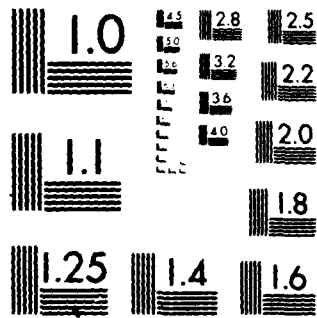


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6 CHEMICAL FACTORS IN THE DEGRADATION AND SELECTIVE DISSOLUTION OF METHACRYLATE-BASED ELECTRON BEAM RESIST POLYMERS: A NUCLEAR MAGNETIC RESONANCE AND ELECTRON SPIN RESONANCE STUDY.

10 BURKHARD E. WAGNER

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The dissolution of selected electron-beam resist polymers was studied by wide-line-NMR/Dynamic Nuclear Polarization signal enhancement techniques under experimentally restrictive conditions. It was demonstrated that $d^6$ -acetone is suitable for NMR-based dissolution studies, and that the amount of polymer required for a dissolution experiment can be reduced by a factor of ten (to 0.2 g) by selection of novel radical spin polarization materials. Studies of scarce experimental or irradiated polymers are now more feasible. -  (Cont'd on reverse side)		

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The beneficial effects of carboxylate- and halocarbon substituents on the dissolution properties of methacrylate resists were demonstrated. An attempt was made to investigate the effect of various parameters on dissolution properties in acetone slurry (irradiation, molecular weight, molecular weight distribution, polymer surface characteristics or morphology), but in the unstirred environment of the experimental set-up, dissolution properties consistently ran counter to those expected from dissolution theory for well-mixed systems. The existence of a gel barrier to dissolution was not only inferred from the dissolution experiments, but also could be confirmed visually in selected samples. The gel barrier phenomenon may affect dissolution behavior inside the freshly-cut channels of the resist, where convection would be least effective. In other dissolution experiments, it was demonstrated that the sensitivity of the instrumentation is not sufficient to make  $^{19}\text{F}$  NMR an acceptable alternative to  $^1\text{H}$ -NMR in dissolution studies of fluoropolymers. *J*

The feasibility of using UV-degradation as a chemically meaningful model for e-beam degradation is suggested. Experiments are relatively easy to perform, and degradation can be followed by electron spin resonance spectroscopy while degradation is occurring. Application to PMMA degradation was demonstrated, and a series of polymers was selected for future studies.

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## INTRODUCTION

The manufacture of integrated circuits is under intensive study at ERADCOM and in private industry. The delicate, micron and sub-micron sized circuit pathways required in future electronic systems are inscribed in the chip in a complicated, multi-step process. A polymer coating is applied over a Si/SiO<sub>2</sub> substrate, a circuit path is inscribed on the polymer (in next-generation methods either by an electron beam or x-rays), the irradiated section is dissolved away in a suitable solvent, and the exposed Si/SiO<sub>2</sub> surface is ready for the etching step, the next of many steps to come.

An electron-beam resist polymer must meet at least three unrelated requirements: 1) the polymer must be reasonably susceptible to radiation damage to permit sufficient writing speed, 2) irradiation must significantly alter the dissolution properties of the irradiated area (differential dissolution properties), 3) the residual protective polymer coating must not undergo structural deformation while the irradiated section is dissolving.

The purpose of this investigation was to develop nmr methods which would allow monitoring of polymer dissolution processes. The first objective was to determine differences in dissolution properties between the standard e-beam resist PMMA, and PMMA in which side groups were substituted by organic functionalities which are known to enhance the radiation degradation of PMMA.

The second objective was to improve dissolution study methods so that only 0.2 g polymer (rather than the previous 3.0 g) would be required. This would allow comparison of the dissolution properties of irradiated and un-irradiated polymers. (Many of the polymers being screened for e-beam resist application are custom synthesized, so that only small quantities are available.)

The third objective was the use of acetone as developer solvent. Previous work on polymer dissolution had utilized CCl<sub>4</sub>, and acetonitrile (CH<sub>3</sub>CN in CD<sub>3</sub>CN form). Since the tiny nmr signal due to dissolved polymer must be seen against the background of the nmr signal due to the solvent, it was not clear whether acetone (C<sub>3</sub>H<sub>6</sub>O) could be used, even in the 99% deuterated form (C<sub>3</sub>D<sub>6</sub>O).

Finally, the work was to provide sufficient familiarization with the 1980 polymer system to allow proposal of methods for determining elementary pathways of polymer degradation involving these chemically diverse systems.

## EXPERIMENTAL

The mainstay of these dissolution studies is wide-line nmr, in which signal intensity is enhanced by Dynamic Nuclear Polarization (DNP) techniques. The prime requirement for successful signal enhancement is the presence of a radical species which is highly efficient in causing spin transitions in the polymer. Unfortunately, few suitable radicals exist, and fewer have

acceptable solubility. During the past two years, several new radicals were screened and found suitable in various solvent systems.

For this work, use of the standard BDPA radical proved unsuitable. High saturation power (25w) was found necessary to give good signal intensity. At this power, heating of the nmr coil gave a time dependent signal intensity varying by ~ 50% (Figure 1). The radical  $\text{TTF}^+\text{BF}_4^-$ , which had been found to be optimal in acetonitrile studies, was insufficiently soluble in acetone.

Use of the new TCNQ radical anion was therefore attempted. The potassium salt proved insufficiently soluble, but the lithium salt proved to be highly effective. Only 8w power was required to give an nmr signal enhancement superior to that observed with BDPA. No coil heating effects were observed at 8w.

The rf saturation circuit had been fine-tuned before my arrival, so that the numerous tube failures experienced during my 1978 ADT were not repeated. The more desirable solid-state rf generator had been requisitioned, but had not yet arrived. The DNP equipment as a whole had not been used since January 1980 (lack of personnel), and one day's time was required to replace various defective components. More frequent use of the equipment would probably be helpful.

The samples were prepared via the technique developed during the 1978 ADT/Counterpart training assignment. The weighed polymer (0.2g) was degassed in the nmr tube, and the tube was repressurized with  $\text{N}_2$ . The solvent containing the required amount of radical was degassed in a separate schlenk tube by means of 3 freeze-pump-thaw cycles, and the tube was repressurized with  $\text{N}_2$ . The required amount of solvent (3ml) was withdrawn via a syringe, and added to the tube containing polymer. (As shown below, the method of addition proved crucial for obtaining a successful experiment.) Data collection (8 repetitive scans of 5 sec duration each) commenced immediately. About 1 point/min was obtained. Nmr conditions were optimized on a dissolved sample: best results were obtained using modulation amplitude 75.4 mv, feed-back 1.2v, time constant 30 msec, frequency 50 cps, phase 116. These conditions were quite distinct from S.O.P. for solution systems. The dissolution curve usually was linear with time for about 20 min, and then trailed off, as expected. Data evaluation and plotting were performed with a Tektronix 4052 minicomputer, and 4662 interactive plotter, using equipment at Rutgers University.

