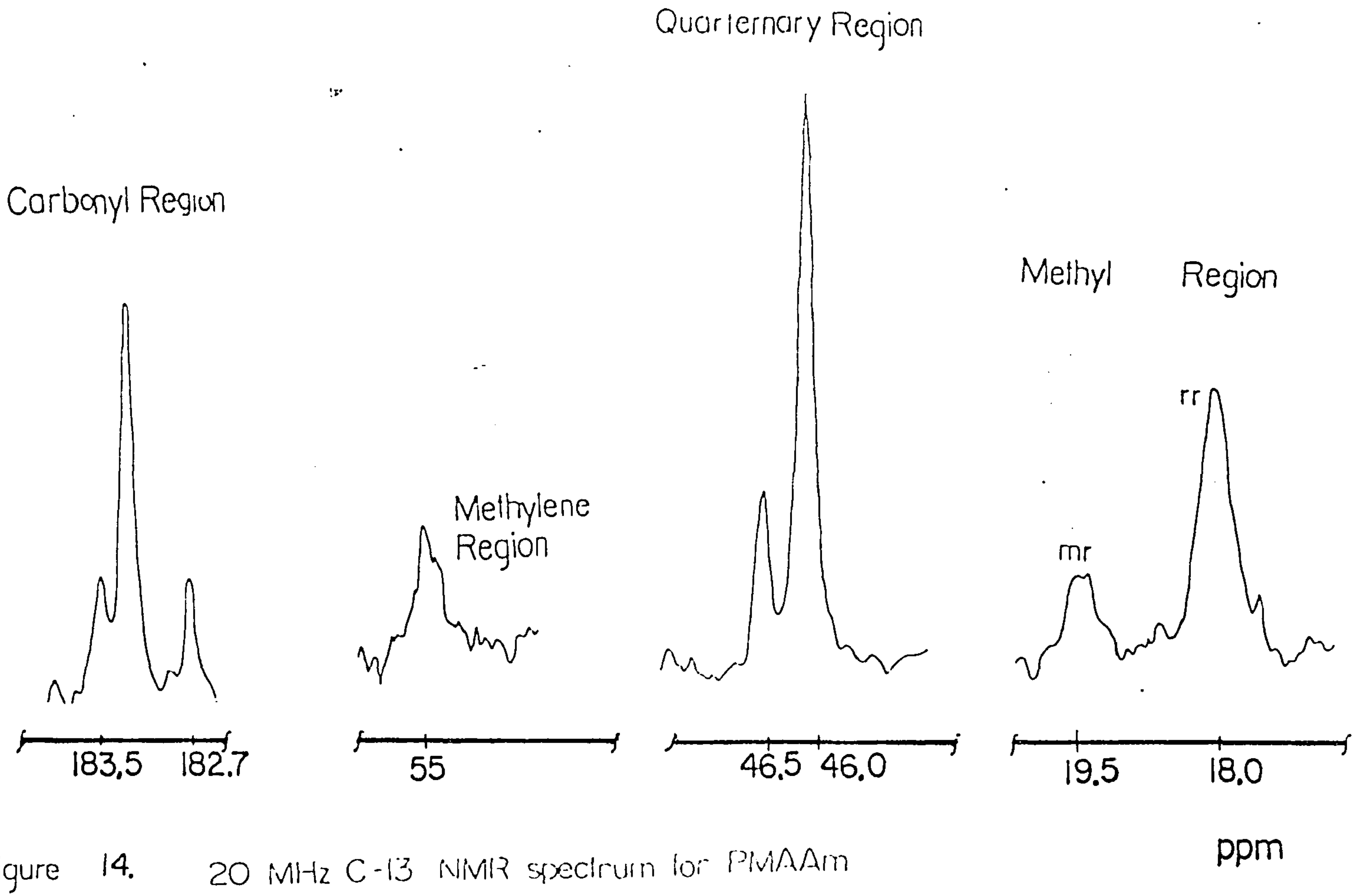


Figure 14. 20 MHz C-13 NMR spectrum for PMAAm produced at room temperature.

Table 2. Spectral data and assignments for PMAAm produced at room temperature.

Parameters:

Relaxation Delay: 1.0 second

Pulse Width: 60°

Line Broadening: 1.0 Hz

Number of Scans: 3,371

Temperature 90°C

Assignment	Shift (ppm)	Quantitative Detd.	 Calc.
Methyl mm	———	0.00	0.01
" mr	19.4	0.18	0.16
" rr	18.0	0.82	0.83
Quarternary mr	46.5		
" rr	46.1		
Methylene r	54.9		
Carbonyl rmrr	182.7		
" rrrr	183.2		
" mrrr	183.5		

$f_r = 0.91$

rr triads. If one assumes a statistical parameter of $f_r = 0.91$ the calculated triad fractions are close to the observed fractions. The sample contains a predominance of syndiotactic character. The conclusion to be reached here is that the lower the polymerization temperature the higher the amount of syndiotactic placement in the polymer.

The C-13 NMR spectrum of poly(N-methyl methacrylamide) is similar to that for PMAAm except that the N-methyl resonance appears at 27.2 ppm. The quarternary and alpha methyl regions show peaks corresponding to the mr and rr triads. Quantitative analysis of the alpha methyl region indicated that the sample contained 64% rr triads.

A C-13 NMR spectrum was recorded for a copolymer containing 95% methyl methacrylate. The spectrum which is given in Figure 15 appears similar to that reported for syndiotactic PMMA (27). Based on quantitative analysis of the alpha methyl region, the copolymer contained 63% rr triads and 37% mr triads. Assignments are listed in Table 3.

Subsequently a copolymer containing 80% MMA and 20% methacrylamide was investigated. The objective of this study was to observe if the NMR spectrum could distinguish the amide carbonyl resonances from the ester carbonyl resonances.

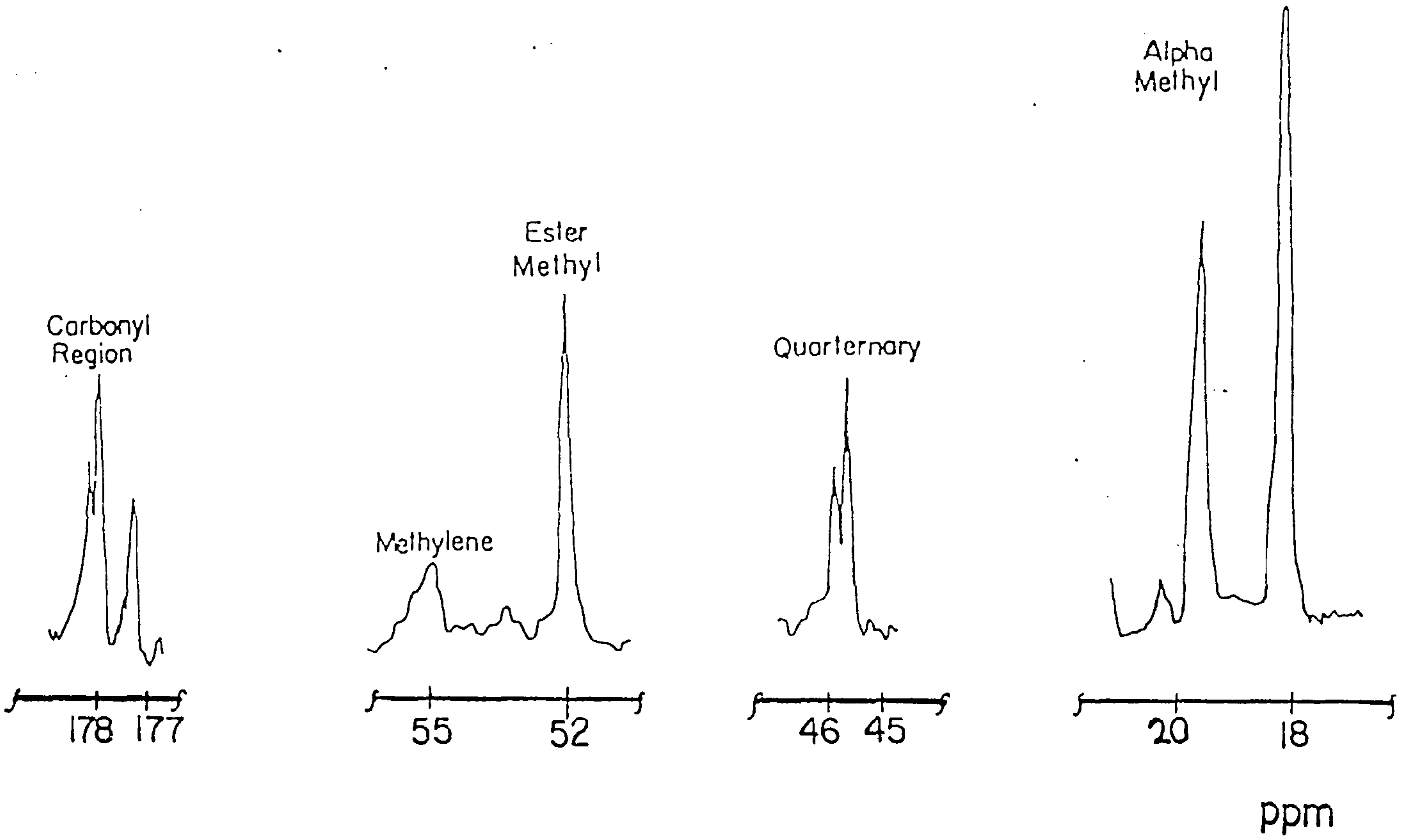


Figure 15. C-13 NMR spectrum for copolymer (95% MMA - 5% MAAm).

Table 3. Carbon 13 NMR assignments for copolymer with 95% methyl methacrylate.

Assignment		Shift (ppm)
Alpha methyl	rr	17.9
"	mr	19.7
Quarternary	rr	45.5
"	mr	45.8
Ester Methyl		51.8
Methylene	r	54.7
Carbonyl	rmrr	177.1
"	rrrr	177.9
"	mrrr	178.1

The solvent used was DMF. Referencing was made by setting the DMF methyl carbon resonance cisoid to the formyl proton at 36.0 ppm.

Carbon-13 spectra were recorded for DMF solutions of two model compounds namely methyl pivalate and pivalamide. The carbonyl resonance for methyl pivalate occurred at 178.4 ppm while that for pivalamide occurred at 180.9 ppm. When both model compounds were studied together as one sample the carbonyl peak for pivalamide appeared at 180.7 ppm and that for methyl pivalate appeared at 178.3 ppm. On the basis of the model compound spectra the carbonyl region of the copolymer may be able to distinguish ester resonances from amide resonances.

The spectrum for the 80% MMA copolymer appears in Figure 16. Quantitative analysis of the alpha methyl region revealed that the sample contained 31% mr triads and 69% rr triads. A total of six resonances were assigned in the carbonyl region. It is apparent that there are two groups of resonances in the carbonyl region. Table 4 lists assignments for the carbonyl region of this copolymer. The weaker resonances appearing at lower field in the carbonyl region are assigned to amide groups in different pentad sequences. The stronger resonances at higher field are assigned to pentad sequences for ester carbons. Only mr and rr centered pentads are considered.

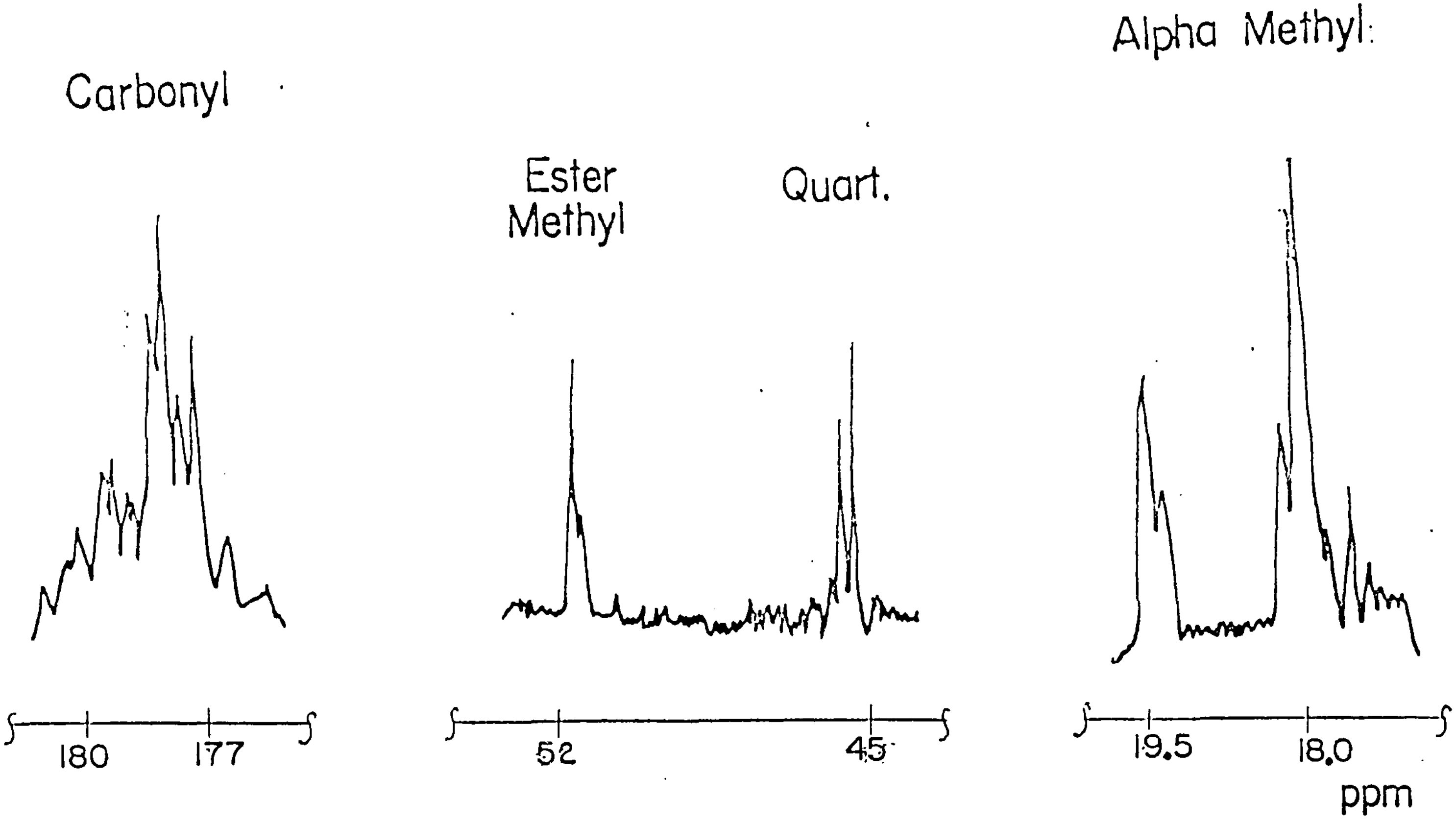


Figure 16. C-13 NMR spectrum for copolymer (80% MMA - 20% MAAm).

Table 4. Carbon-13 assignments for carbonyl region for copolymer with 80% MMA and 20% MAAm.

Shift (ppm)	Assignment
177.1	ester rmrr
177.6	ester mrmr
177.9	ester rrrr
178.3	ester rrrm
179.5	amide rrrr
179.8	amide rrrm

Since it was desirable to have some knowledge of the sequence of the comonomer units in the copolymer, a computer simulation of copolymer sequence was carried out. The copolymer containing 80% MMA will have a 4:1 ratio of MMA units to MAAm units. The following five unit blocks were stored in the computer:

A-M-M-M-M-

M-A-M-M-M-

M-M-A-M-M-

M-M-M-A-M-

M-M-M-M-A-

where A stands for methacrylamide and M stands for methyl methacrylate. Fifteen unit sequences were then constructed utilizing the five unit blocks shown above. A total of 65 unique fifteen unit sequences were found.

An inherent assumption was made in the simulation. It was assumed that one unit in every five units along the chain must be methacrylamide. No block copolymer would have been possible with this simulation.

Probabilities of having certain fifteen unit sequences were then calculated. The quantity P(X-Y) denotes the probability that three methacrylamide units in a fifteen unit chain will be separated by two strings of methyl methacrylate units (i.e.):

$$-A-(M)_X-A-(M)_Y-A-$$

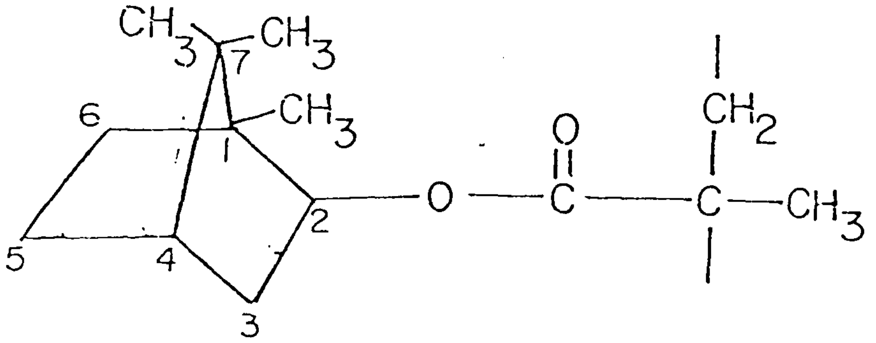
One string contains X methyl methacrylate units while the other contains Y units.

The calculated probabilities for fifteen unit sequences are listed in Table 5. From the probability values listed it appears that sequences where the value of X is about 4 or 5 and where the value of Y is about 4 or 5 are highly probable. This result reflects the fact that the copolymer contains four methyl methacrylate units in every five. On the other hand sequences where the value of X is high such as 7 or 8 and the value of Y is low such as 0 or 1 are much less likely to occur. In other words for a random copolymerization of methacrylamide with methyl methacrylate the methacrylamide units are not likely to bunch together given that the total of methacrylamide is only 20%. If a sequence has a value of Y equal to zero then that sequence has two methacrylamide units adjacent to one another. Of the 65 sequences generated, five of them had adjacent methacrylamide units.

Table 5. Probabilities of different 15 unit sequences for the copolymer containing 80% MMA and 20% MAAm.

Sequence	P(X-Y)
(4-4)	0.0462
(4-5)	0.0615
(4-6)	0.0462
(4-7)	0.0308
(4-8)	0.0154
(5-3)	0.0615
(5-5)	0.0308
(5-6)	0.0308
(5-7)	0.0154
(6-2)	0.0462
(6-3)	0.0462
(6-6)	0.0154
(7-1)	0.0308
(7-2)	0.0308
(7-3)	0.0308
(8-0)	0.0154
(8-1)	0.0154
(8-2)	0.0154
(8-3)	0.0154
(3-4)	0.0615
(4-2)	0.0462
(5-2)	0.0462
(6-1)	0.0308
(7-0)	0.0154
(3-3)	0.0308
(5-1)	0.0308
(6-0)	0.0154
(1-4)	0.0308
(2-3)	0.0308
(5-0)	0.0154
(4-0)	0.0154
(1-3)	0.0154
(2-2)	0.0154
Total	1.0007

Finally poly(isobornyl methacrylate) was investigated by C-13 NMR. The study of this polymer by C-13 NMR provides a challenge due to the complexity of the bicyclic ring. The structure of poly(isobornyl methacrylate) is given below with appropriate numbering in the isobornyl ring:



The C-13 NMR spectrum for poly(isobornyl methacrylate) appears in Figure 17. Assignments are reported here for the first time and are listed in Table 6.

The alpha methyl carbon, the methylene carbon in the main chain and the carbonyl carbon were assigned without doubt. The same may be said about carbon 2 in the isobornyl ring. The remaining carbons in the frame of the isobornyl ring were assigned on the basis of the C-13 chemical shifts reported for exo-2-hydroxy norbornane (28).

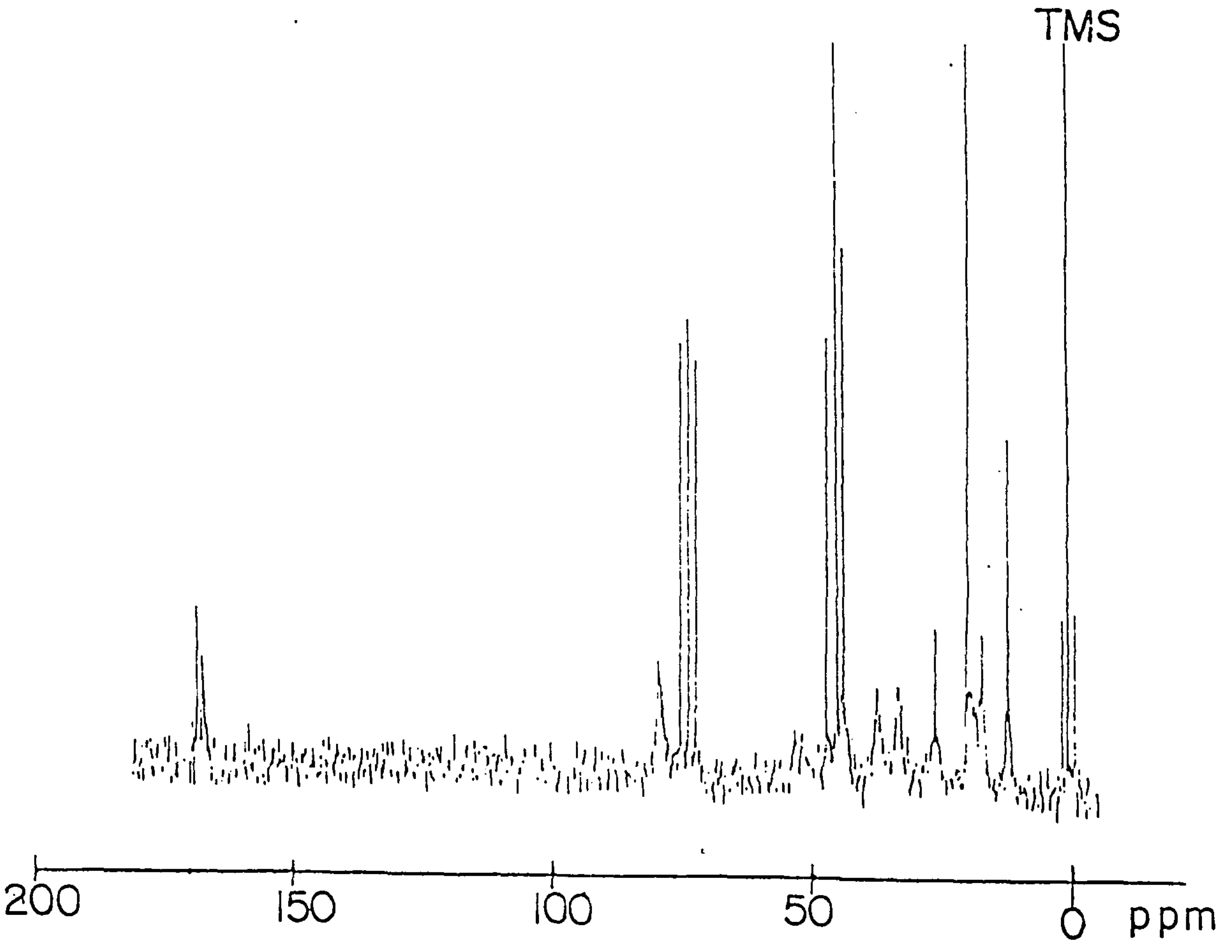


Figure 17. C-13 NMR spectrum of polyisobornyl methacrylate in $CDCl_3$.

Table 6. C-13 NMR assignments for poly(isobornyl methacrylate).

Main chain:	Resonance (ppm)	Assignment
	17.7	alpha-methyl
	45.6	quarternary
	55	methylene
	176.3,177.5	carbonyl (mr,rr)
Ring:	12.3	Methyl group on carbon 1
	20.3	Methyl groups on carbon 7
	27.3	Methylene carbon (6)
	33.0	Methylene carbon (5)
	34.7	Tertiary carbon (4)
	39.0	Methylene carbon (3)
	46.8	Quarternary carbon (7)
	48.9	Quarternary carbon (1)
	83.0	Ester carbon (2)

The number inside the parenthesis above indicates the number of a particular carbon in the bicylic ring as shown in the structure of the polymer.

III. Molecular Weight and Polymer Degradation

Titkova and coworkers (29) reported results of viscosimetric studies of PMAAm in aqueous salt solutions. The polymer showed poor solubility in many common organic solvents. It was also determined that the higher the molecular weight of the polymer the poorer was its solubility. Intrinsic viscosity - molecular weight relations were reported for the polymer in 0.4M aqueous magnesium perchlorate and 8M aqueous urea solutions at 25°C. The relations are indicated below:

In 0.4M Magnesium Perchlorate: $[\eta] = (3.28 \times 10^{-4})M^{0.55}$
In 8M Urea: $[\eta] = (1.71 \times 10^{-4})M^{0.63}$

Figures 18 and 19 show plots of reduced viscosity against concentration for 8M urea and 0.4M magnesium perchlorate solutions of redox polymerized PMAAm.

Upon extrapolation to zero concentration the polymer had an intrinsic viscosity of 0.80 dl/g in 8M urea which indicates a molecular weight of 685,000. The same sample had an intrinsic viscosity of 0.50 dl/g in the perchlorate solution which indicates a molecular weight of 621,000.

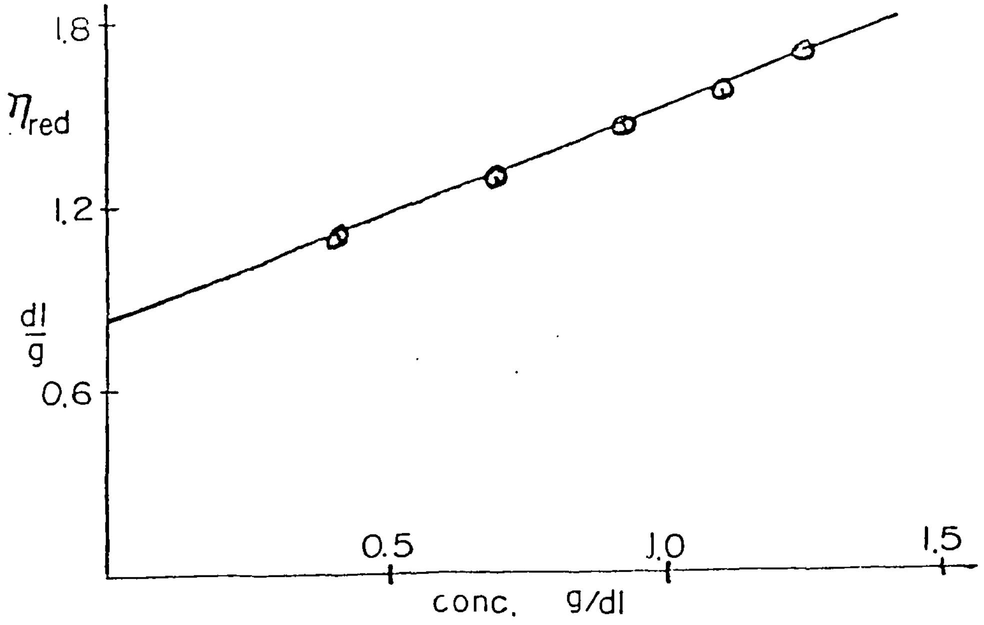


Figure 18. Reduced viscosity vs. concentration for redox PMAAm in 8M urea.

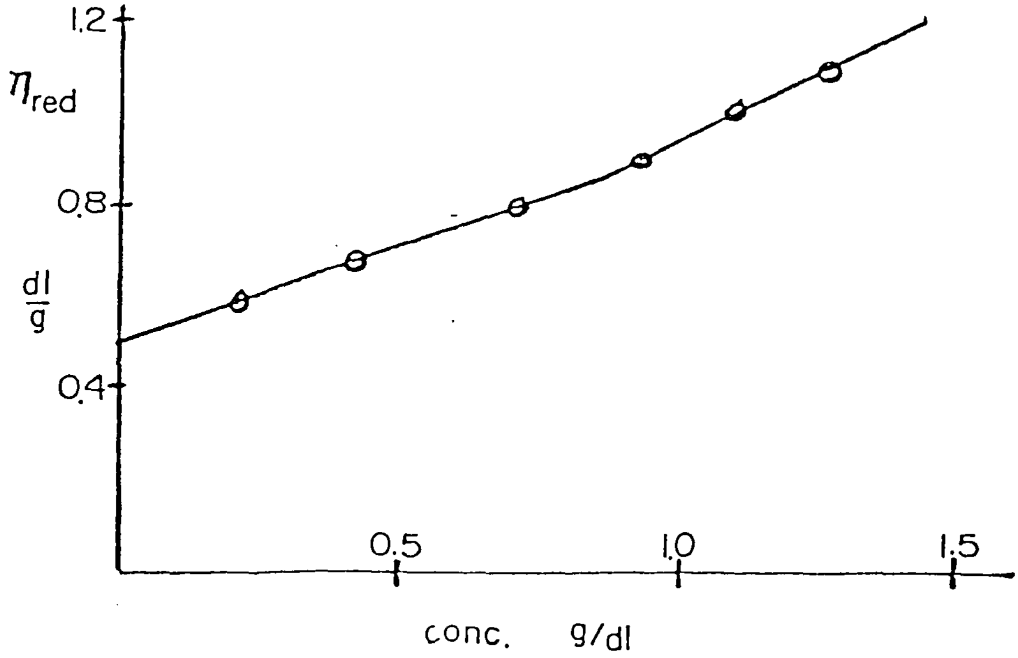


Figure 19. Reduced viscosity vs. concentration for redox PMAAm in 0.4M $Mg(ClO_4)_2$.

The first objective was to study the effect of ultraviolet radiation on the polymer in dilute solution. Two ultraviolet irradiations were performed. In each case the polymer was irradiated for six hours in 0.4M magnesium perchlorate solution while stirring in a quartz flask. The polymer concentration was 0.75 g/dl. In one study the solution was purged with nitrogen prior to irradiation. In the other study the solution was purged with oxygen before irradiation.

Figures 20 and 21 show plots of reduced viscosity against concentration for irradiated PMAAm solutions. After irradiation under nitrogen the intrinsic viscosity of the sample decreased to 0.40 dl/g which indicates a molecular weight of 404,000. After irradiation under oxygen the intrinsic viscosity decreased to 0.36 dl/g which indicates a molecular weight of 343,000. In a qualitative sense it is apparent that the polymer undergoes reduction in molecular weight during irradiation in a dilute solution. A larger decrease in molecular weight was observed for irradiation under oxygen.

For electron beam lithography solid polymer films are usually irradiated with high energy electrons. It would then be appropriate to study the solid state radiation degradation of the polymer. Molecular weight studies were performed on redox PMAAm before and after irradiation with gamma rays. NMR measurement showed that this

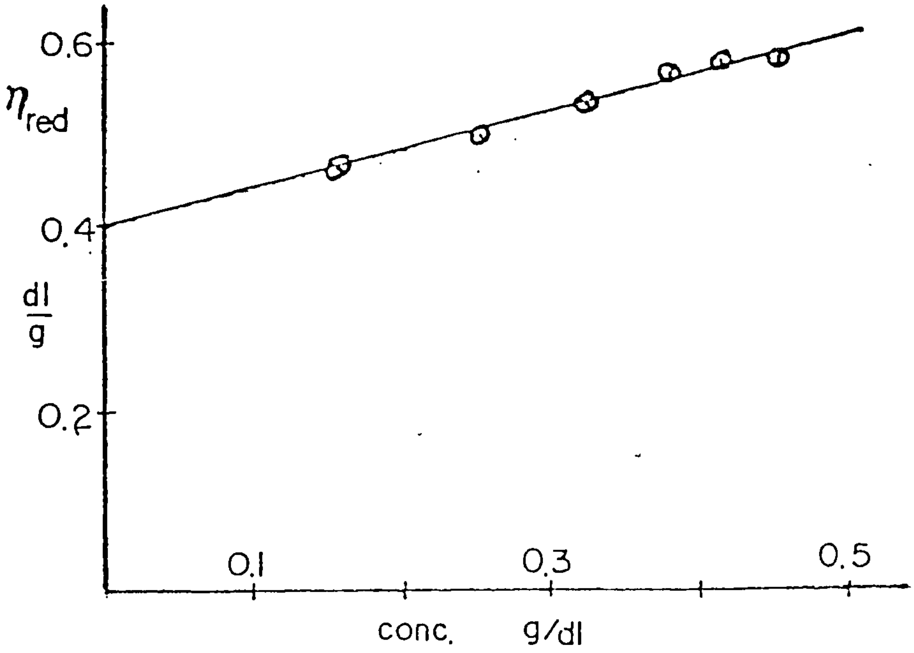


Figure 20. Reduced viscosity vs. concentration for redox PMAAm after irradiation in solution under nitrogen.

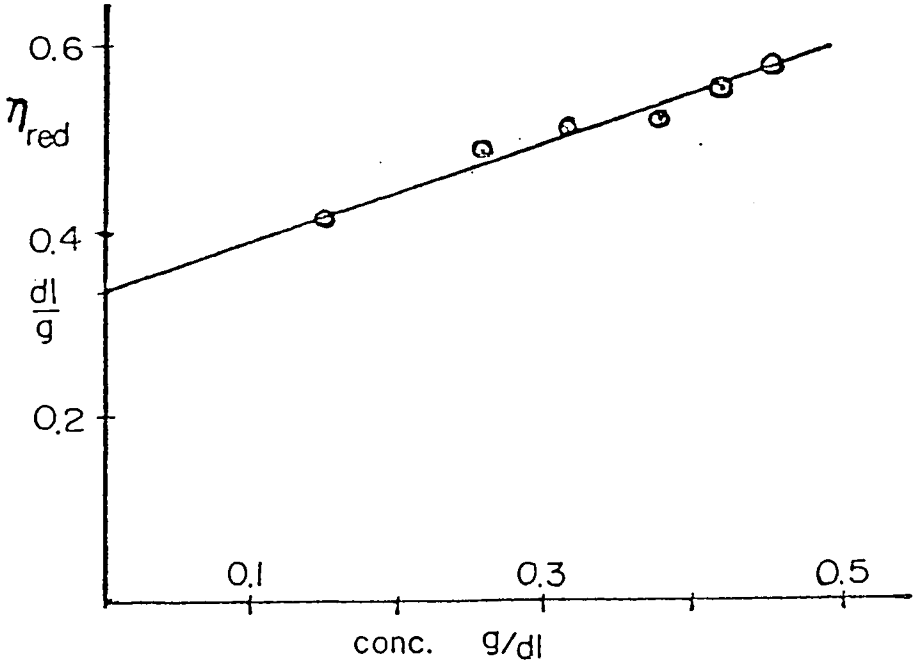


Figure 21. Reduced viscosity vs. concentration for redox PMAAm after irradiation in solution under oxygen.

sample contained 82% rr triads and 18% mr triads. Radiation (G_s-G_x) values and quantum efficiencies were determined.

The solid polymer was irradiated for periods of two, four, six and eight hours. Viscosimetric measurements were made in 8M urea solutions at 25°C. Molecular weight changes are indicated in Table 7.

Table 7. Gamma irradiation of redox PMAAm.

Time hours	$[\eta]$ dl/g	$\bar{M}_v \times 10^{-5}$	$\frac{1}{M_v} \times 10^{6}$	N	Dose Mrad
none	0.73	5.9	1.7	——	——
2	0.51	3.3	3.0	0.79	0.58
4	0.44	2.6	3.8	1.27	1.16
6	0.36	1.9	5.3	2.10	1.74
8	0.31	1.5	6.7	2.93	2.32

The term N is the net number of main chain scissions per polymer molecule after irradiation and is given by:

$$N = \frac{M_{(0)}}{M_{(t)}} - 1$$

The radiation dosage rate received by polymer samples was 0.29 Mrad/hour.

A plot of N against cumulative dose is given in Figure 22. Also a plot of the reciprocal viscosity average molecular weight is given in Figure 23. In each case an approximately linear relationship is observed. The radiation G value difference was determined from the graph of reciprocal molecular weight versus dose. The slope of the graph is 2.13×10^{-6} mole/g-Mrad. The G value difference is related to slope by:

$$G_s - G_x = (\text{Slope})\times(9.65\times10^5)$$

For PMAAm the value of G_s-G_x is 2.05 events per 100 eV.

A method for calculating the quantum efficiency for main chain cleavage of polymers during photochemical reactions was given by Otsu and Tanaka (30). The value of N may be related to the quantum efficiency through the following relation:

$$N = \phi_{cs} M_0 I t$$

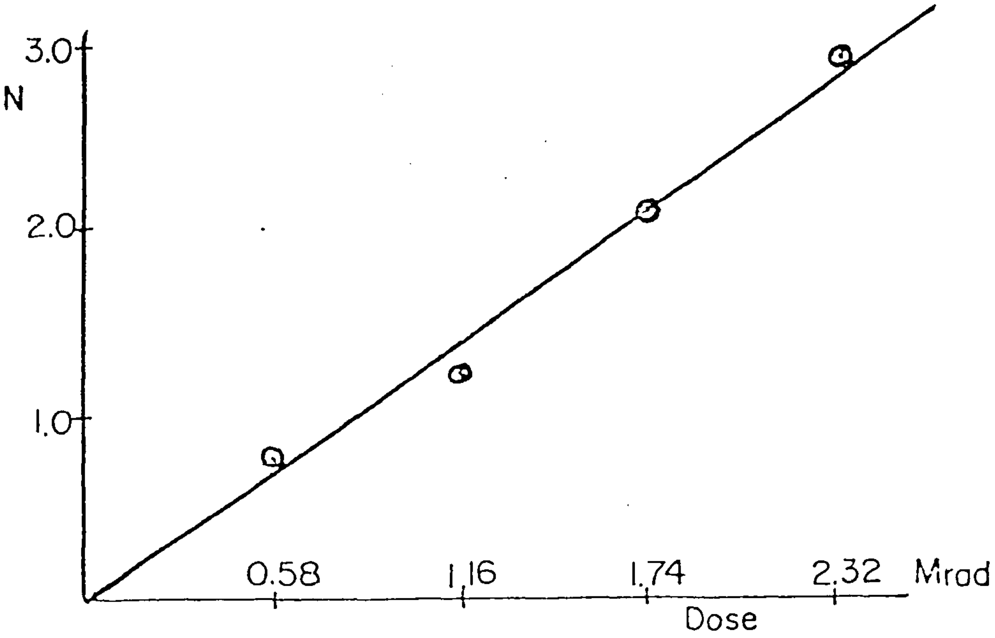


Figure 22. N vs. cumulative dose for redox PMAAm.