## RESULTS AND DISCUSSION

The dissolution curves in general were quite linear with little scatter, even when only 0.2g polymer were used. There was no induction period; therefore, gel formation within the polymer surface was minimal. This is a requirement for application of a polymer as electron-beam resist. Typical dissolution curves are shown in subsequent sections and the Appendix. The acetone-proton background signal was substantial, but signal-noise ratio was

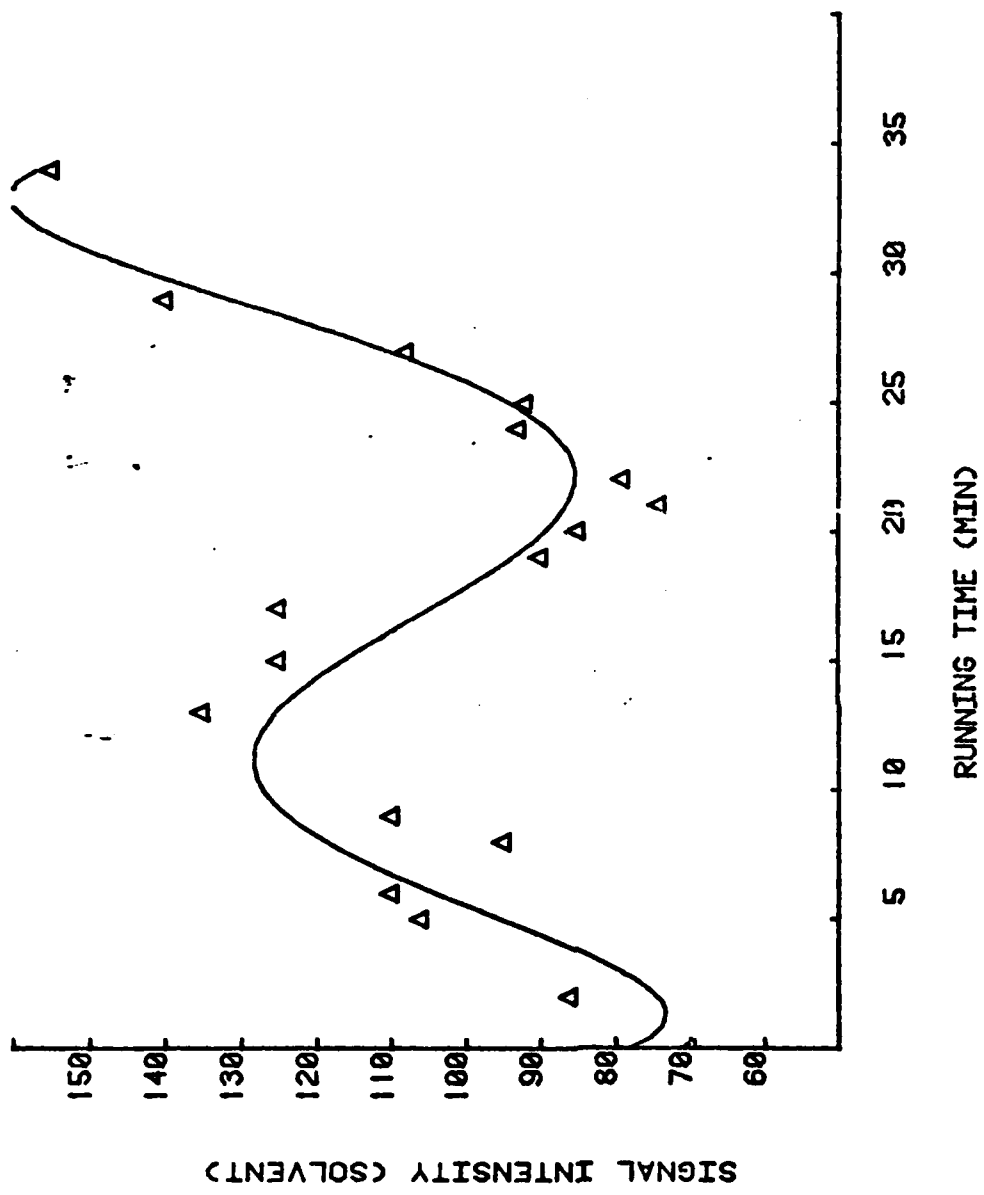
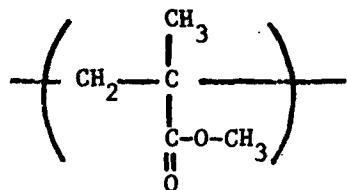


Figure 1. Effect of continuous 25W saturation power on signal intensity.

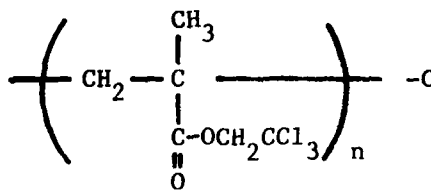
sufficient to permit detection of the signal intensity added by the polymer (5 units signal intensity for PMMA against a 40 unit background signal; 50 units of signal intensity for other systems against a 25-50 unit background)

Effect of substituents on PMMA

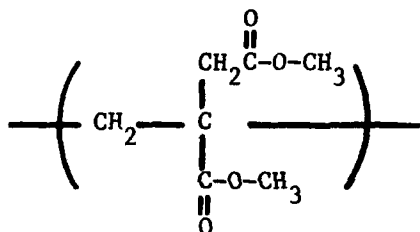
Three types of polymer were studied: PMMA, TRICE, and PDMI.



Polymethylmethacrylate  
PMMA  
Batch 2041



Polytrichloroethyl  
methacrylate  
TRICE



Polydimethylitaconate  
PDMI - Batch YJ011A

All three samples had comparable molecular weights, but differed in the substituent on the main chain.

A comparison of dissolution curves (Figures 2-4) reveals that TRICE and PDMI have comparable dissolution rates in acetone under equivalent experimental conditions, but dissolve about 8 times faster than unsubstituted PMMA (slope 1.6 vs 0.2). The presence of one floppy, polar side-chain (PDMI) is equivalent to that of two (TRICE) as far as dissolution is concerned. The results of Figures 2-4 demonstrate the feasibility of the polymer dissolution method, the use of small amounts of polymer, and the use of  $d^6$ -acetone solvent. However, further work within each of the polymer systems demonstrated that physical as well as chemical factors could influence polymer dissolution properties.