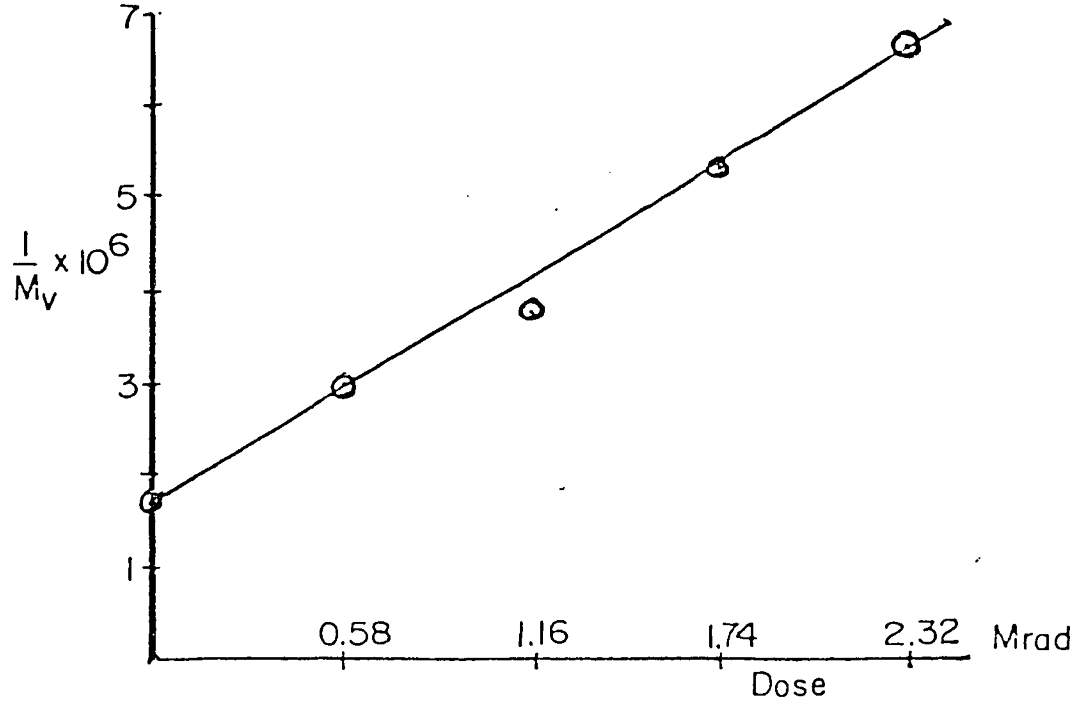


Figure 23. Reciprocal molecular weight vs. dose for redox PMAAm.

ϕ_{cs} is the quantum efficiency for main chain cleavage, M_0 is the initial molecular weight of the sample, I is the radiation dosage rate received by the sample and t is time. ϕ_{cs} for redox PMAAm is 2.04×10^{-6} mole/g-Mrad or 2.04×10^{-14} mole/erg. The latter number indicates the number of moles of main chain bonds broken per erg of energy absorbed.

The degradation of PMAAm produced by benzoyl peroxide initiated polymerization was also investigated. NMR measurement revealed that this sample contained 53% rr triads and 47% mr triads. The objective of this experiment was to see if there is any influence of polymer tacticity on the degradation.

The influence of tacticity on the use of PMMA as an electron beam resist has been reported (31). Isotactic PMMA exhibited the greatest sensitivity to the electron beam.

Table 8 contains results of viscosity experiments for gamma irradiated PMAAm produced by polymerization with benzoyl peroxide (PMAAm-BP). Viscosity experiments were performed on 8M aqueous urea solutions.

Table 8. Gamma irradiation of PMAAm-3P.

Time hrs.	M_v	N	Dose Mrad
none	38,000	———	———
2	34,000	0.118	0.58
4	32,000	0.188	1.16
6	37,000	0.027	1.74
8	31,000	0.226	2.32

The molecular weight of this PMAAm sample is very low to begin with. Drastic changes in molecular weight after irradiation do not occur. However there seems to be a general trend toward lower molecular weight.

A plot of M_v^{-1} against dose appears in Figure 24. An anomolous point may be observed in the plot for PMAAm-3P. A simple relation between scissions and dose is not the case here as it was for redox PMAAm. It should be noted that it is not fair to compare results of degradation for polymer samples that are drastically different in molecular weight. The effect of tacticity on degradation of PMAAm is not clear at this point.

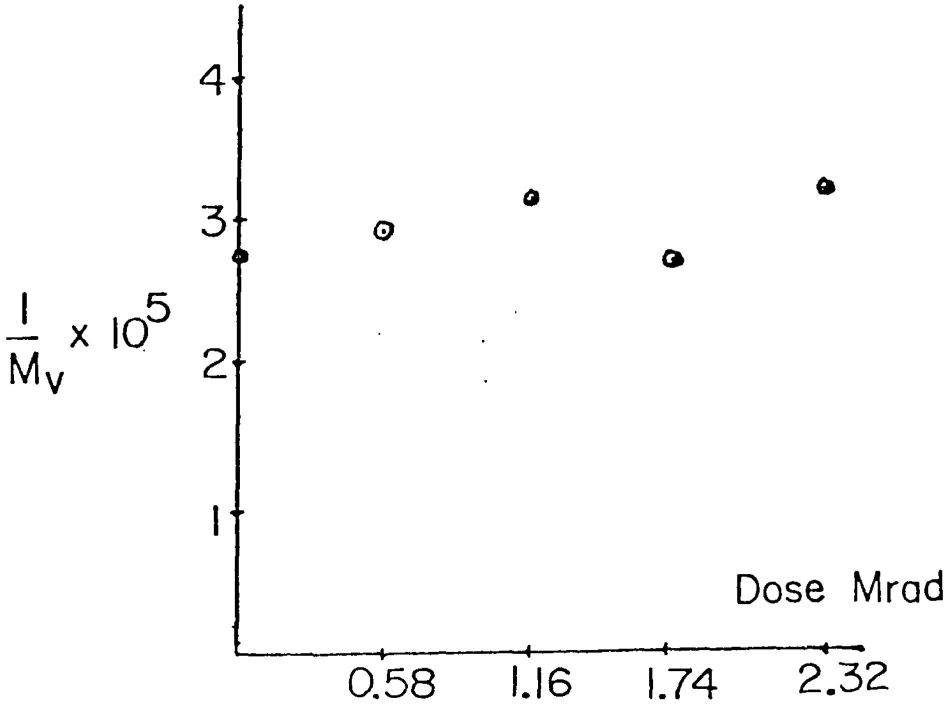


Figure 24. Reciprocal molecular weight against dose for PMAAm-BP.

A methyl methacrylate copolymer containing 5% methacrylamide was also irradiated with gamma rays. Molecular weight measurements were made by gel permeation chromatography with DMF as solvent. Figure 25 shows the GPC traces for copolymer samples before and after irradiation.

Table 9 contains the molecular weight results. As the irradiation time increases the trend is for the copolymer to go to lower molecular weight. The number average molecular weight is low to begin with and does not decrease much over the course of irradiation.

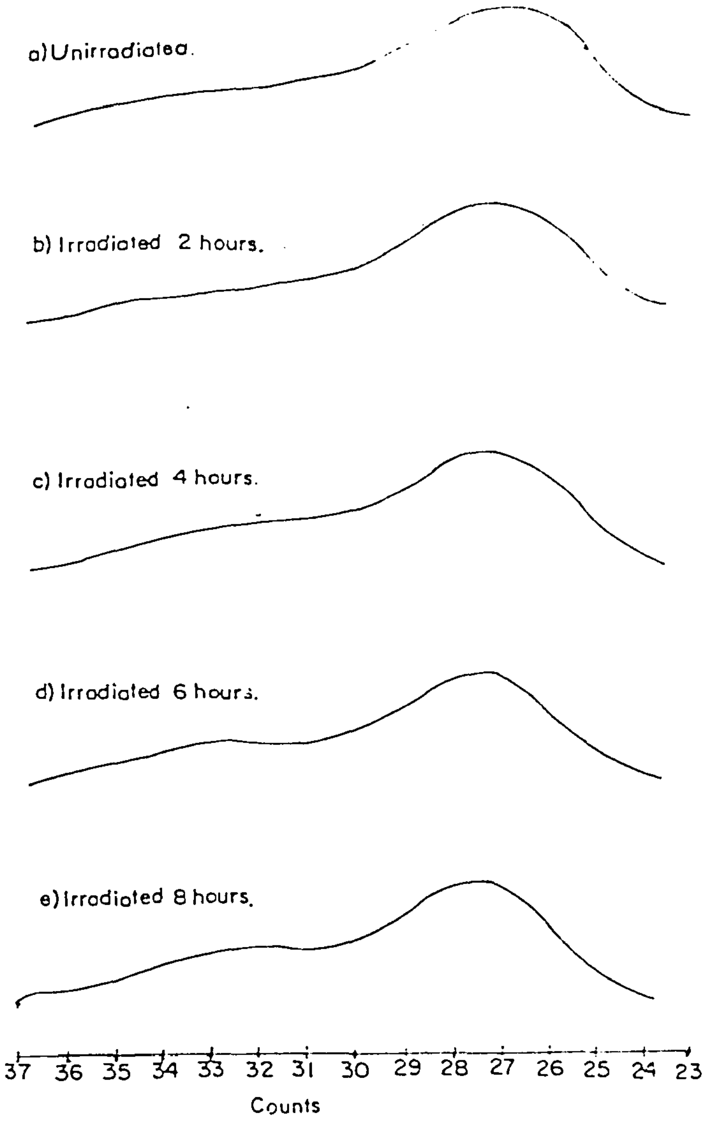


Figure 25. GPC traces for copolymer with 95% MMA and 5% MAAm.

Table 9. Molecular weight results for 5% methacrylamide copolymer.

Irrad. Time hrs.	Dose Mrad	$\overline{M}_n$ g/mole	N_n	$\overline{M}_w$ g/mole	N_w
0	0.00	24,000	——	198,000	——
2	0.58	24,000	0.00	175,000	0.13
4	1.16	23,000	0.04	160,000	0.24
6	1.74	20,000	0.20	146,000	0.36
8	2.32	18,000	0.33	130,000	0.52

A plot of reciprocal number average molecular weight against dose for the copolymer is given in Figure 26. The value of G_s-G_x is 0.83 events/100 eV.

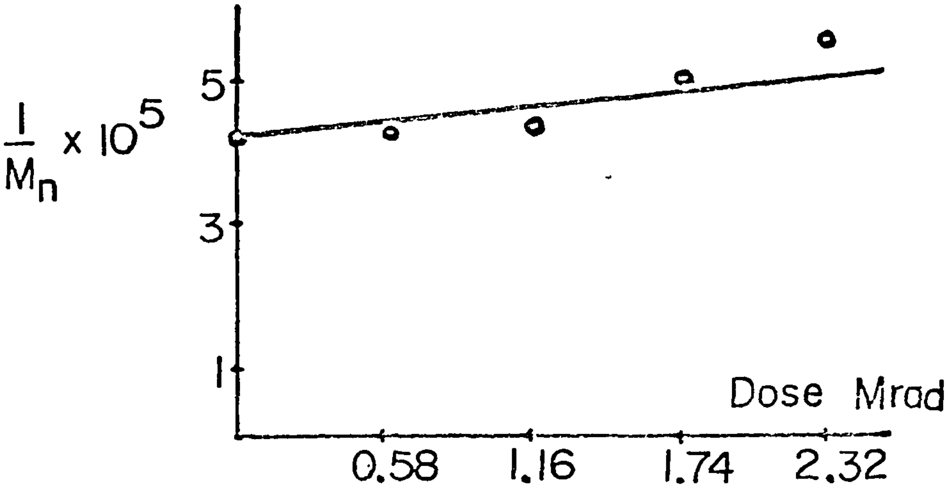


Figure 26. Reciprocal number average molecular weight vs. dose for copolymer.

A plot of reciprocal weight average molecular weight against dose for this copolymer appears in Figure 27. The G value difference for the weight average plot is related to the slope by:

$$(G_s - 4G_x) = (\text{slope})x(1.93x10^6)$$

The value of $G_s - 4G_x$ is 0.55. The individual values are $G_s = 0.92$ and $G_x = 0.09$ events/100 eV.

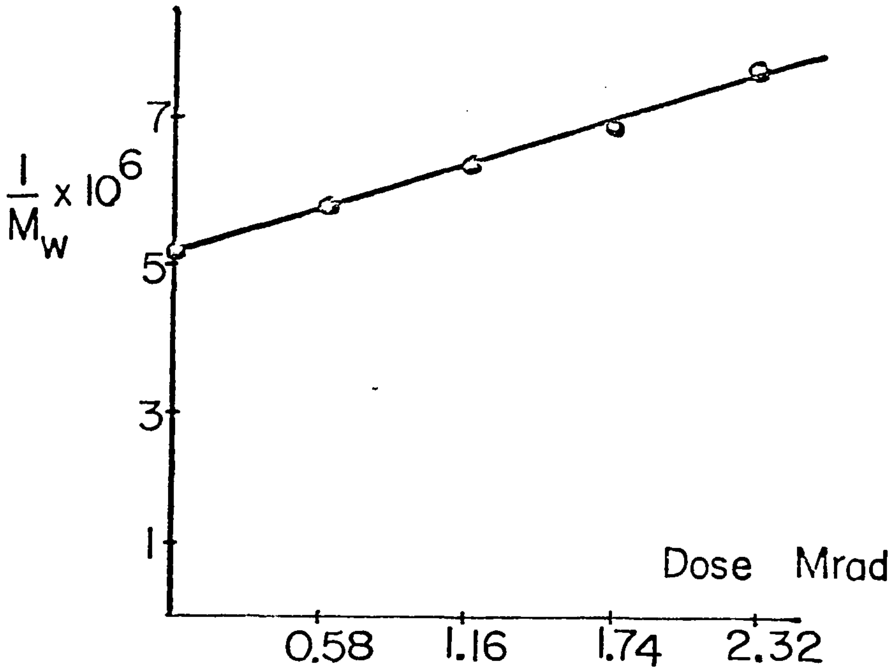


Figure 27. Reciprocal weight average molecular weight vs. dose for copolymer.

Based on molecular weight studies by GPC it appears that this copolymer does not degrade as readily as does PMAAm. It is also apparent that a small amount of crosslinking occurs during the irradiation as evidenced by the nonzero value of G_x.

Poly(isobornyl methacrylate) was also irradiated with gamma rays and number average molecular weights were measured by membrane osmometry. Toluene was used as solvent. Table 10 lists irradiation times and molecular weights.

Table 10. Molecular weight results for poly(isobornyl methacrylate).

Time hrs.	$M_n \times 10^{-5}$	N	Dose Mrad
none	1.91	———	———
2	1.91	0.00	0.58
4	1.74	0.10	1.16
6	1.28	0.49	1.74
8	1.11	0.72	2.32

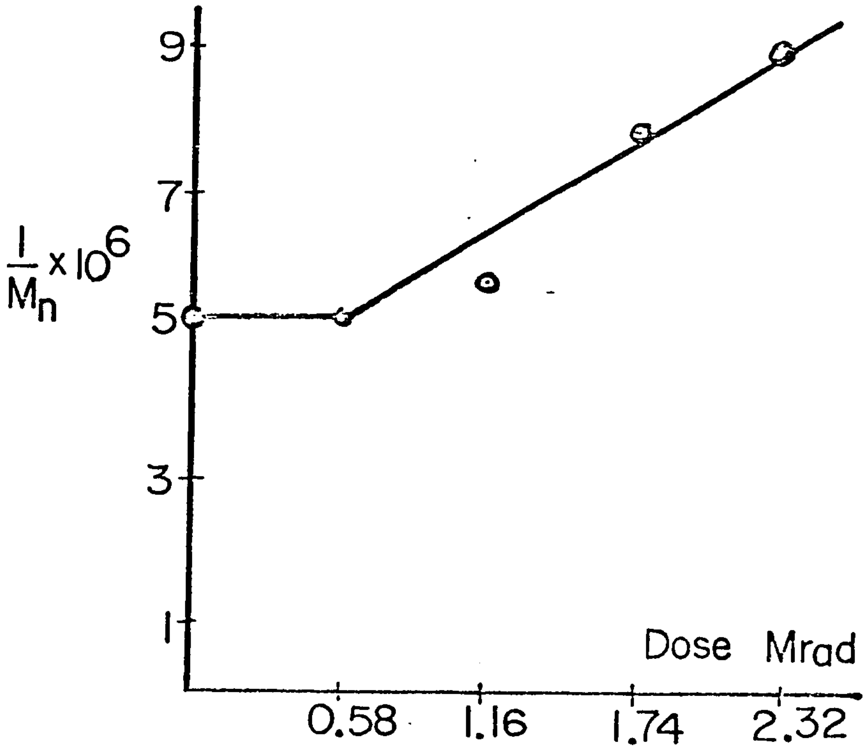


Figure 28. Reciprocal number average molecular weight vs. dose for poly(isobornyl methacrylate).

A plot of reciprocal number average molecular weight versus dose for poly(isobornyl methacrylate) is given in Figure 28. The value of $G_s - G_x$ is 2.1 events per 100 eV.

IV. ESR Results and Discussion

A. Polymethacrylamide and Copolymers

Consider the ESR spectra for polymethacrylamide in the solid state and in THF glass. The solid polymer was irradiated for 45 minutes at liquid nitrogen temperature using ultraviolet light. Figure 29 shows spectra for the solid polymer at -130°C and -10°C. A five line spectrum was obtained at all temperatures studied in this range. The approximate hyperfine splitting is about 22 gauss. The line width is about 10 gauss.

A rigid glass of PMAAm in THF was irradiated at liquid nitrogen temperature. A well resolved ESR spectrum was obtained at -150°C and is shown in Figure 30. Essentially the same spectrum as this was obtained at other temperatures up to -100°C. Above -100°C the THF glass melts. As a result the spectrometer tuning is lost and the spectrum disappears. The measured hyperfine coupling was 22 gauss and the line width was 10 gauss. Integration of the first derivative curve indicated that the intensities distribution of the spectral lines was $1:3:7:3:\frac{1}{2}$. This result is close to the binomial intensity distribution of 1:4:6:4:1.