Dissolution of TRICE

We wished to determine the effect of irradiation on dissolution

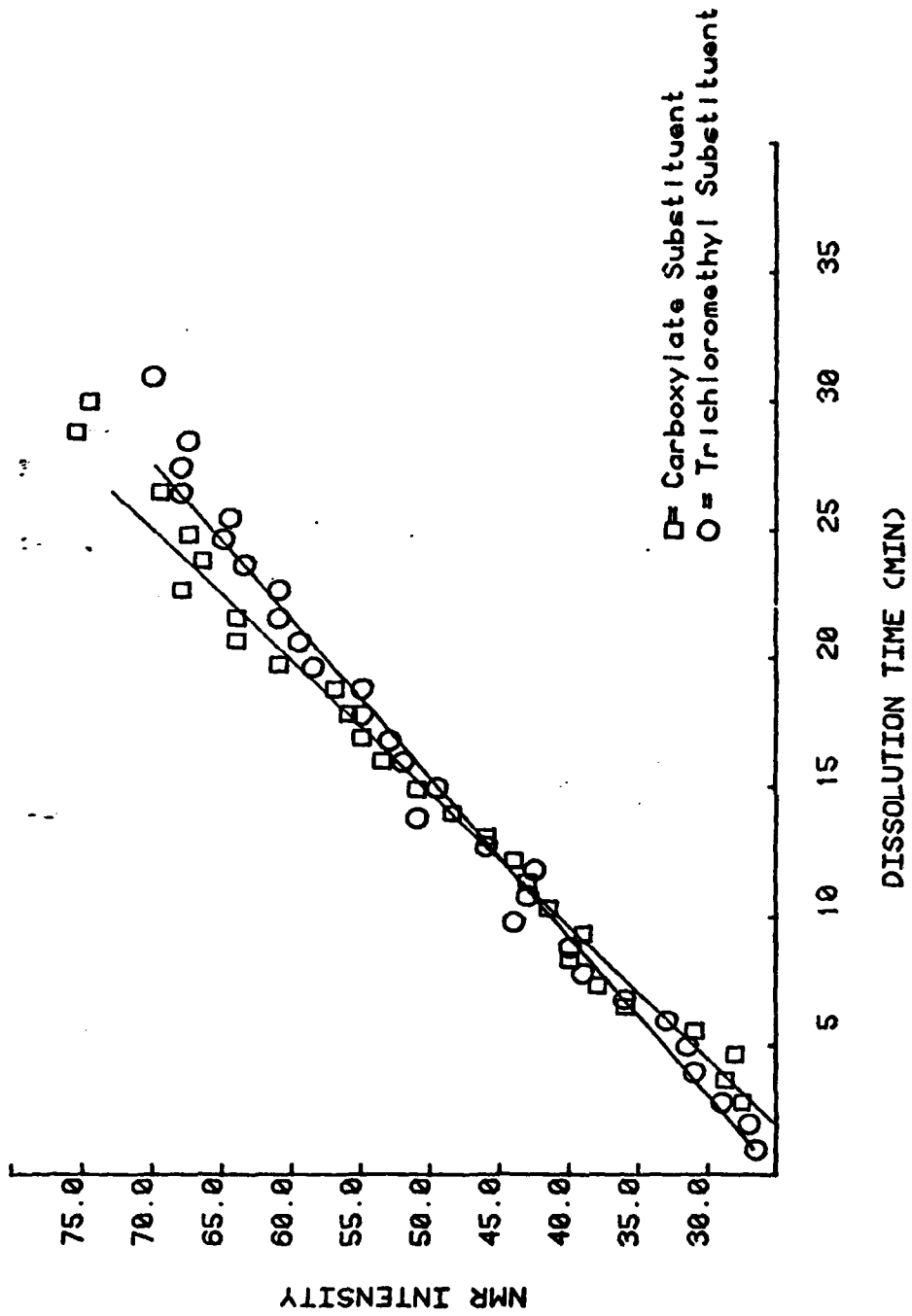


Figure 2. Effect of substituent type on PMMA dissolution in acetone.

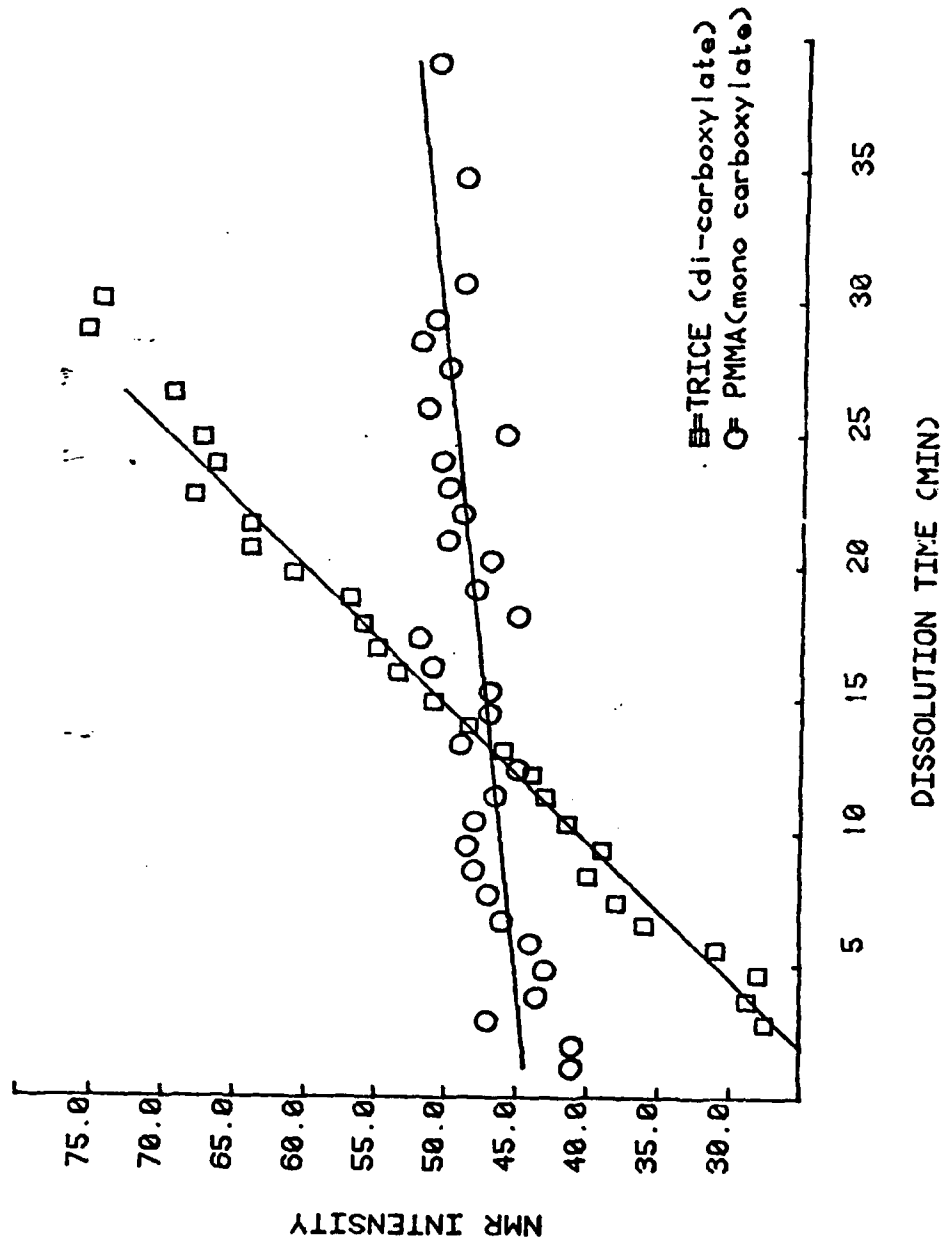


Figure 3. Effect of second carboxylate group on PMMA dissolution in acetone.