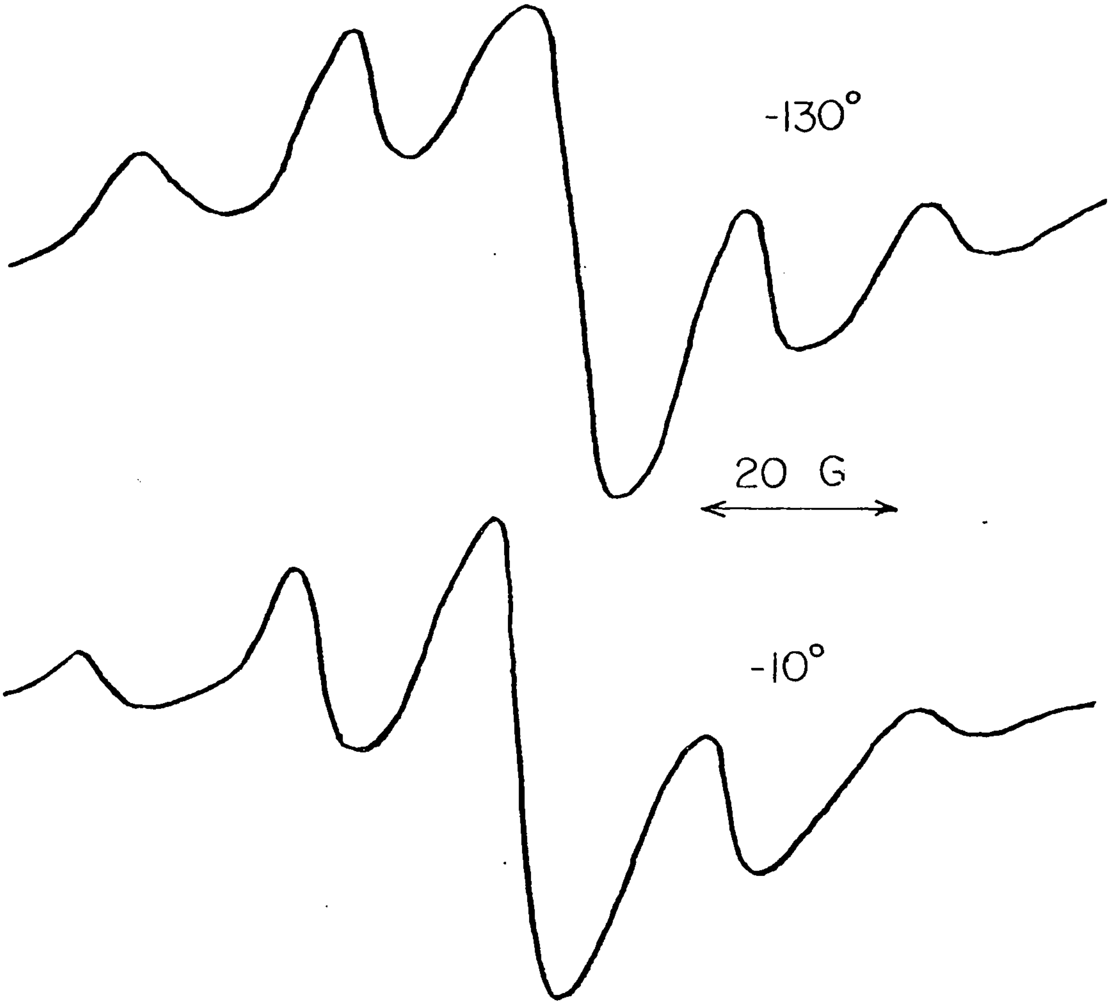


Figure 29. ESR spectrum of irradiated powder of polymethacrylamide.

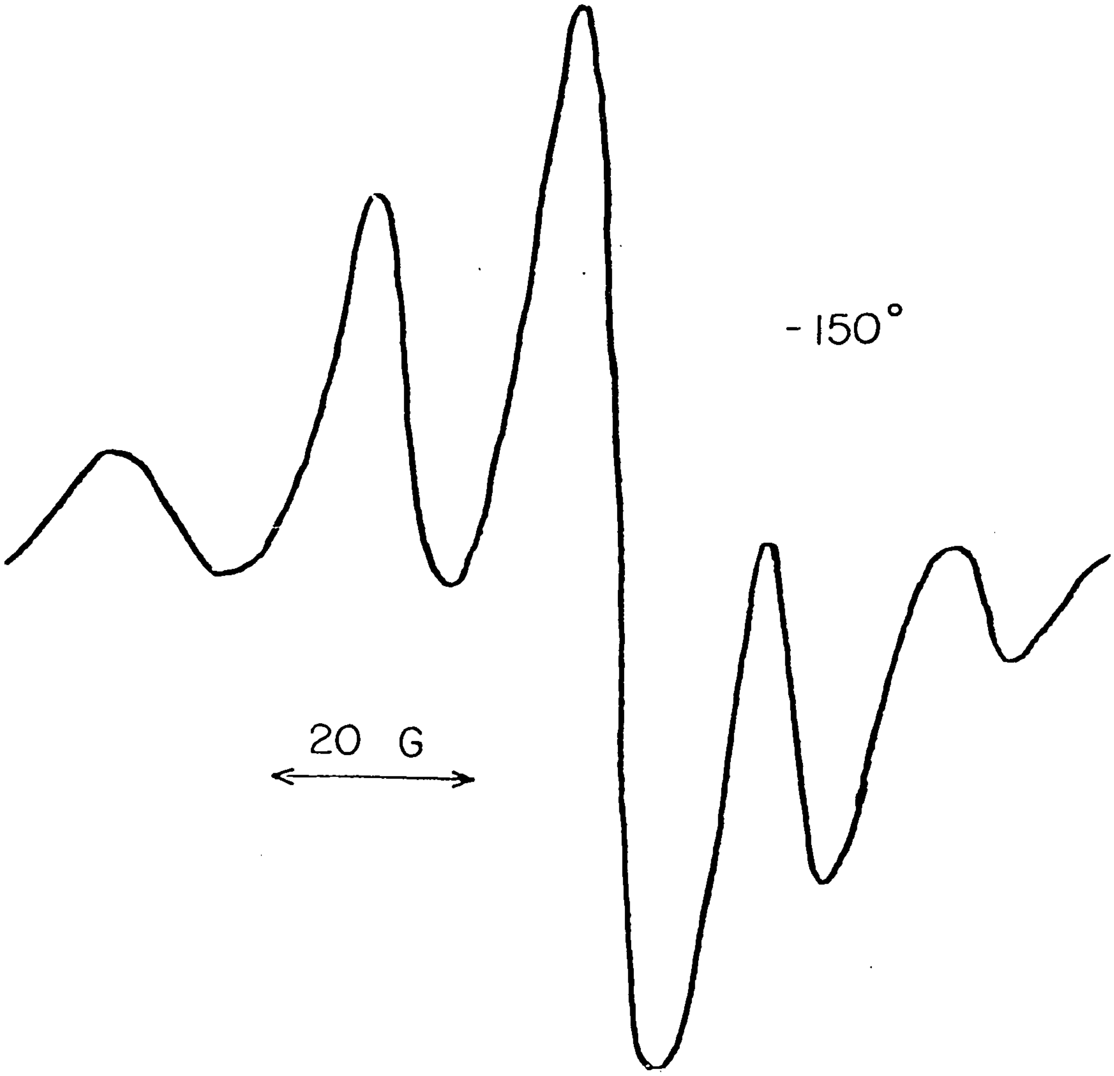


Figure 30. ESR spectrum of irradiated glass of polymethacrylamide in THF.

It would appear that the ESR spectrum from irradiated PMAAm is very similar to the spectrum for polymerizing methacrylamide. This result suggests that "Radical 1" may be responsible for the spectrum from the irradiated polymer.

The assignment of "radical 1" to the five line spectrum is further substantiated by the application of the McConnell relation (32) described in Figure 31.

$$a_{\beta H} = \rho(B_1 + B_2\cos^2\theta)$$

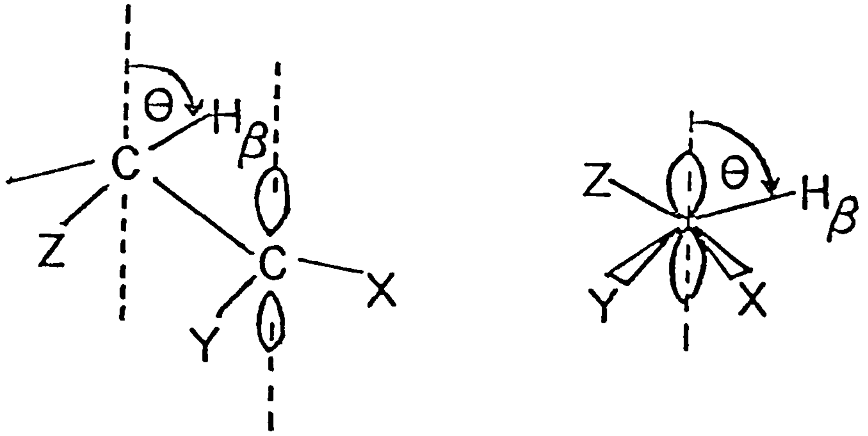
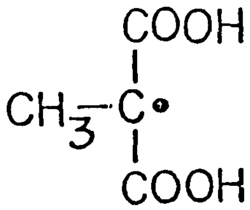


Figure 31. McConnell's relation for beta protons.

The term a_{β} is the hyperfine coupling by a beta proton and ρ is the unpaired electron density at the carbon atom bearing the unpaired electron. B_1 is a constant equal to 3.8 gauss and B_2 is a constant equal to 51.0 gauss. Theta is the angle between the unpaired electron orbital and the projection of the C–H bond in the plane perpendicular to the carbon-carbon bond.

Consider the methyl protons of radical 1. Heller (33) investigated alkyl free radicals with a methyl group attached to a carbon atom bearing an unpaired electron (e.g.):



$$\mathrm{CH_3{-}\overset{\displaystyle COOH}{\underset{\displaystyle COOH}{C}}\bullet}$$

It was determined that the energy barrier for rotation about the C–CH_3 bond was not greater than 0.1 kcal/mole.

If the methyl group experiences free rotation then the hyperfine couplings by the methyl protons would all be the same since each proton has the same interaction with the unpaired electron. However if the methyl group rotation were to stop, the splittings by each of the methyl protons could all be different.

The ESR studies revealed that for free radicals of this type, the methyl group experienced a nearly free rotation around liquid helium temperature. Therefore it would be safe to assume that at temperatures above liquid nitrogen temperature that the methyl group executes free rotation. Thus all the methyl protons of "radical 1" should be equivalent.

For the methyl protons, the hyperfine coupling from the spectrum (Figure 30) is 22 gauss. The C-H bonds in the rotating methyl group have an average value of $\cos^2\theta$ given by the following relation:

$$\overline{\cos^2\theta} = \frac{\pi}{2}\int_0^{2\pi} \cos^2\theta \, d\theta = 0.5$$

Substituting values for $\cos^2\theta$, a_β, B_1 and B_2 into McConnell's relation yields a value of 0.75 for the unpaired electron density.

For a radical with five beta protons giving a five line spectrum with binomial intensity distribution one must consider that one of the beta methylene protons does not interact significantly with the unpaired electron. The coupling by one of the beta methylene protons could be either 22 gauss or 44 gauss. If the coupling were 22 gauss then one would obtain the spectral stick diagram shown in Figure 32.

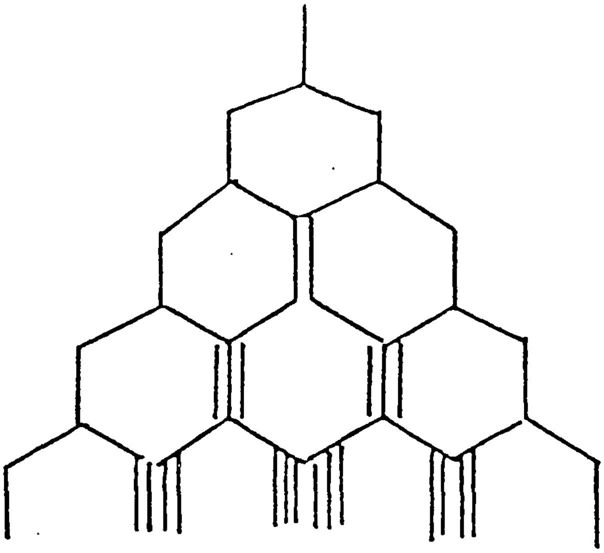


Figure 32. Spectral stick diagram for radical 1 where the methylene proton splitting is 22 gauss.

Here one would have five lines with 22 gauss spacing and an intensities ratio of 1:4:6:4:1. On the other hand if the coupling by a methylene proton were 44 gauss one would obtain the spectral diagram shown in Figure 33.

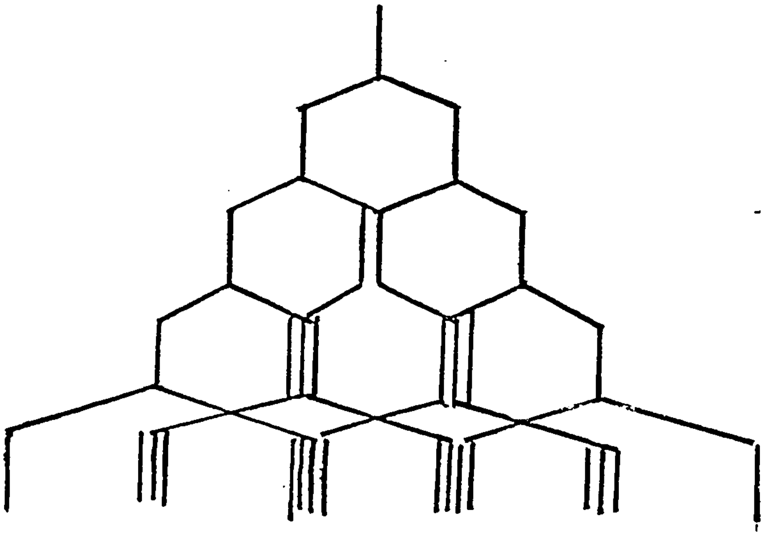


Figure 33. Spectral stick diagram for radical 1 where the methylene proton splitting is 44 gauss.

Here one would have six lines with 22 gauss spacing and an intensities ratio of 1:3:4:4:3:1. The experimental spectrum is clearly composed of five lines with a coupling of 22 gauss. The conclusion is that the coupling by a methylene proton is 22 gauss.

According to McConnell's relation, if the coupling by a methylene proton is 22 gauss then the C-H' bond must be at an angle of 45° with respect to the unpaired electron orbital. The conformation of radical 1 is depicted in Figure 34.

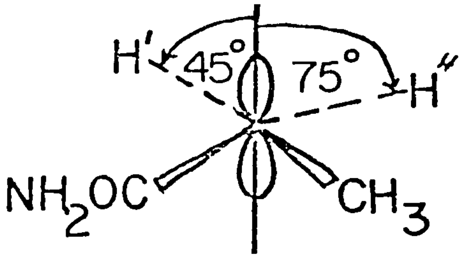


Figure 34. The conformation of radical 1.

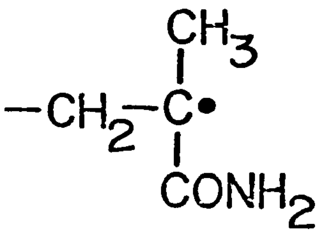
It would appear that one of the beta methylene protons is equivalent with the methyl protons. The C-H'' bond must be at an angle of 75° with respect to the unpaired electron orbital. McConnell's relation would indicate that the coupling by H'' is given by:

$$a_{\beta}(H'') = 0.75(3.8 + 51.0 \cos^2 75^\circ) = 5.4 \text{ G}$$

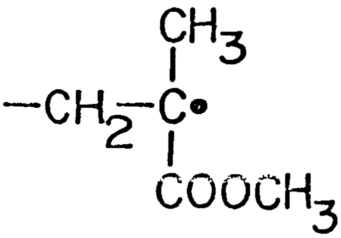
The coupling by H'' would be too low to be observable in the condensed phase.

"Radical 1" must exist in a structural conformation which allows the three methyl protons and one methylene proton to interact equivalently with the unpaired electron. "Radical 1" is thereby assigned to the five line ESR spectrum for irradiated PMAAm.

ESR spectra of irradiated copolymers of methacrylamide with methyl methacrylate appear in Figures 35, 36 and 37. Each sample was irradiated in a THF glass at liquid nitrogen temperature. Measurements were made from -150°C to -100°C. Each copolymer exhibited a five line spectrum. For the irradiated copolymers the following radicals may result:



$-CH_2-\overset{CH_3}{\underset{CONH_2}{C}}\cdot$



$-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot$

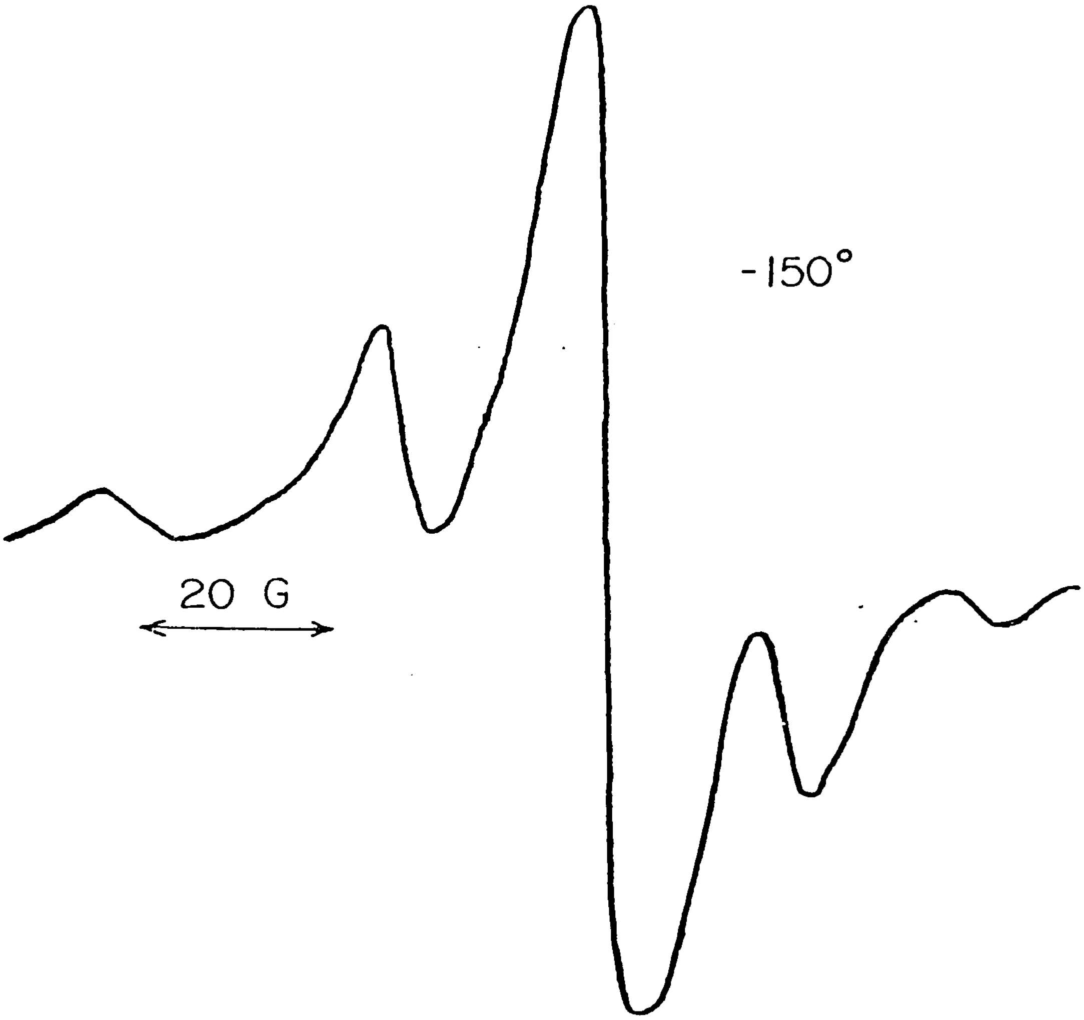


Figure 35. ESR spectrum of irradiated copolymer containing 65% methacrylamide and 35% methyl methacrylate, in THF glass.