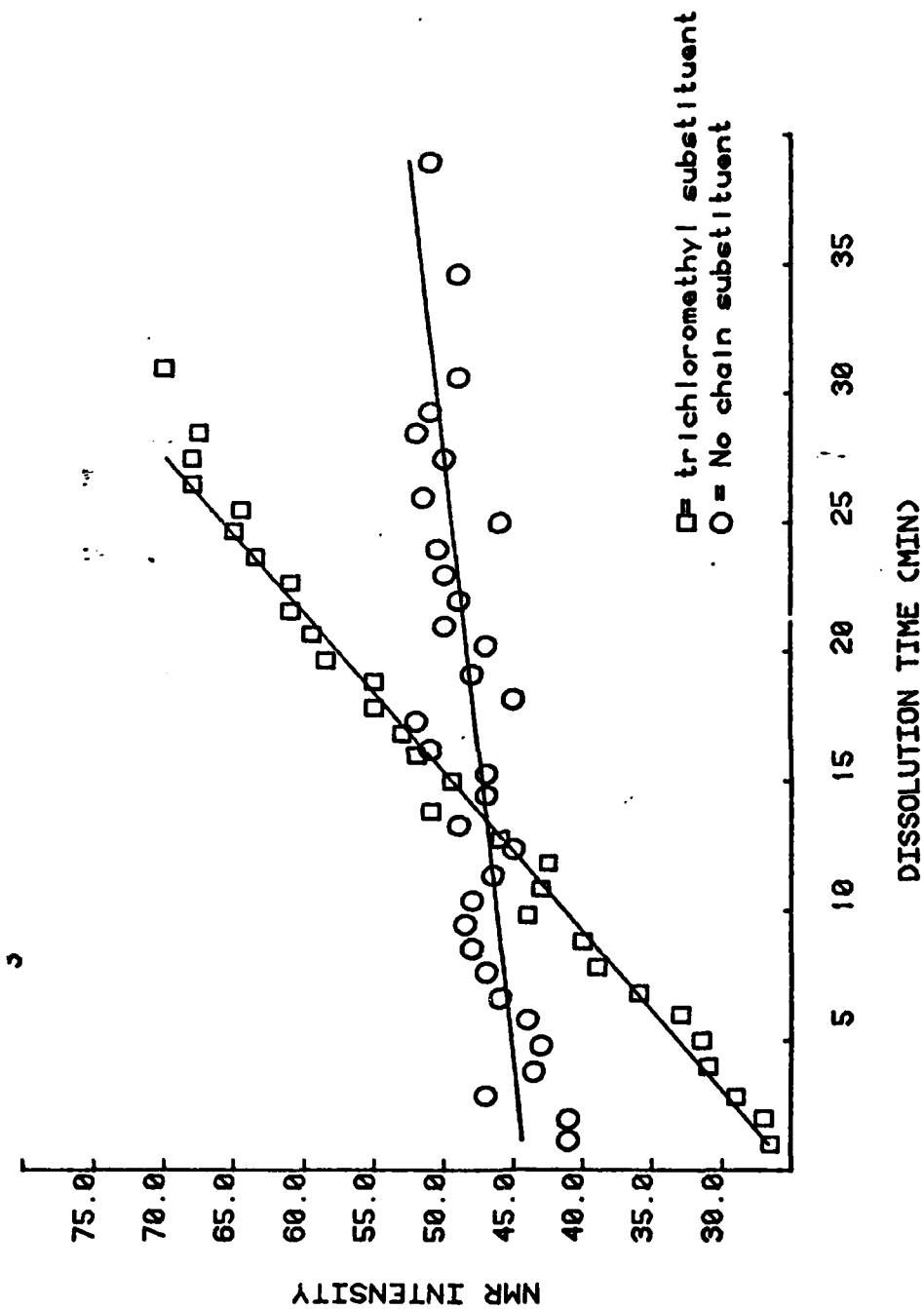


Figure 4. Effect of  $\text{CCl}_3$  group on PMMA dissolution in acetone.

properties of TRICE. When irradiated, polymer molecular weight decreases, and dissolution rates should increase. The dissolution of unirradiated as well as irradiated TRICE (1.13, 2.34, and 4.8 MRADS) was therefore investigated in acetone. The dissolution data are sufficiently linear over the first ten minutes dissolution time (linear correlation coefficient 0.99, 0.97, 0.92, 0.95) that the effect of irradiation should be discernible. (Figures A-1 - A-4, Appendix A). A fairly linear decrease in dissolution rates with increasing radiation dosage (decreasing molecular weight) is observed (Figure 5).

Unfortunately, this relationship between dissolution rate and polymer molecular weight runs counter to both dissolution theory and common sense. The explanation for the observed phenomenon was found when a layer of viscous sludge was observed to form around the dissolving polymer. This layer disappeared on shaking of the sample for a few minutes. Thus, the dissolution of polymer in the unstirred slurry is very much affected by diffusion effects. Certain combinations of solvents and polymers may give rise to a viscous layer of dissolved polymer which prevents access of fresh solvent to the polymer.

The above hypothesis received further experimental support in the following comparative experiment: A) 0.2g polymer particles were well dispersed (fluidized) in 3ml solvent (the needle of the syringe containing 3ml solvent was embedded in the polymer bed, and the plunger was depressed rapidly to fluidize the polymer in the emerging solvent). The dissolution curve was run, and was found to be normal. B) 3ml solvent was added on top of the polymer bed without shaking (careful dribbling of solvent over the bed of polymer without shaking). The dissolution curve of this mixture was run as well. As shown in Figure 6, there is a dramatic difference in dissolution rates between these two chemically identical samples. The dissolution which occurred in the first few minutes in the system containing settled polymer sets up a concentration layer which retards further dissolution. The apparent decrease in polymer dissolution rates with decreased molecular weight is attributed to more efficient gel formation at lower molecular weights.

#### Dissolution of PDMI

Based on the observations with TRICE, factors affecting diffusion were investigated. These were polymer morphology (powder vs high surface area pellets), polymer molecular weight distribution ( $M_w/M_n$ ) at constant  $M_w$ , and effect of irradiation.

Sample reproducibility was investigated first. Two batches of pelletized materials were run on successive days ("new acetone" vs "old acetone"). Moderate differences in dissolution rates and in extent of dissolution linearity were observed (Figure 7).

Differences in dissolution rates due to differences in polymer morphology were examined next. Small pellets of PDMI dissolved slightly



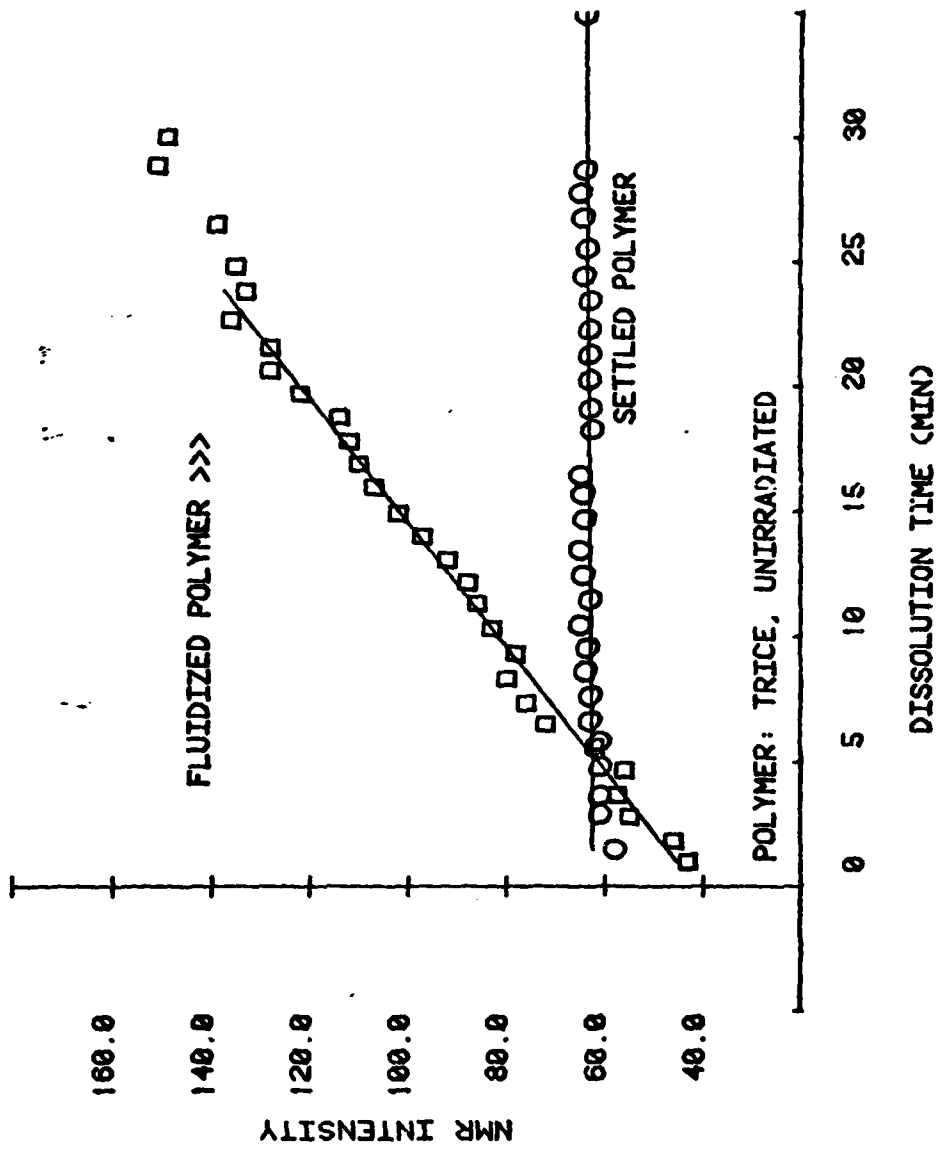


Figure 6. Effect of initial dispersal of polymer on dissolution.

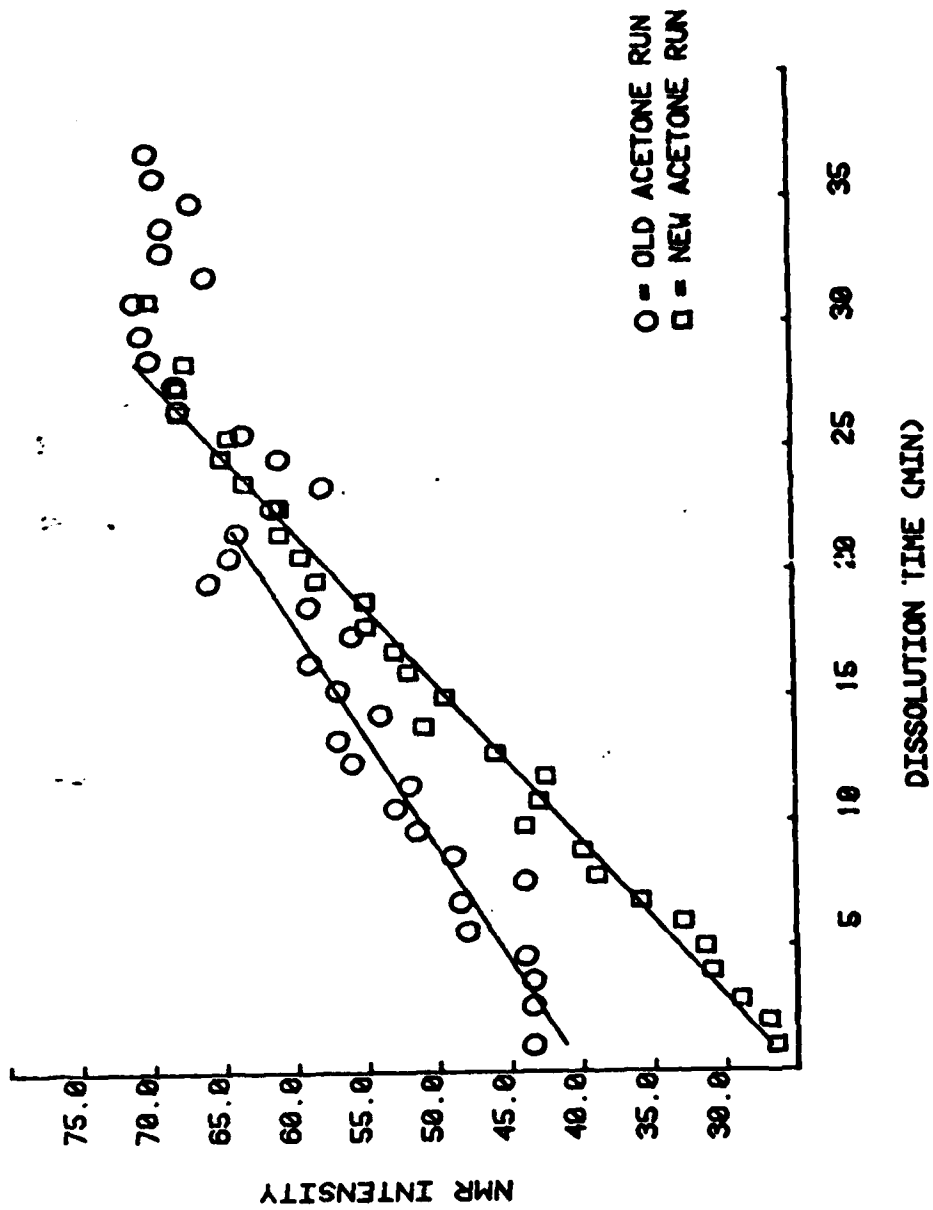


Figure 7. Reproducibility of PMI (YJ011A) dissolution: new vs. old acetone.

faster than ground powder, and gave more linear dissolution curves besides (Figure 8). The granular material would be expected to allow more diffusion of solvent and, therefore, more even dissolution. However, the difference in dissolution rates is not dramatic.

The dissolution of irradiated PDMI (0.96 MRADS,  $M_w = 366,000$ ) was compared to that of unirradiated PDMI (0 MRADS,  $M_w = 642,000$ ). Again, the unirradiated polymer exhibits the higher dissolution rate when the dissolution is studied in unstirred systems (Figure 9). In a well-stirred environment, the irradiated polymer would be expected to dissolve at  $1\frac{1}{2}$  to 2 times the rate of the unirradiated sample.

Two batches of PDMI differing in the width of their molecular weight distribution (MWD), but not in weight-average molecular weight, were examined. Sample PDMI (YJ011A) has a broader MWD ( $M_w/M_n = 2.5$ ) than sample PDMI (PjWLA) ( $M_w/M_n = 1.3$ ). Due to the closeness in weight-average molecular weight ( $M_w$  650,000), and due to the fact that the samples are chemically identical, similar dissolution rates should be expected. As shown in Figure 10, the dissolution rates differ by about 20%, with the narrower MWD material having the higher dissolution rate.

It is not clear whether the 20% difference in dissolution rate is significant enough to merit discussion. It is interesting to note that the PDMI sample with broader molecular weight distribution has the lower dissolution rate. That material has more of the low molecular weight components, which in all the relevant previous examples had given rise to depressed dissolution rates due to gel formation. Therefore, the results in Figure 10 conform to the pattern observed in previous samples.

#### Implication of the Gel Barrier Effect on Device Manufacture

In four out of four cases, it was observed that irradiated polymers with decreased molecular weights gave lower dissolution rates than found for the parent material. These effects were noted when the dissolution study was carried out in quiescent, convection-free polymer/liquid slurries. It is not clear whether the observed phenomenon plays any role in the selective dissolution of e-beam-degraded polymer during the manufacture of an integrated circuit chip. If the solvent is well agitated during the dissolution process, and flows smoothly over the surface of the chip, then a barrier of viscous gel should not be formed. It is not clear whether movement of solvent in the bulk of the solution must also imply free movement of solvent within the crevasses of the polymer layer where dissolution is occurring at the fastest rate (= the irradiated section). A decreased rate of polymer degradation below the expected value is not necessarily undesirable. One of the areas of concern in polymer resist dissolution is penetration of solvent now residing in the freshly cut channels into the undesirable region under the layer of unirradiated polymer, giving rise to undercutting of the protective polymer coating. (Figure 11) The formation of a gel barrier would decrease the undercutting effect, since it would be precisely in the crevasses that solvent motion would be minimal, and a gel barrier could build up.