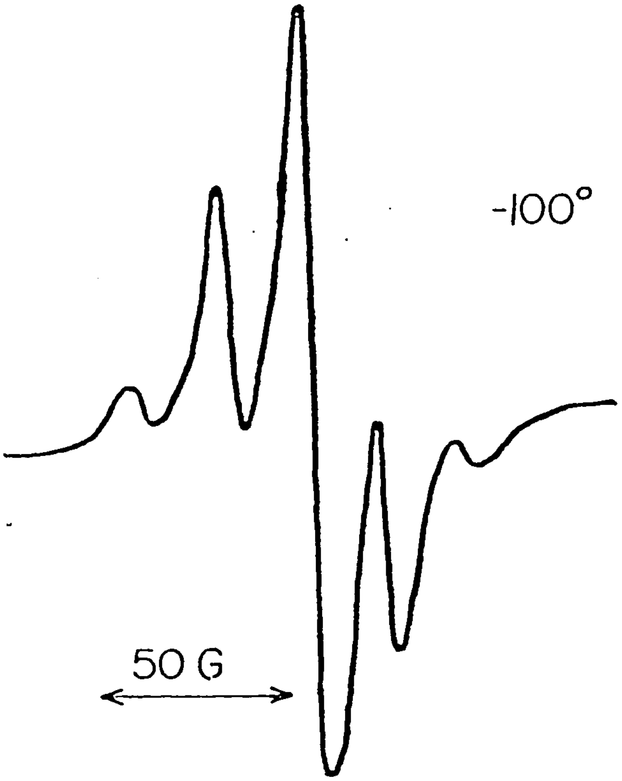


Figure 36. ESR spectrum of irradiated copolymer containing 41% methacrylamide and 59% methyl methacrylate, in THF glass.

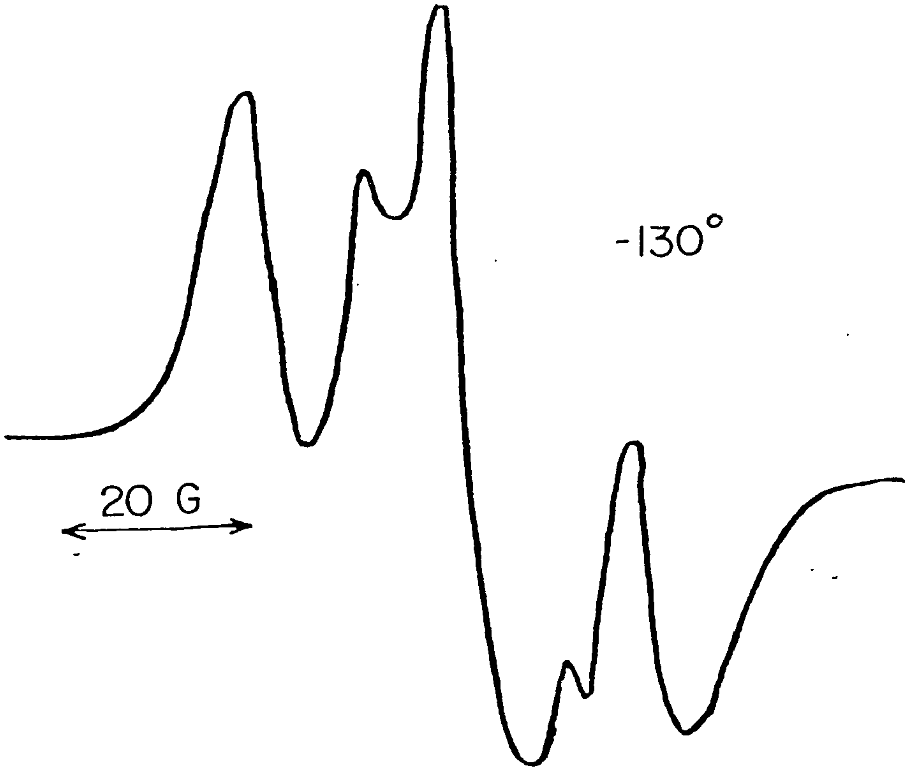


Figure 37. ESR spectrum of irradiated copolymer containing 18% methacrylamide and 82% methyl methacrylate, in THF glass.

The copolymers with 65% and 41% methacrylamide both yield ESR spectra very similar to the spectrum for the homopolymer of methacrylamide. It is believed that "radical 1" may give rise to these spectra. However the spectrum from the copolymer containing 18% methacrylamide appears to be slightly different. The intensities of the second and fourth lines for latter copolymer are out of proportion with the rest of the spectral lines. Also the splitting from line two to line three is only 8 gauss which is substantially different from the 22 gauss coupling observed for radical 1.

B. Spin Trapping Results

ESR studies were first carried out on the trapping compound itself, nitroso-t-butane (NtB). Figures 38 and 39 show spectra recorded for a solution of 0.1M NtB in hexane before and after irradiation respectively. The three line spectrum is assigned to the di-t-butyl nitroxide free radical. The coupling by the nitrogen nucleus is 15.7 gauss. For a given concentration of NtB and spectrometer amplitude, irradiation of the sample for one hour doubles the peak height of the spectrum. A solution of 0.1M NtB in water was irradiated at room temperature and spectra were recorded from -20°C to 0°C. The first and second derivative curves for the latter sample appear in Figures 40 and 41 respectively. The three line spectrum is assigned to the di-t-butyl nitroxide free radical. The coupling by the nitrogen nucleus is 17.5 gauss. It would appear that the dielectric constant of the solvent influences the magnitude of the splitting in this free radical. Subsequently a mixture of solid NtB suspended in water was irradiated and spectra were recorded. The ESR spectrum given in Figure 42 shows a total of nine lines in three sets of three lines. The central peak of each set is very intense. The N-14 splitting in the di-t-butyl nitroxide radical is assigned to the three intense lines (a_N=16.5 gauss). The small

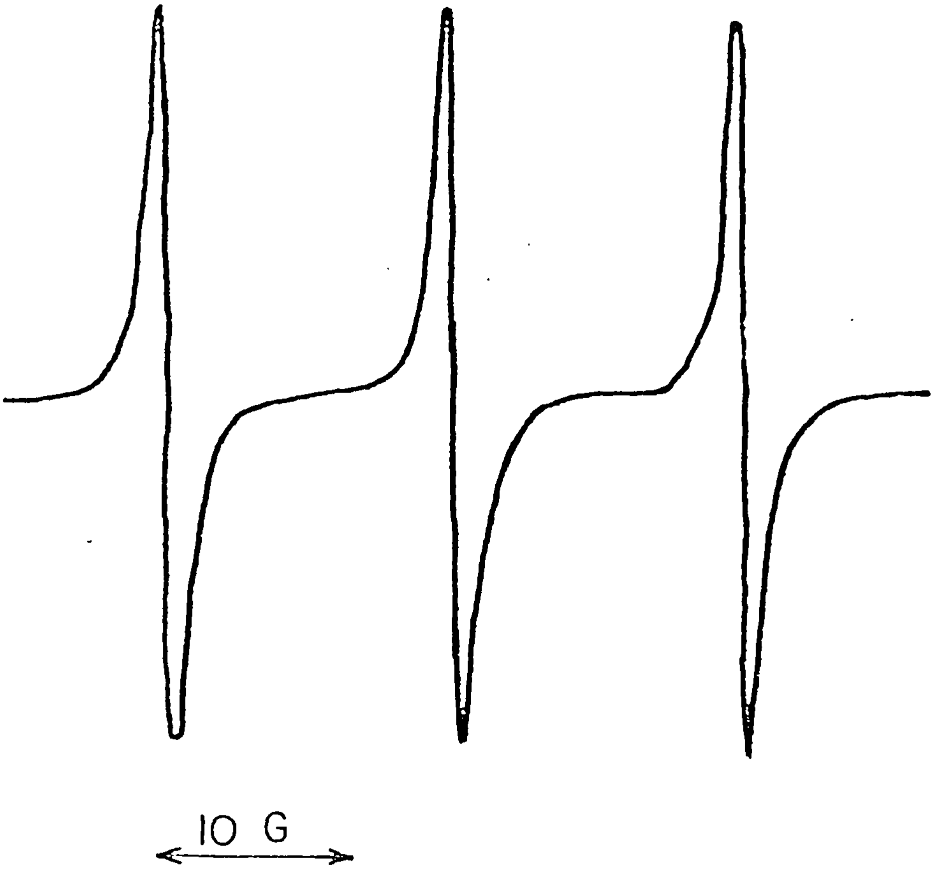


Figure 38. ESR spectrum of nitroso-t-butane in hexane before irradiation at room temperature.

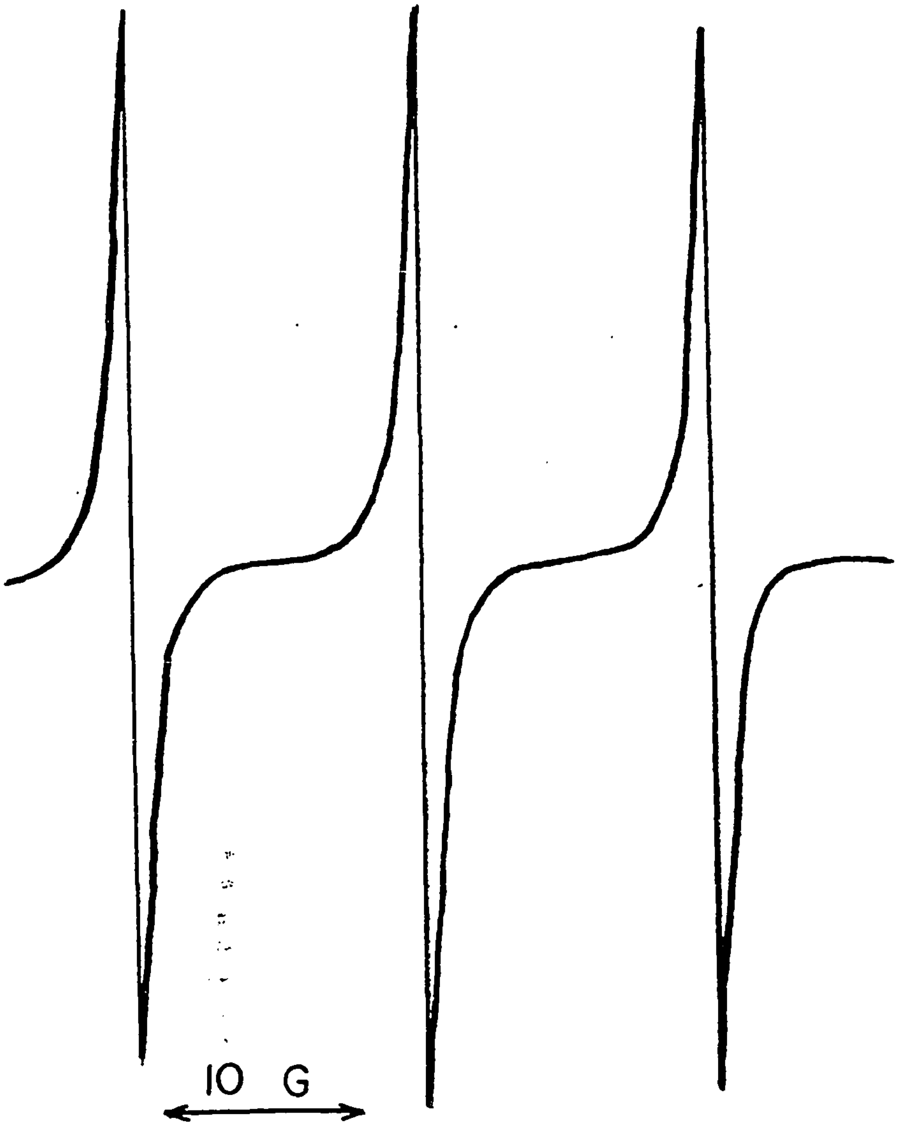


Figure 39. ESR specrtum of nitroso-t-butane in hexane solution after UV irradiation at room temperature.

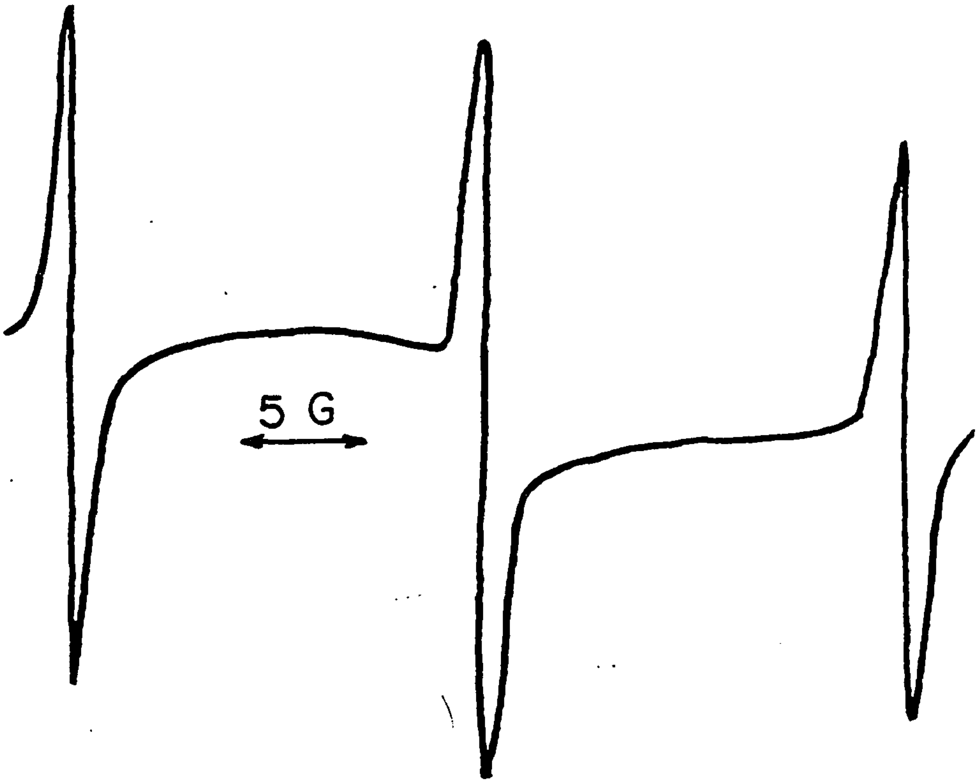


Figure 40. ESR spectrum of irradiated solution of 0.1M NtB in water recorded at -10°C.

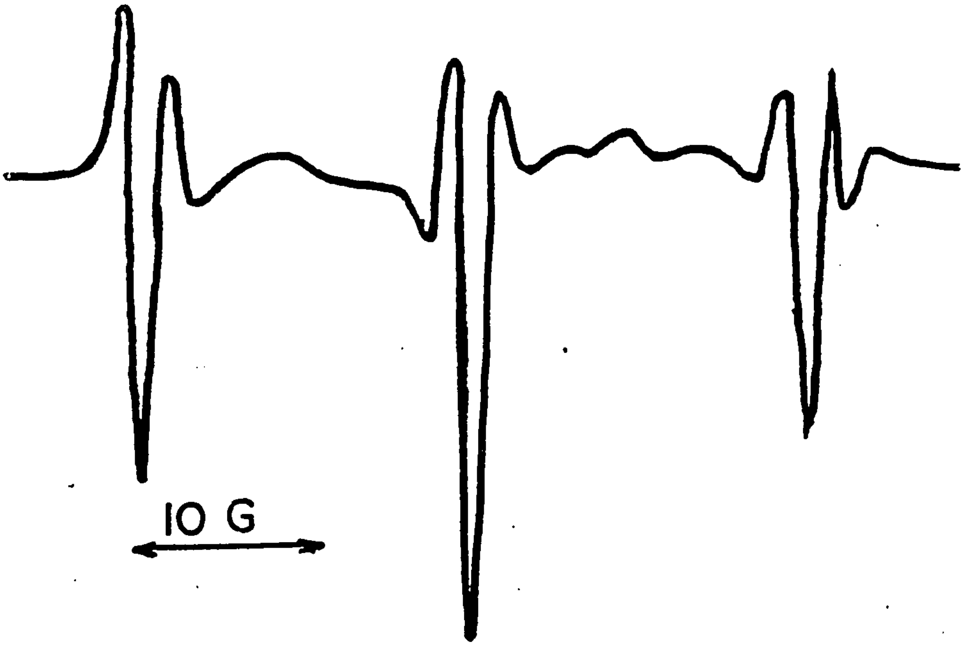


Figure 41. ESR second derivative curve of irradiated 0.1M solution of NtB in water, recorded at -16°C.