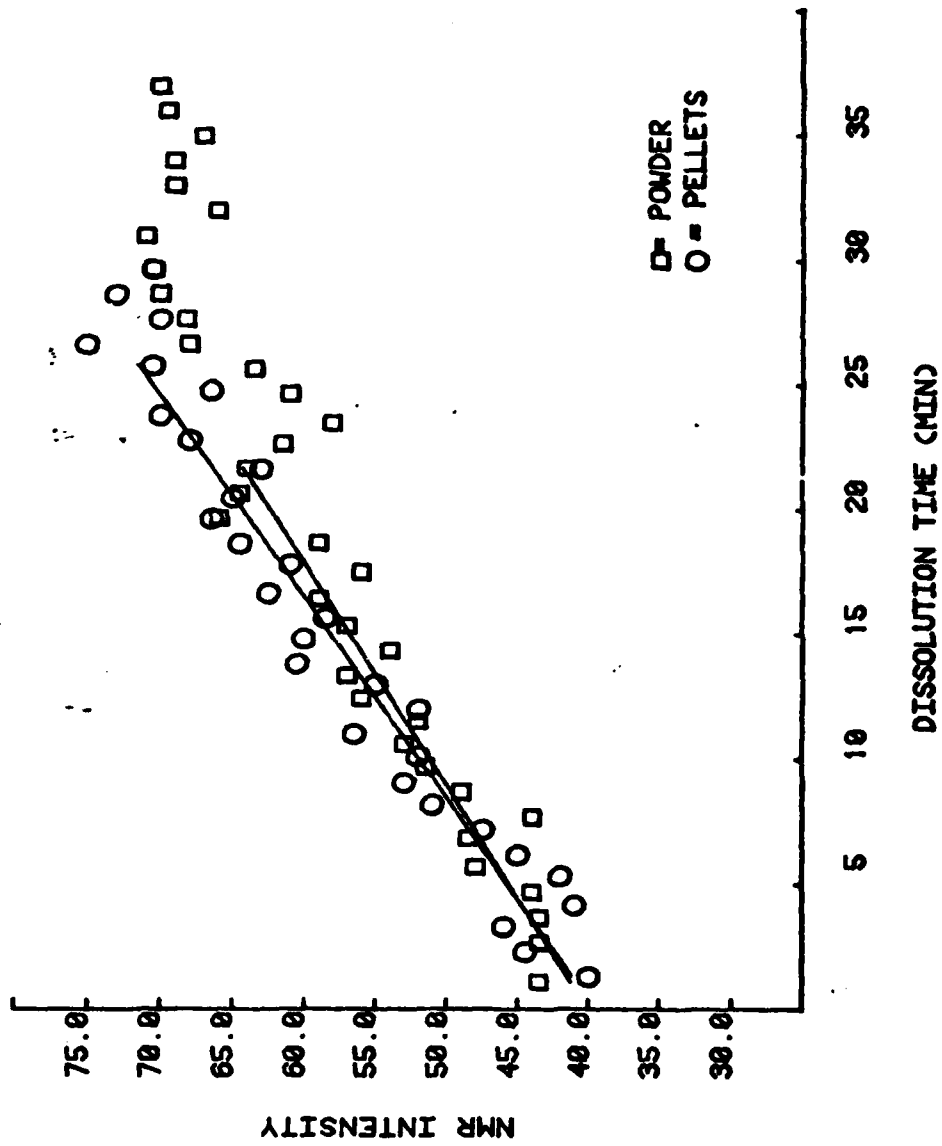
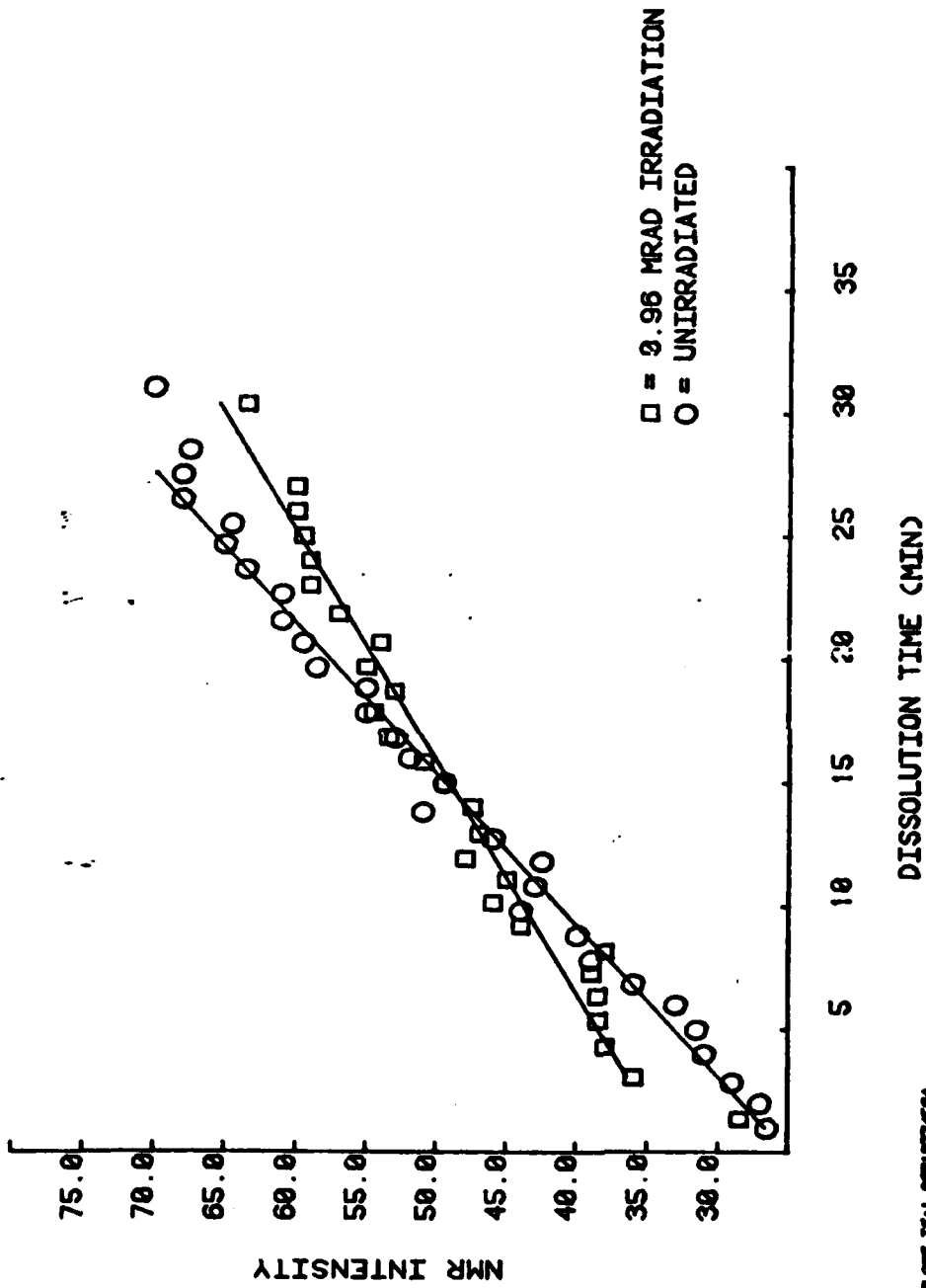


Figure 8. Effect of YJ011A morphology on dissolution rate.



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Figure 9. Effect of 0.96 MRAD irradiation on YJ011A dissolution rate.

EFFECT OF PDMI MOLECULAR WEIGHT DISTRIBUTION ON DISSOLUTION RATE

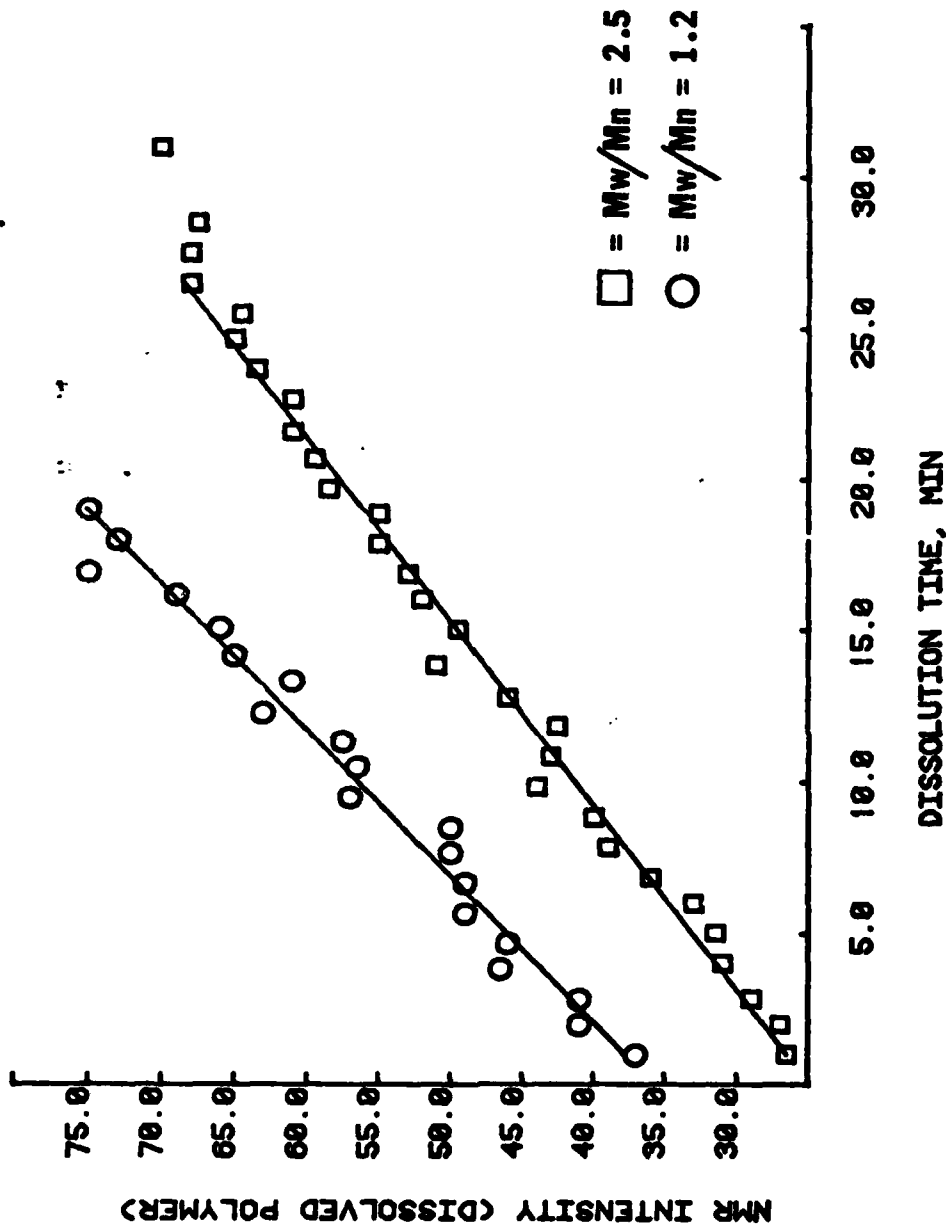


Figure 10. Effect of PDMI molecular weight distribution on dissolution rate.

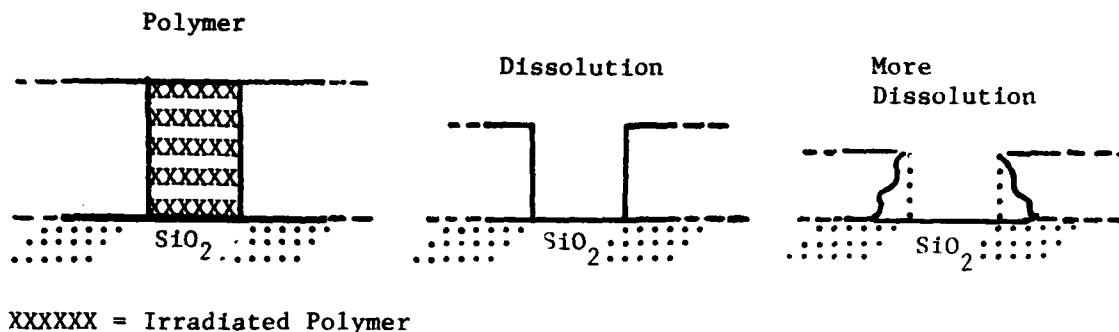


Figure 11. Undercutting during polymer dissolution.

#### Other Dissolution Studies

Several of the experimental polymers contain fluorocarbon substituents whose  $^{19}\text{F}$  nmr signal could be used to monitor dissolution. A comparison between BDPA radical (the previous champion) and  $\text{Li}^+$  TCNQ established that the latter gave rise to a 30% larger  $^{19}\text{F}$  nmr signal enhancement than the former. Nevertheless, we were not able to observe  $^{19}\text{F}$  nmr signals during the early stages of dissolution of poly(hexafluoroisopropyl-methacrylate-co-methyl methacrylate) within the 40 sec signal acquisition time required for this work. A  $^{19}\text{F}$  signal was seen only for the fully dissolved polymer (0.2g) using 80 sec signal acquisition time. It would have been beneficial to use  $^{19}\text{F}$  nmr to follow polymer dissolution, since the standard polymer solvents do not contain fluorine, and so could not give rise to a large  $^{19}\text{F}$  NMR background signal.

During the last two days of ADT, some of the polymer dissolution studies were repeated using halocarbon solvents ( $\text{CCl}_4$  or  $d^1\text{-CCl}_3\text{H}$ ) in order to establish the effect of solvent composition on gel barrier formation. Attempts to utilize TCNQ as radical failed due to low solubility. Dissolution experiments using BDPA radical proved more successful, although nmr signal enhancements were reduced considerably over those observed in acetone/TCNQ $^-$ . The signal:noise ratio was considerably worse, and irregularities in signal size due to coil-heating were observed (see Experimental Section). Polymer solubility in all cases was much lower than in acetone (Figures A-5 - A-6, Appendix A). Therefore, dissolution experiments would have to have been followed for considerably longer periods than were feasible. Nevertheless, it did appear that gel barrier formation was less extensive than in acetone. Confirmatory work will be required.