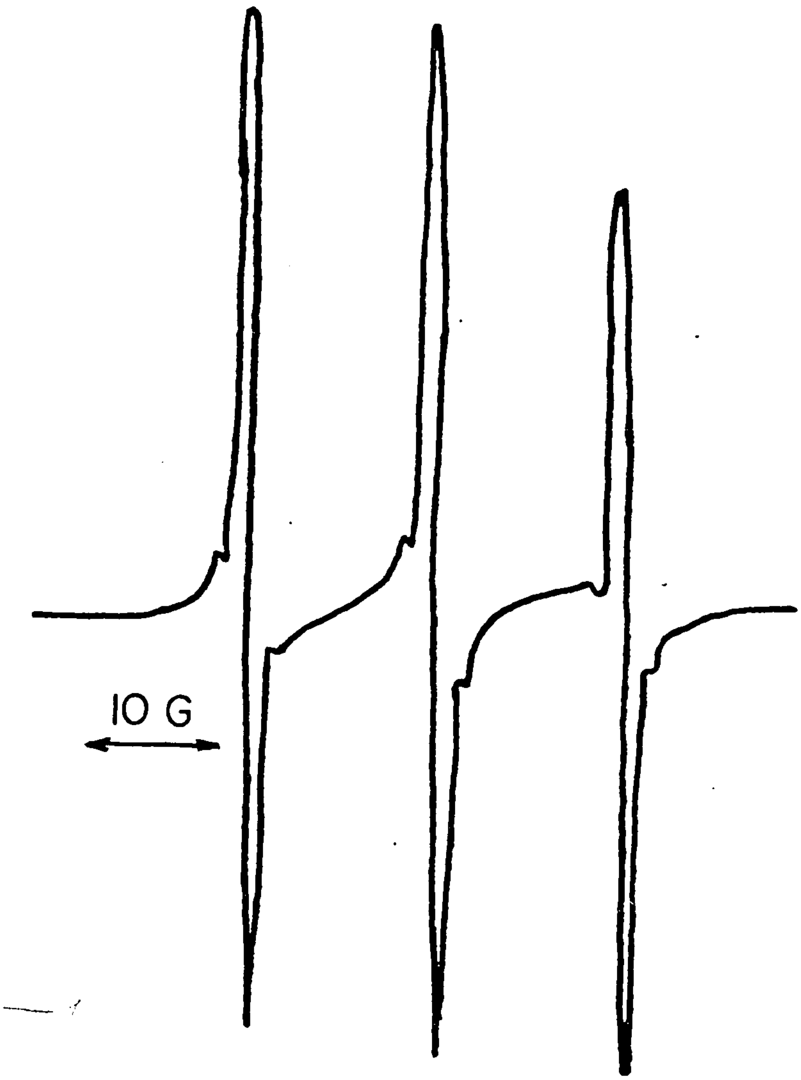
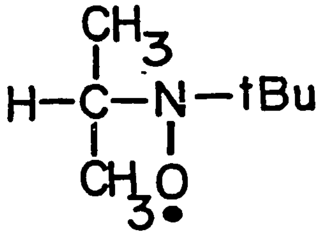


Figure 42. ESR spectrum of irradiated solid NtB suspended in water at -8°C.

satellite lines are ascribed to C-13 couplings with the unpaired electron (a_C=4.4gauss). The ratio of the N-14 peak height to the C-13 peak height is close to 100. This result is consistent with that reported for the di-t-butyl nitroxide radical (34).

ESR spin trapping studies utilizing NtB were used to help identify free radical intermediates from the irradiated low molecular weight model compounds. Aqueous solutions of isobutyramide and pivalamide with NtB were irradiated at room temperature and ESR spectra were recorded from -10°C to 0°C.

The spectrum of irradiated isobutyramide with NtB appears in Figure 43. A three line spectrum which shows evidence of further splitting to six lines is obtained. The spectrum is believed to arise from the t-butyl, isopropyl nitroxide free radical:



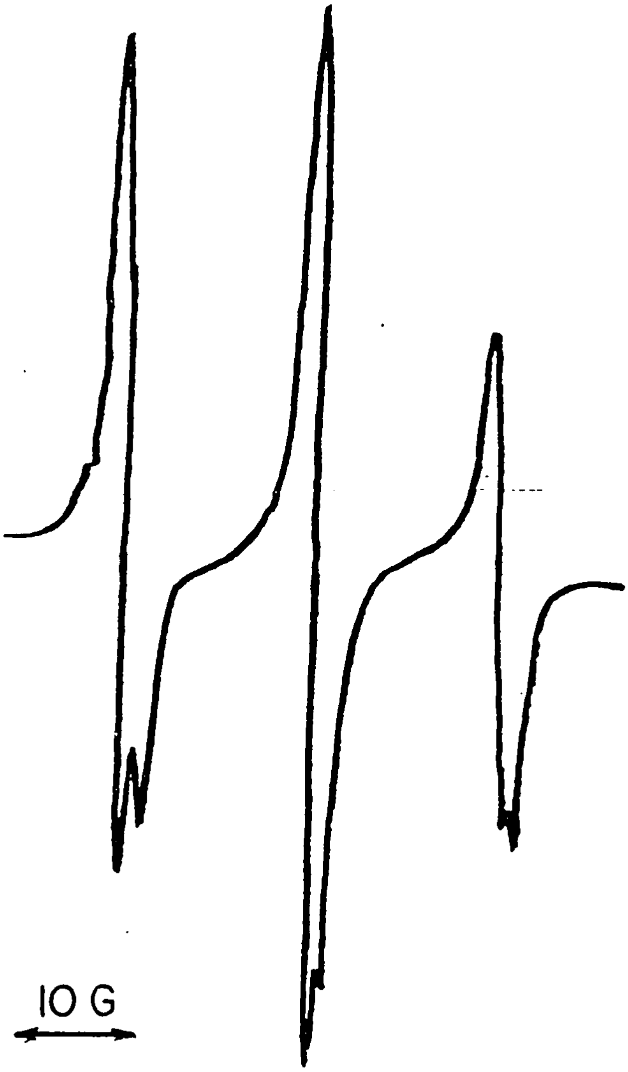


Figure 43. ESR spectrum of irradiated mixture of isobutyramide with NtB in water at -5°C. Mole ratio of isobutyramide to NtB is 7:1.

The splitting due to the nitrogen nucleus is 17.0 gauss and the beta proton splitting is about 2 gauss. To verify that it is indeed the isopropyl group that becomes trapped by NtB during the irradiation, a separate experiment was performed where a mixture of isopropyl chloride with NtB was irradiated. The ESR spectrum of the aforementioned mixture appears in Figure 44. A three line spectrum is observed which shows evidence of further splitting. The coupling by the nitrogen nucleus is 16.0 gauss and the beta proton coupling is about 2 gauss. The result of the latter experiment provides evidence that the isopropyl group becomes trapped by NtB during the irradiation of isobutyramide. The ESR spectrum of the t-butylisopropyl nitroxide radical has been reported (35). A six line spectrum was observed. The N-14 coupling was 16.8 gauss and the proton coupling was 1.8 gauss. The spectrum of irradiated isobutyramide with NtB is assigned to the t-butylisopropyl nitroxide radical.

The spectrum of irradiated pivalamide with NtB appears in Figure 45. A three line spectrum is observed with no further splitting. The spectrum is assigned to the di-t-butyl nitroxide radical. The N-14 coupling is 15.0 gauss. To confirm this result a mixture of NtB with t-butyl chloride was irradiated and ESR spectra were recorded. The sample containing the t-butyl chloride and NtB also yielded a three line spectrum (Figure 46) with N-14 coupling of 15.5 gauss.

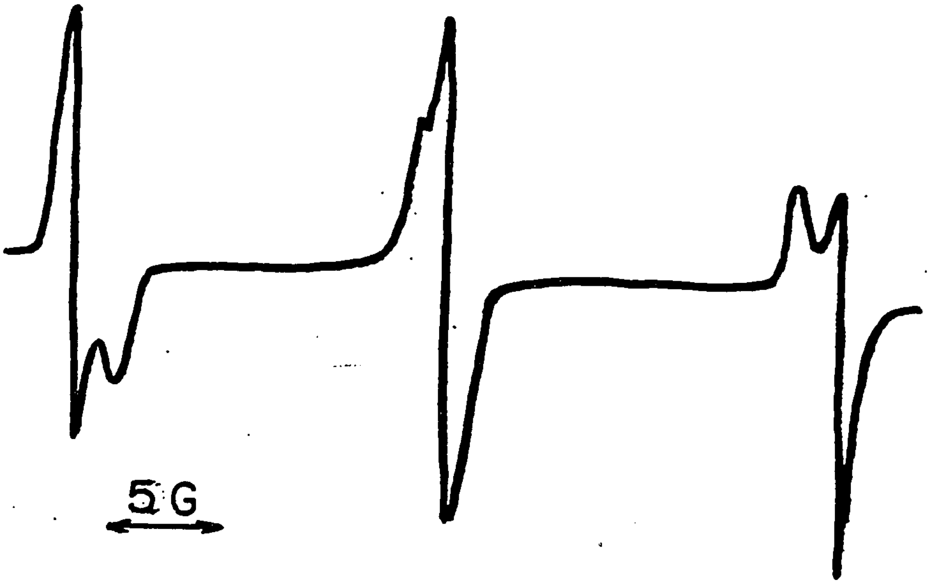


Figure 44. ESR spectrum of irradiated mixture of isopropyl chloride with NtB at room temperature.

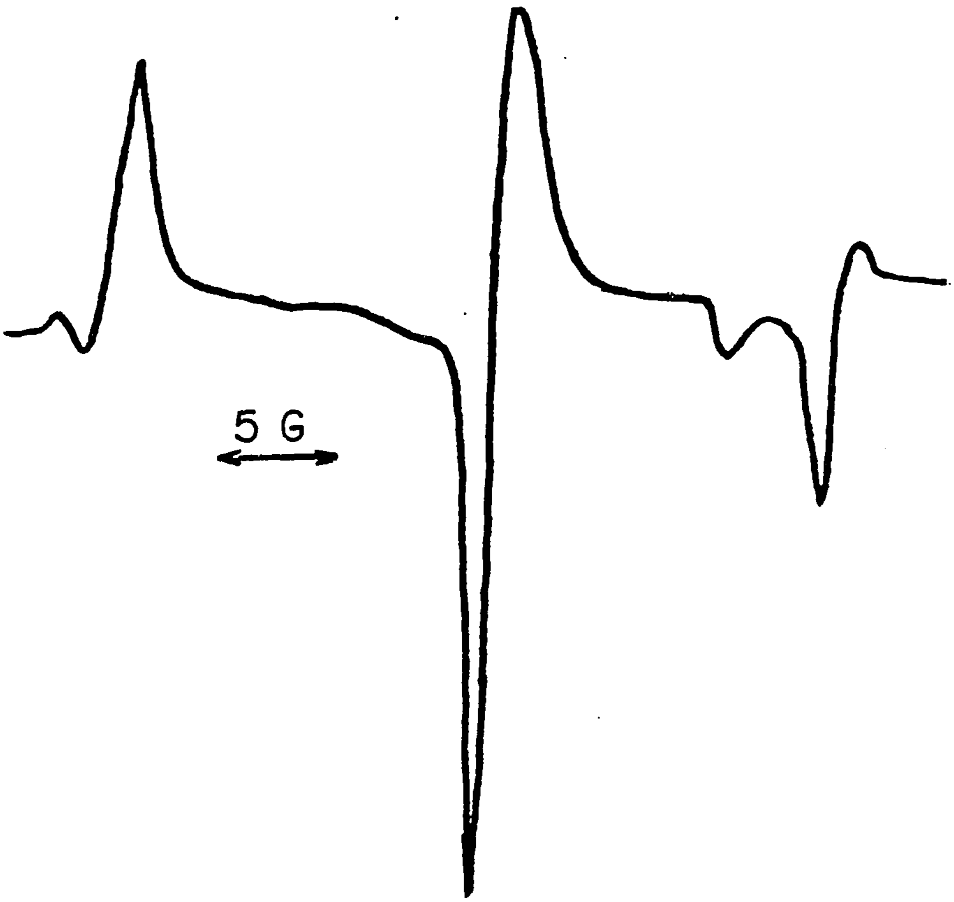


Figure 45. ESR spectrum of irradiated mixture of pivalamide with NtB in water at -4°C. Mole ratio of pivalamide to NtB is 4:1.

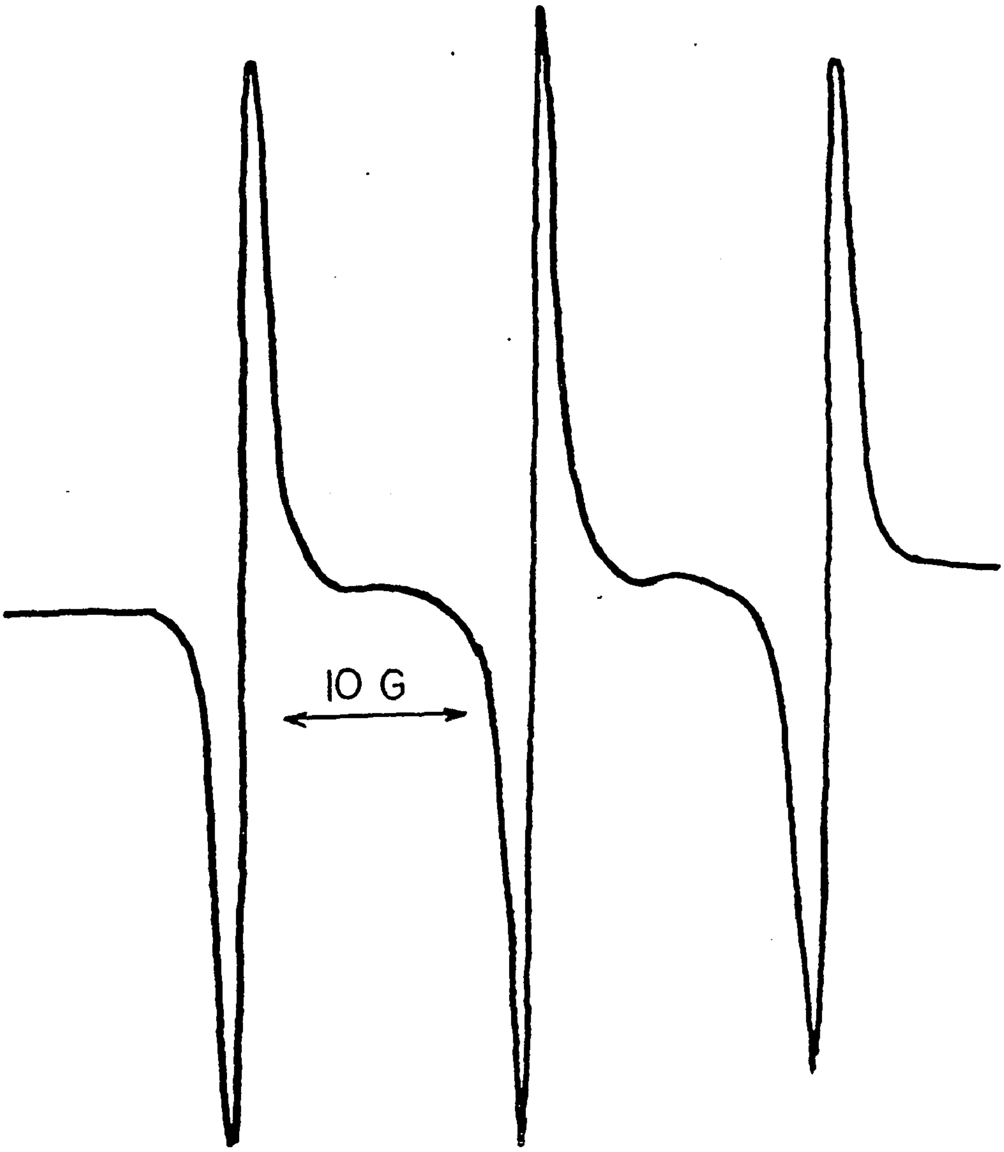
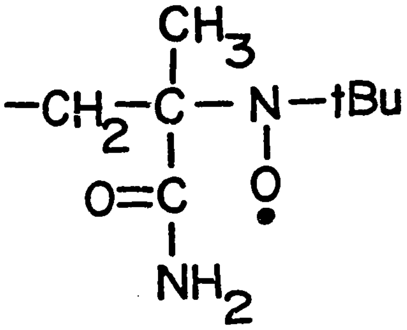


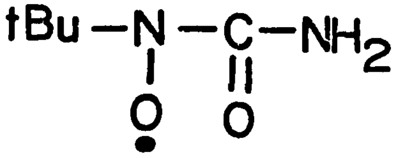
Figure 46. ESR spectrum of irradiated t-butyl chloride with NtB at room temperature.

An aqueous solution of PMAAm with NtB was irradiated at room temperature. Spectra were recorded from -10°C to 0°C. Figure 47 shows the spectrum observed at -10°C. A total of five lines are seen. Two partially overlapped spectra are present. One spectrum corresponds to peaks labeled 1, 3, 5. This spectrum is assigned to the NtB adduct of radical 1:



The N-14 coupling is 15.5 gauss. This result is in line with that obtained for the NtB adduct of the propagating radical in methacrylamide (Figure 8).

The second spectrum corresponds to peaks labeled 2, 3' which is superimposed on 3 and 4. This spectrum is assigned to the NtB adduct of the amide free radical:



$$\mathrm{tBu{-}N(O^{\bullet}){-}C({=}O){-}NH_2}$$

The observed N-14 coupling is about 10.7 gauss. This result is in line with that obtained for the irradiation spin trapping study of formamide (Figure 11).

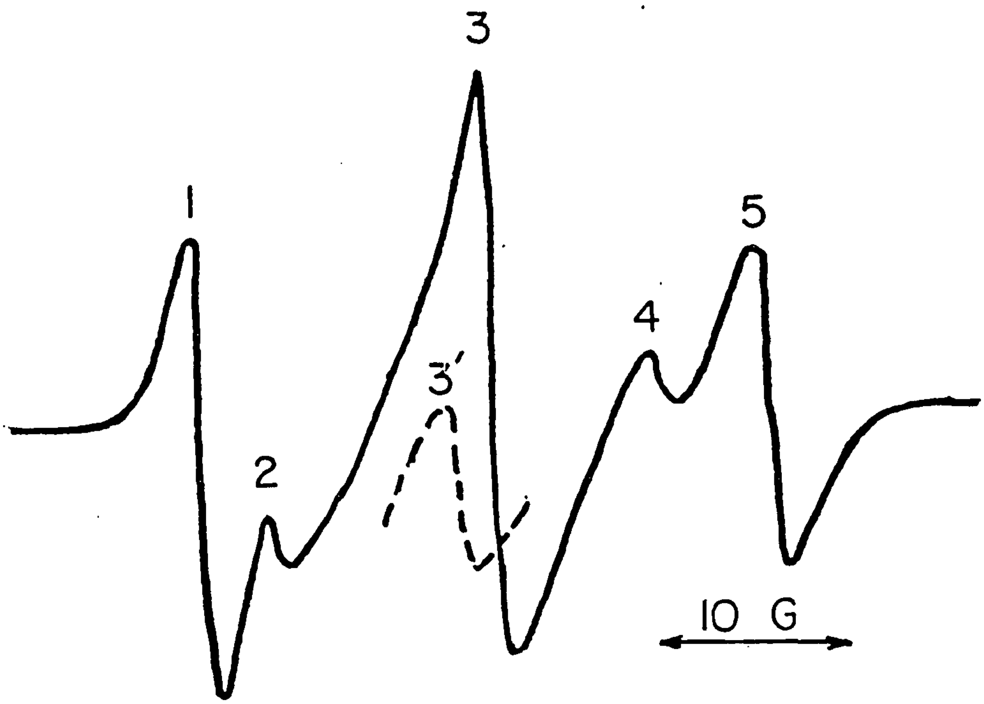
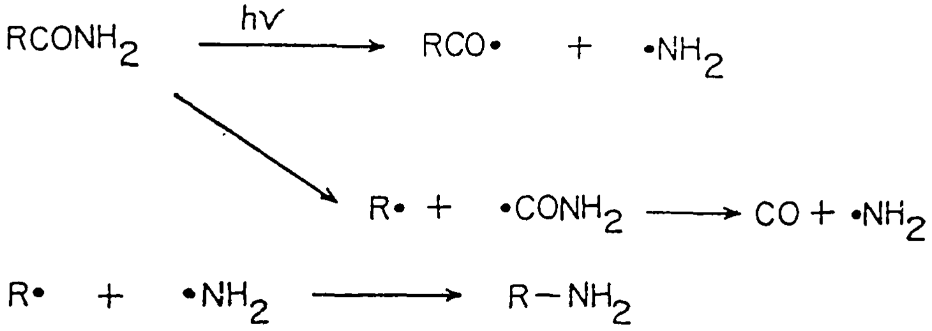


Figure 47. ESR spectrum of irradiated mixture of polymethacrylamide and NtB in water at -10°C.

C. Discussion of Amide Photochemistry

It would be appropriate at this time to briefly discuss the basic processes in amide photochemistry and to correlate the results obtained thus far. During the photolysis of aliphatic amides, carbon monoxide, hydrogen and aliphatic amines are generated (36)(37). A reaction scheme for the photolysis of amides is given below:



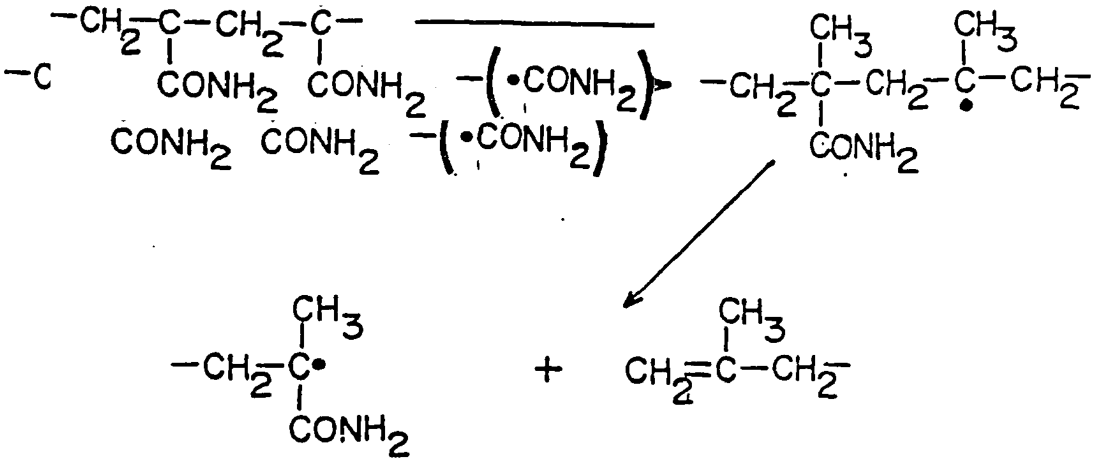
The amide group controls the photodecomposition. Cleavage may occur at the carbon-carbon bond or the carbon-nitrogen bond at the carbonyl group.

The results of the irradiation spin trapping studies for isobutyramide and pivalamide indicate that the alkyl group attached to the amide group is trapped by NtB. Hence one might suspect that cleavage of the carbon-carbon bond at the amide group occurs during irradiation of these compounds. However the spin adduct of the amide group could not be detected during these experiments. Perhaps the amide radical is sufficiently reactive that it decomposes before it can be trapped by NtB.

When PMAAm was irradiated in the presence of the trapping compound, the spin adducts of "radical 1" and the amide radical were detected. Apparently during the irradiation of the polymer the amide radical is generated.

The results of the spin trapping experiments support the belief that when amide compounds are irradiated, the cleavage of the carbon-carbon bond at the carbonyl group occurs.

Finally how might one account for the formation of "radical 1" during the irradiation of PMAAm? A suggested mechanism for the irradiation degradation of PMAAm is given below:



The primary step of the degradation involves cleavage of an amide group from the polymer chain. The intermediate tertiary free radical then quickly undergoes main chain scission at the carbon-carbon bond beta to the site of the unpaired electron. "Radical 1" and a fragment with terminal unsaturation are the results. The fact that "radical 1" is generated during the degradation suggests that PMAAm undergoes chain scission when it is irradiated.

V. Conclusion

The results obtained herewith point to the fact that PMAAm is a polymer of the degrading type under ultraviolet and gamma irradiation. ESR spectroscopy revealed that "radical 1" is an important intermediate during the ultraviolet irradiation of PMAAm and its copolymers with methyl mrthacrylate. A well resolved five line ESR spectrum with approximate binomial intensity distribution was obtained for PMAAm in a rigid glass at low temperature. McConnell's relation was used as a basis for the assignment of "radical 1" to the five line spectrum. The fact that "radical 1" appears after irradiation suggests that main chain cleavage is an important process for the polymer. The ESR spin trapping study of PMAAm not only provided support for the formation of "radical 1" during irradiation but also inferred the mechanism by which "radical 1" may arise. The spin trapping experiment also indicated that the amide radical is generated during the irradiation of PMAAm. The chemical processes involved during the irradiation of the polymer have been elucidated.

The viscosimetric studies of redox polymerized PMAAm indicated that the polymer underwent significant reduction in molecular weight after exposure to gamma irradiation.

Table 11 lists radiation G values for the polymers studied here as well as some polymers studied elsewhere (38)(39)(40)(41).

Table 11. Radiation G values for degrading polymers.

Polymer	G Value (events/100 eV)
Polymethacrylamide	$G_s - G_x = 2.0$
MMA (95%) - co MAAm (5%)	$G_s = 0.92$, $G_x = 0.09$
Poly(isobornyl methacrylate)	$G_s - G_x = 2.1$
PMMA	$G_s - G_x = 1.3$ *
Poly(n-hexyl methacrylate)	$G_s - G_x = 0.38$ *
Poly(methyl-α chloro acrylate)	$G_s - G_x = 5.3$ (low dose) * $= 2.1$ (high dose)
Poly(1,1,1-trichloroethyl α chloro acrylate)	$G_s - G_x = 2.1$ *
Poly(1-butene sulfone)	$G_s - G_x = 6.5$ *

* Indicates a literature value.

It is known that the sensitivity of a polymeric resist to the electron beam increases with the G value of the polymer. Comparison shows that PMAAm and poly(isobornyl methacrylate) have higher G values than PMMA and poly(n-hexyl methacrylate). However the polymers investigated here do not degrade as readily as do poly(1-butene sulfone) and poly(methyl α chloro acrylate) (PMCA). PMCA is an interesting case. After absorption of one megarad of radiation, the value of $G_s - G_x$ decreases by a factor of two. After irradiation the material becomes less sensitive to radiation. PMCA undergoes dissociative electron capture with the removal of a chloride ion. Then beta scission occurs to yield the polymeric methyl α chloro acrylate radical. The number of scissions per polymer after one megarad dose is 1.1. One chlorine atom is lost for every chain scission that occurs. The reason for the decrease in sensitivity is not clear.

The copolymer containing methacrylamide and methyl methacrylate yielded a fairly low G value. It should be pointed out that this copolymer had a large dispersity ($M_w/M_n > 7$). Perhaps the broad distribution of the copolymer obscures the true effect of the radiation on this sample.

Based on studies performed by Matsuda and co-workers (8) PMAAm had a sensitivity of 2.3×10^{-7} coulombs/cm^2 which is about two orders of magnitude better than that for PMMA (5×10^{-5} coulombs/cm^2). With the combination of characteristics such as high glass transition temperature and good adhesion properties, perhaps PMAAm may have potential for use as a positive resist for fabrication of integrated circuit components.

VI. Experimental Section

A. Materials

Methacrylamide and methyl methacrylate monomers were obtained from Aldrich Company. N,N-dimethyl methacrylamide and N-methyl methacrylamide were obtained from Polysciences Company. Butyl methacrylate and isobornyl methacrylate were received from Scientific Polymer Products.

Methacrylamide was recrystallized from toluene prior to use. Methyl methacrylate was distilled before use. The other methacrylate monomers were passed through a column (supplied by SP2 Company) to remove the inhibitor. The initiators benzoyl peroxide and potassium persulfate were supplied by Fisher Company and were used without further purification. Tetrahydrofuran of high purity was distilled and stored over molecular sieves in the dark under nitrogen.

Model compounds isobutyramide and pivalamide were purchased from Aldrich Company and were recrystallized from methanol prior to use. The trapping agent, nitrosotertiary butane, was obtained from Aldrich Company. This compound was stored in the refrigerator and was used without further purification. Magnesium perchlorate (Tridom Co.) and urea (Fisher Co.) were used as they were received for viscosity experiments. PMMA standards used for GPC were obtained from Polysciences Company.

B. Preparation of Polymers

Polymethacrylamide (PMAAm)

Water soluble PMAAm was prepared by free radical polymerization of methacrylamide in refluxing toluene with benzoyl peroxide as initiator (42). The polymer which is insoluble in toluene precipitates as it is formed in the reaction mixture. This fact will limit the molecular weight of the polymer produced. A 66% yield was obtained. After isolation the polymer was washed with hot methylene chloride to remove traces of monomer and initiator. This PMAAm sample was used for ESR studies and molecular weight measurements.

A second sample of PMAAm was prepared using redox polymerization at room temperature. A 20% aqueous solution of methacrylamide was first purged with nitrogen. Potassium persulfate and sodium bisulfite were then added to initiate the reaction. The mass ratio of monomer to initiator was 100:1. The solution was stirred vigorously. The next morning the reaction mixture was found gelled. The solid glob of material was placed in a beaker with distilled water and heated to boiling to dissolve it. The polymer precipitated upon cooling. The material was cut into small pieces and placed in the oven at 100°C. After two hours the dry sample was removed from the oven. A 50% yield was obtained. This PMAAm proved soluble in 8M urea and 0.4M magnesium perchlorate solutions. The kinetics of persulfate initiated polymerization of methacrylamide had been reported by other workers (43). Redox PMAAm was used for molecular weight experiments.

Copolymers with MMA

Three copolymers with varying compositions of MAAm and MMA were prepared and used for ESR studies. The copolymerizations took place at 70°C in 95% ethanol with benzoyl peroxide as initiator. The reported reactivity ratios for copolymerization of MAAm (M_1) with MMA (M_2) are r_1=0.47, r_2=1.5 (44) and r_1=0.43, r_2=1.68 (45). The copolymer samples prepared could be described this way:

Copolymer 1:	f_1=0.789	F_1=0.65
Copolymer 2:	f_1=0.583	F_1=0.41
Copolymer 3:	f_1=0.285	F_1=0.18

F denotes the fraction of the comonomer in the copolymer and f denotes the fraction of the comonomer in the feed. Figure 48 shows the plot of F_1 against f_1, the copolymer composition curve for MAAm and MMA.

All copolymerizations were carried to 10% or less conversion to insure the production of homogeneous co-

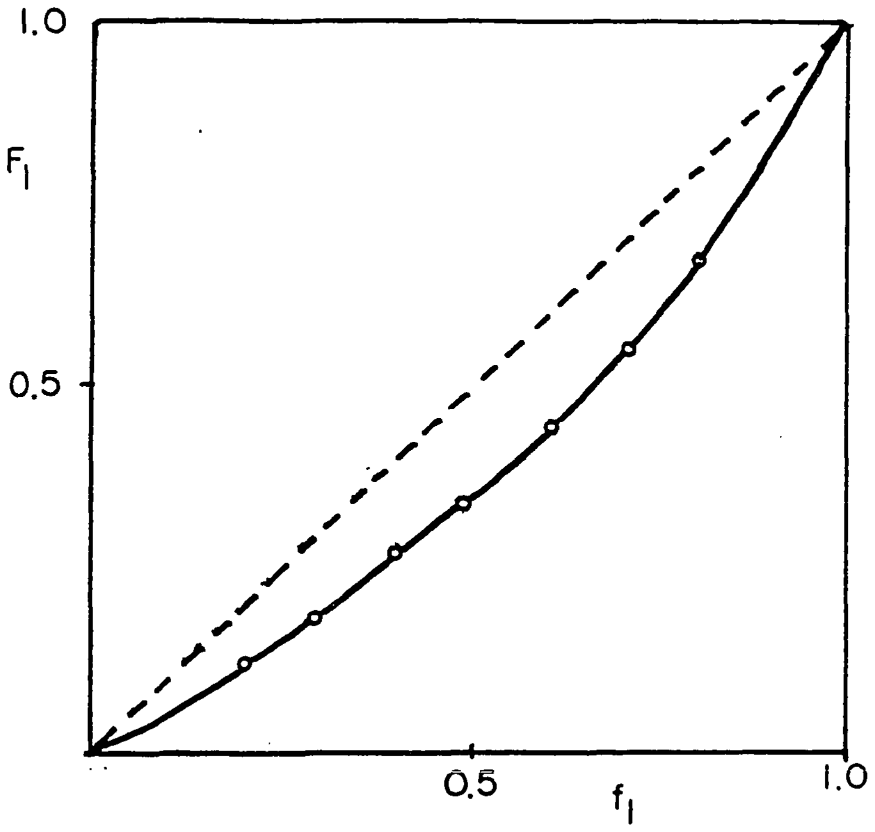


Figure 48. Copolymerization curve for MAAm (M_1) and MMA (M_2).

Table 12. Copolymer yields.

Copolymer	% conv.	f_1 @start	f_1 @ end
1	7.0	0.789	0.798
2	8.0	0.583	0.598
3	6.0	0.285	0.292

polymer. Table 12 lists the f_1 values at the start and end of each copolymerization. Considering monomer reactivities, the copolymer composition and the extent of conversion, the change in f_1 over the course of copolymerization was calculated. In each case there is not much change in f_1 during the course of the reaction. The value of f_1 increases since MMA is the more reactive monomer. Subsequently a copolymer with 5% MAAm was prepared and used for a molecular weight study.

Poly(N-Methyl Methacrylamide)

Ten grams of N-methyl methacrylamide were mixed with 20 ml of distilled water and initiator (0.07g potassium persulfate and 0.03g sodium bisulfite). The solution was stirred and the temperature was held at 35°C. The next day the mixture was found gelled. The gel was then dried on a watch glass over a heat plate. A 55% yield was obtained. This polymer was soluble in 8M aqueous urea and distilled water.

Copolymer of MAAm with N,N-Dimethyl Methacrylamide

80 ml of distilled water were mixed with 0.1 mole of each comonomer and initiator (0.15g potassium persulfate and 0.06g sodium bisulfite). The solution was stirred and the temperature was held at 35°C. The next day a small amount of solid had formed in the mixture.

The copolymer dissolved in water with stirring at or above room temperature.

Poly(n-Butyl Methacrylate)

Poly(butyl methacrylate) was prepared by free radical polymerization in bulk. 100 ml of monomer were purged with nitrogen and 0.1g of benzoyl peroxide was added. The mixture was stirred while heating to 85°C. After an hour the polymer was precipitated on pentane. The polymer was dissolved in hot methyl ethyl ketone, precipitated on methanol and then isolated. A 40% yield was obtained.

Copolymer of Butyl Methacrylate with MAAm

Butyl methacrylate (0.5 mole) and MAAm (0.5 mole) were dissolved in 250 ml of ethanol. The solution was then purged with nitrogen. Benzoyl peroxide (0.25g) was added. The mixture was heated to 85°C with stirring. After two and one half hours the copolymer was precipitated on water and then dried in the oven. A 15% yield was obtained.

Poly(Isobornyl Methacrylate)

10 ml of isobornyl methacrylate were heated to 85°C in a test tube with 0.1g of benzoyl peroxide. Within 15 minutes the reaction mixture solidified. The test

tube was broken. The solid material was crushed to bits under the heat press at 200°C. The polymer was found to be insoluble in DMF but was soluble in toluene.

C. Thermal Characterization

PMAAm and the copolymers with MMA were characterized by differential scanning calorimetry with the Dupont 990 thermal analyzer. The heating rate was 10°C per minute under air. Each sample exhibited a DSC trace similar to the one depicted in Figure 49.

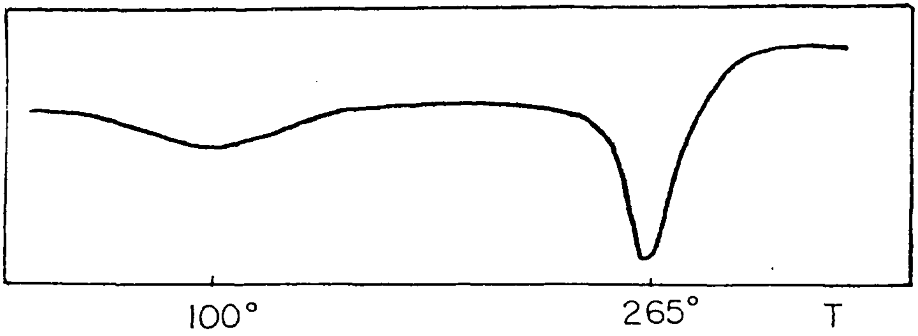


Figure 49. DSC sketch for copolymers of MAAm with MMA and PMAAm.

Each sample exhibited two endotherms. The broad peak around 100°C is thought to be due to the release of absorbed water molecules. A sample which was dried prior to taking the DSC did not show this peak. The sharp peak around 265°C is thought to be due to the thermal decomposition of the sample. The thermal degradation of PMAAm and its copolymers had been reported by other workers (46)(47).

D. Ultraviolet Spectra

Ultraviolet spectra were recorded for aqueous solutions of methacrylamide, PMAAm, isobutyramide, pivalamide and magnesium perchlorate. Quartz cells with one cm. path length were used. Spectra were recorded on the Cary 118C instrument.

The spectrum of PMAAm at a concentration of 0.3 g/l is depicted in Figure 50. A plot of absorbance at 220 nm against concentration is given in Figure 51. The absorptivity coefficient for PMAAm is 3.6 l/g-cm.

The UV spectrum of MAAm at a concentration of 0.105 g/l appears in Figure 52. A plot of absorbance at 230 nm against concentration is shown in Figure 53. The absorptivity coefficient for MAAm is 13.3 l/g-cm.

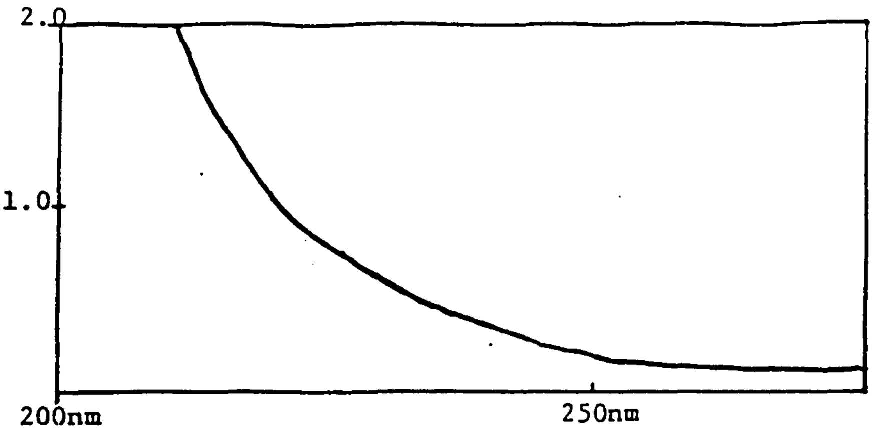


Figure 50. Absorbance vs. wavelength for PMAAm, conc.=0.3g/l.

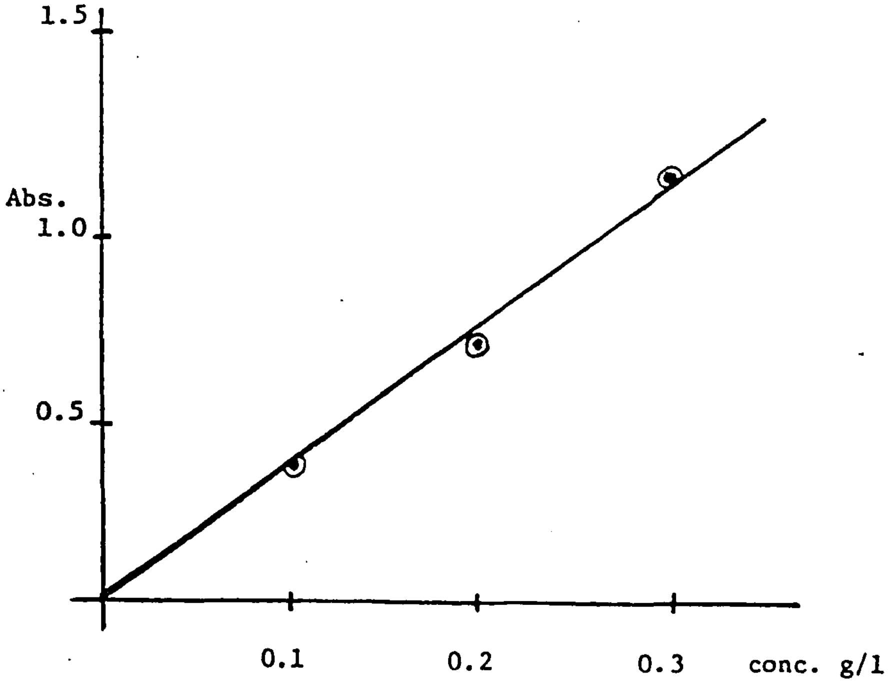


Figure 51. Absorbance @ 220 nm vs. concentration for PMAAm.

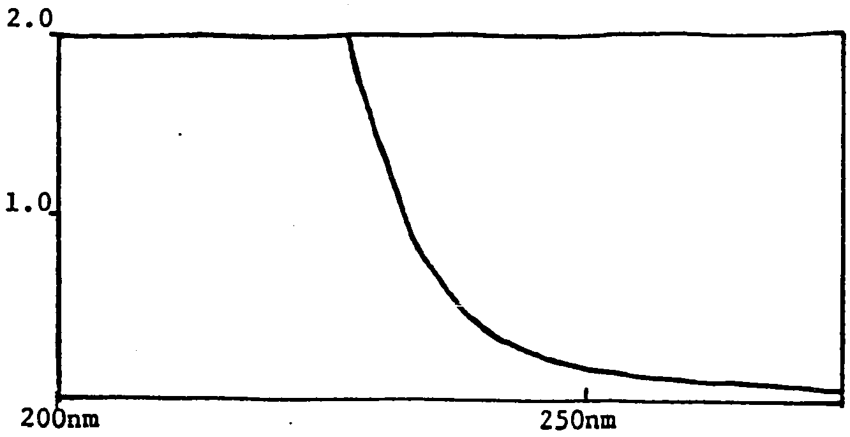


Figure 52. Absorbance vs. wavelength for MAAm, conc.=0.105 g/l.

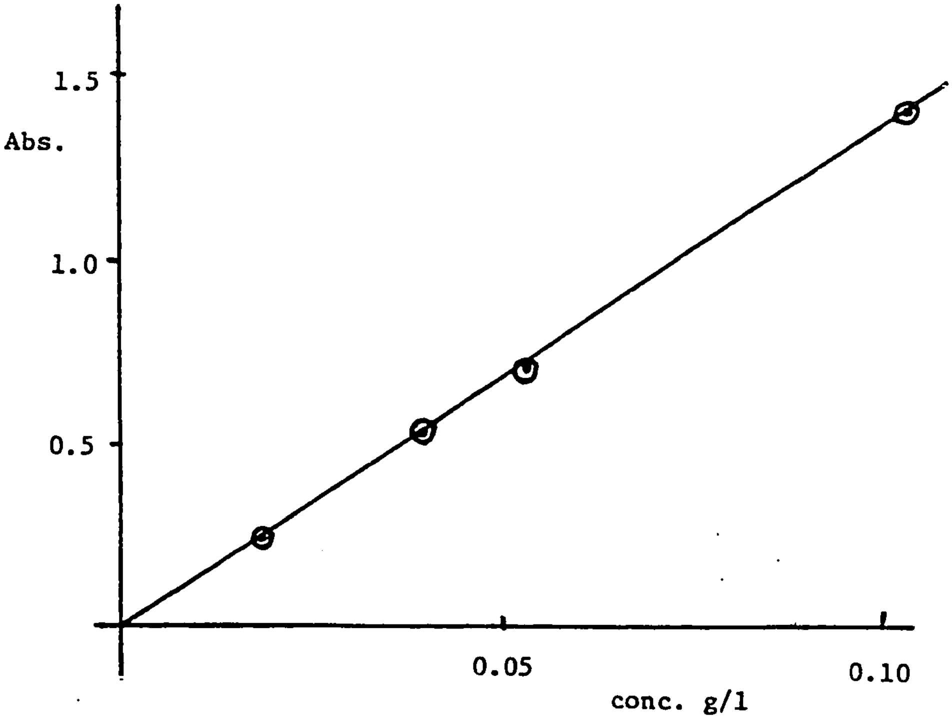


Figure 53. Absorbance @ 230 nm vs. concentration for MAAm.

An ultraviolet study of irradiated PMAAm was carried out. An aqueous solution of PMAAm was irradiated for various time intervals and spectra were recorded. The solute concentration was 0.3 g/l. The results are summarized in Table 13.

An increase of ultraviolet absorption is observed in the range of 300 nm to 200 nm for solutions irradiated up to two hours. The change in spectrum indicates a modification of polymer structure; possibly due to the formation of double bonds in the material.

Table 13. Ultraviolet absorbance for irradiated PMAAm.

Sample Irradiation Time	Absorbance Values		
	@ 300 nm.	@ 260 nm.	@ 220 nm.
none	0.04	0.12	1.20
15 min.	0.08	0.16	1.36
30 min.	0.08	0.16	1.36
1 hour	0.10	0.20	1.38
2 hours	0.12	0.22	1.24

A spectrum was recorded for an aqueous solution of magnesium perchlorate. The solution had an absorbance of 0.16 at 220 nm.

Spectra were recorded for isobutyramide and pivalamide in aqueous solutions. Both compounds exhibited spectra similar to PMAAm. Plots of absorbance at 220 nm against concentration are shown in Figures 54 and 55. Isobutyramide had an absorptivity coefficient of 0.84 l/g-cm. Pivalamide had an absorptivity coefficient of 0.86 l/g-cm.

E. ESR Spectra

ESR spectra were recorded on the JEOL ESR spectrometer at various temperatures from -160°C to room temperature. All samples for ESR work were degassed and then sealed under vacuum in quartz sample tubes or quartz capillary tubes. A 200 Watt mercury-xenon lamp was used for ultraviolet irradiations.

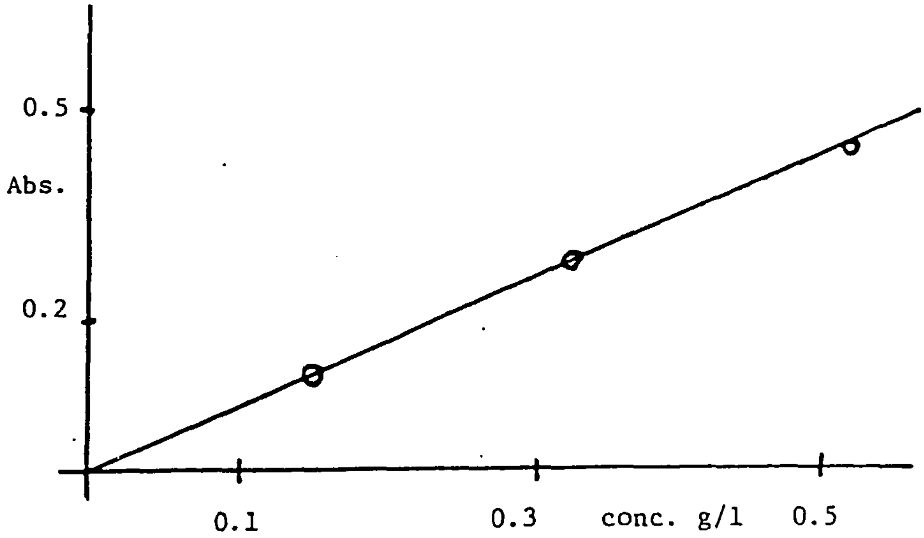


Figure 54. Absorbance @ 220 nm vs. concentration for pivalamide.

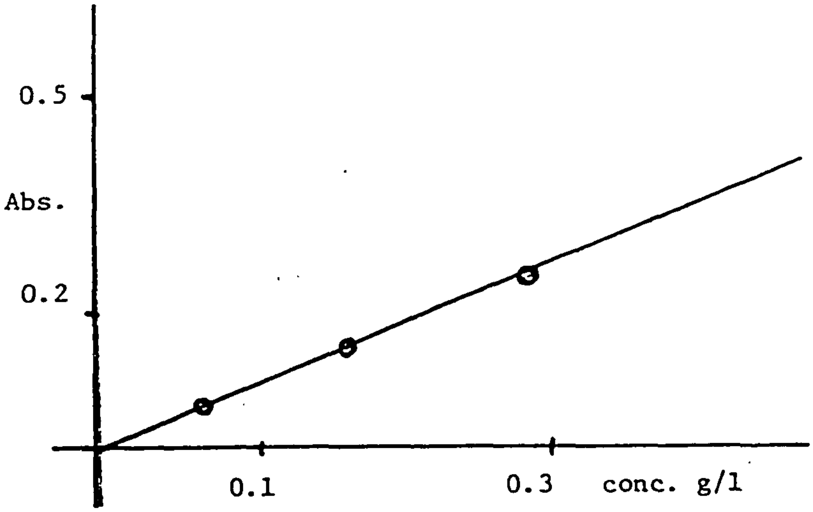


Figure 55. Absorbance @ 220 nm vs. concentration for isobutyramide.

F. Molecular Weight

Viscosity average molecular weights were determined for PMAAm samples using the Hewlett-Packard autoviscometer. The viscometer tubes were supplied by Cannon Company (tube numbers: 1D-657 and 50E-530). The temperature was maintained at 25°C with a temperature bath equipped with a thermoregulator. Efflux times were measured with a photoelectric attachment with automatic recorder. Intrinsic viscosities were determined by the graphical intercept method. The solvents used for viscometric studies of PMAAm were 8M aqueous urea and 0.4M aqueous magnesium perchlorate.

The molecular weights of MMA copolymer samples were investigated by gel permeation chromatography with the Waters GPC instrument. Several narrow molecular weight distribution samples of PMMA were injected into the GPC and a calibration curve for PMMA in DMF was prepared. Figure 56 shows the natural logarithm of molecular weight against the elution volume. It was then assumed that the copolymer (95% MMA) obeyed the PMMA calibration curve.

The molecular weights of poly(isobornyl methacrylate) samples were investigated by membrane osmometry. Toluene was used as solvent. Number average molecular weights were determined by the graphical intercept method from plots of reduced osmotic pressure against

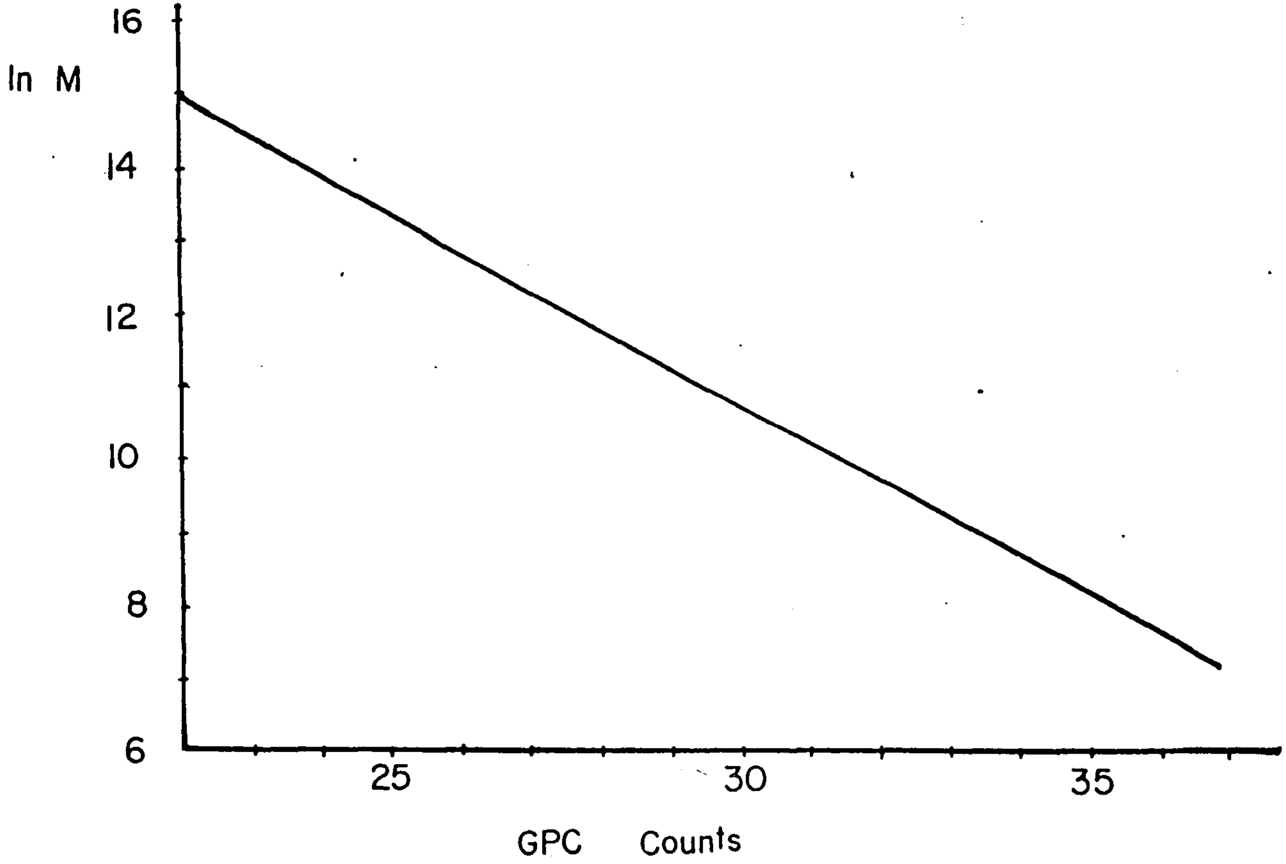


Figure 56. GPC calibration plot for PMMA in DMF.

concentration.

G. Film Preparations

The following samples were made into films using a heat press:

1. PMMA
2. Copolymer (MAAm 18% - MMA 82%)
3. Copolymer (MAAm 40% - MMA 60%)
4. Poly(butyl methacrylate)
5. Copolymer of butyl methacrylate with MAAm

PMMA was pressed at 125°C under 30,000 psi for 15 minutes. Copolymers with methacrylamide were pressed at 170°C under 35,000 psi for 15 minutes. Poly(butyl methacrylate was pressed at 50°C under 30,000 psi for 10 minutes. The copolymer of butyl methacrylate with MAAm was pressed at 150°C for 10 minutes under 30,000 psi. PMAAm, poly(N-methyl methacrylamide) and the copolymer with MAAm and dimethyl methacrylamide could not be softened. Thus no films could be prepared from these samples.

H. Mechanical Properties

The Instron tensile testing device was used to characterize polymer films. The instrument was calibrated with a five pound weight prior to use. Stress, strain, modulus and ultimate strength for six samples

Table 14. Mechanical properties of polymer films.

Sample	Modulus dynes/cm^2	Ultimate Strength psi (Range)	Percent Elongation at break
PMMA	$(1.03 \pm 0.55) \times 10^{10}$	$(2.1 \text{ to } 4.3) \times 10^3$	3.6
MAAm 18% MMA 82%	$(6.41 \pm 3.41) \times 10^9$	$(0.6 \text{ to } 1.9) \times 10^3$	1.3
MAAm 40% MMA 60%	$(8.06 \pm 2.73) \times 10^9$	$(0.7 \text{ to } 4.5) \times 10^3$	2.1
Poly-butyl MA	$(3.61 \pm 1.86) \times 10^8$	$(0.8 \text{ to } 2.8) \times 10^3$	143.3
BMA and MAAm	$(6.83 \pm 3.28) \times 10^9$	$(0.8 \text{ to } 3.3) \times 10^3$	1.9

of each film tested. Table 14 lists values for modulus, ultimate strength and percent elongation for the polymers studied.

PMMA, the copolymers of MAAm with MMA and the copolymer of butyl methacrylate with MAAm exhibited stress-strain curves indicative of brittle fracture. The aforementioned materials had high modulus values and low percent elongation at the break. On the other hand poly (butyl methacrylate) exhibited plastic deformation with lower modulus values than the other samples.

It would appear that the incorporation of MAAm into a copolymer with MMA lowers the modulus by less than one order of magnitude. Incorporation of MAAm into a copolymer with butyl methacrylate leads to an increase in modulus of the sample by one order of magnitude. The copolymers formed good films and had high strength.

I. Gamma Irradiations

A cesium 137 gamma irradiator was used to irradiate solid polymers. Samples were sealed under vacuum and irradiated for periods of two, four, six and eight hours. Radiation G values and the quantum efficiency for degradation were determined from molecular weight measurements. The radiation dosage rate was determined by the dosimetry procedure given by Tsay and Cdian (48). The dosage rate received by polymer samples was 0.29 Mrad/hr.

J. Carbon 13 Spectroscopy

20.1 MHz, natural abundance, proton decoupled carbon 13 spectra were obtained on the IBM NR-80 instrument. PMAAm samples were studied in aqueous urea solutions with D_2O for lock. The urea carbonyl resonance appears at 163.0 ppm and does not interfere with the carbonyl resonances from the polymer. The C-13 shift for dioxane (reference) was set at 67.4 ppm.

Copolymers were studied in DMF solution with D_2O capillary tube for lock. Referencing was made by setting the DMF methyl carbon cisoid to the formyl proton at 36.0 ppm. Poly(isobornyl methacrylate) was studied in $CDCl_3$ solution at 40°C with TMS for reference. Concentrations were in the range of 10% to 15%. Pulse widths of 60° and relaxation delays of one second were used. Normally 3,000 to 10,000 scans were taken for a given sample. Spectra for samples in D_2O and DMF solutions were recorded at 80°C to 90°C.

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