## CONCLUSIONS AND RECOMMENDATIONS

### Polymer Dissolution Studies

- 1) The experimental conditions used in these experiments did indeed prove restrictive, but did not prevent dissolution studies.
- 2) The formation of a gel barrier in convection-free zones of a resist undergoing selective dissolution may counteract the innate dissolution properties of e-beam resist polymers, and may lead to unanticipated dissolution patterns.
- 3) If the aim of a dissolution study is the comparative characterization of polymers (molecular weight, molecular weight distribution, effect of substituents, effect of varying copolymerization, effect of irradiation), then these studies should be conducted in solvents not conducive to gel formation. The utility of the solvent for e-beam resist applications is not relevant in this type of study.
- 4) The experiments outlined in this section of the report were made possible by the availability of radicals highly sensitive to rf saturation. Work should continue to improve the solubility characteristics of the radicals by use of appropriate substituents and/or anions.
- 5) While considerable work has been done to upgrade the performance characteristics and sensitivity of the instrumentation, further improvements (solid-state rf generator, rewound copper coil) would improve system sensitivity by perhaps another factor of two.
- 6) A silicon chip with thin PMMA coating was crushed to give a powder suitable for degradation studies. It would be highly worthwhile to run the dissolution experiment on this material as a feasibility study. Time ran out before the experiment could be attempted.
- 7) A screening of a cross section of the many types of e-beam resist materials being sent to ERADCOM would allow a correlation of chemical structure with dissolution properties, as shown in Figures 2-4 for the investigated isolated examples. An increase in staffing would be required to perform these dissolution studies on an in-house basis.

### Degradation of Electron-Beam Resist Materials

Current work in the industry focuses on preparation of substituted methacrylates or copolymers of various methacrylate species. Much success was achieved at ERADCOM in the mid-seventies by using  $\gamma$ -irradiation as a model for electron beam irradiation, and by causing polymer degradation at 77°K (where molecular rearrangements are precluded) and letting the samples warm up to room temperature. During this period, the radical rearranges, gives cross-linking, or gives more chain scission, depending on the exact chemical composition of the sample.

During the course of this training period it was concluded that UV-light degradation could be employed as a method of causing radical formation at 77°K. A rough correlation between electron-beam degradation and UV-degradation can be expected, but this is only a bonus. The real importance of UV-degradation is that subsequent radical rearrangement, cross-linking, and chain-scission processes should depend mainly on the structure of the polymer, and only peripherally on whether the original radiation damage was caused by  $\gamma$ , B- or UV irradiation.

Experimentally, UV-irradiations are much easier and faster to perform than B or  $\gamma$ -irradiation. The polymer degradation can be carried out inside the spectrometer, and even the irradiation experiment, as well as the subsequent radical decay, can be observed. The b- and  $\gamma$ -degradations need to be conducted in shielded reactors.

As a feasibility study, the UV-degradation of PMMA was conducted at Rutgers University, and studied inside the esr spectrometer. The degradation curve (Figure 12) has a linear slope and later tails off on further irradiation, just like the  $\gamma$ -degradation curve. The esr spectrum of the radical is fairly well resolved after only 19 min of irradiation (Figure 13). The spectrum shows a variety of radicals (R-CH<sub>2</sub>. main chain scission: triplet with 20G splitting;  $\overset{\cdot}{\underset{H}{C}}$  - structure with >100G splitting). Further irradiation would have increased the intensity of the spectrum, and would have permitted the morning study under controlled temperature conditions.

#### Polymer Resist UV-Degradation

- 1) UV-irradiation of the PMMA e-beam resist gives rise to degradation whose kinetics can be followed easily, and where radical structures can be determined as the experiment progresses.
- 2) The types of radicals formed on UV-degradation of PMMA, and the kinetic curve, appear to parallel the degradation processes observed on e-beam degradation.
- 3) The UV-degradation experiments can be performed at Rutgers University. They can also be performed at Fort Monmouth with some minor changes in experimental procedures, if the ERADCOM esr machine can be freed for these studies, and if manpower is available.
- 4) To test out the feasibility of UV-degradation studies using technologically relevant e-beam resist materials, the comparative study of the following polymers is suggested to determine relative radical formation processes, radical stability, and radical rearrangement processes:

UV-DEGRADATION RATE OF 2041 PMMA

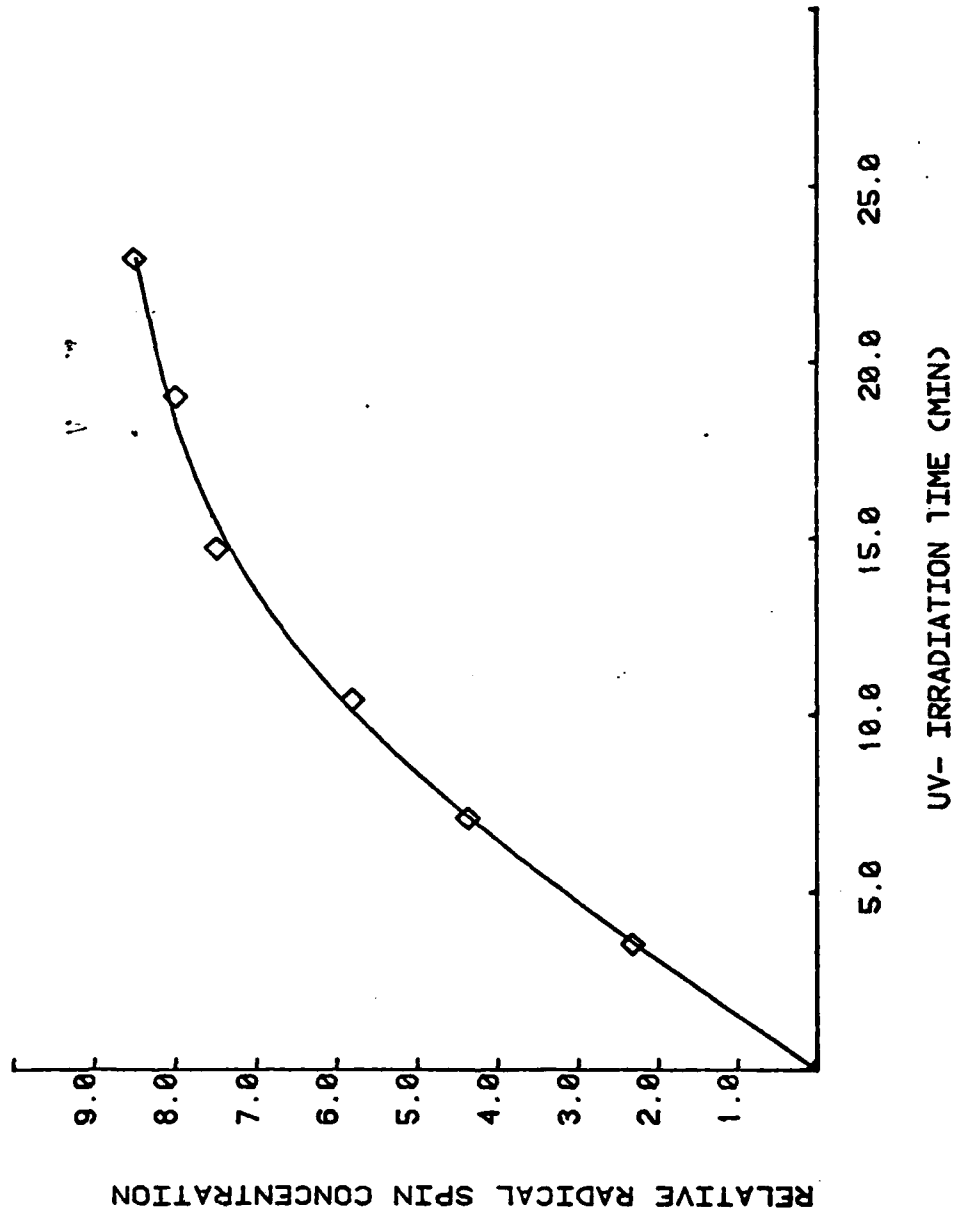


Figure 12. UV-degradation rate of 2041 PMMA.

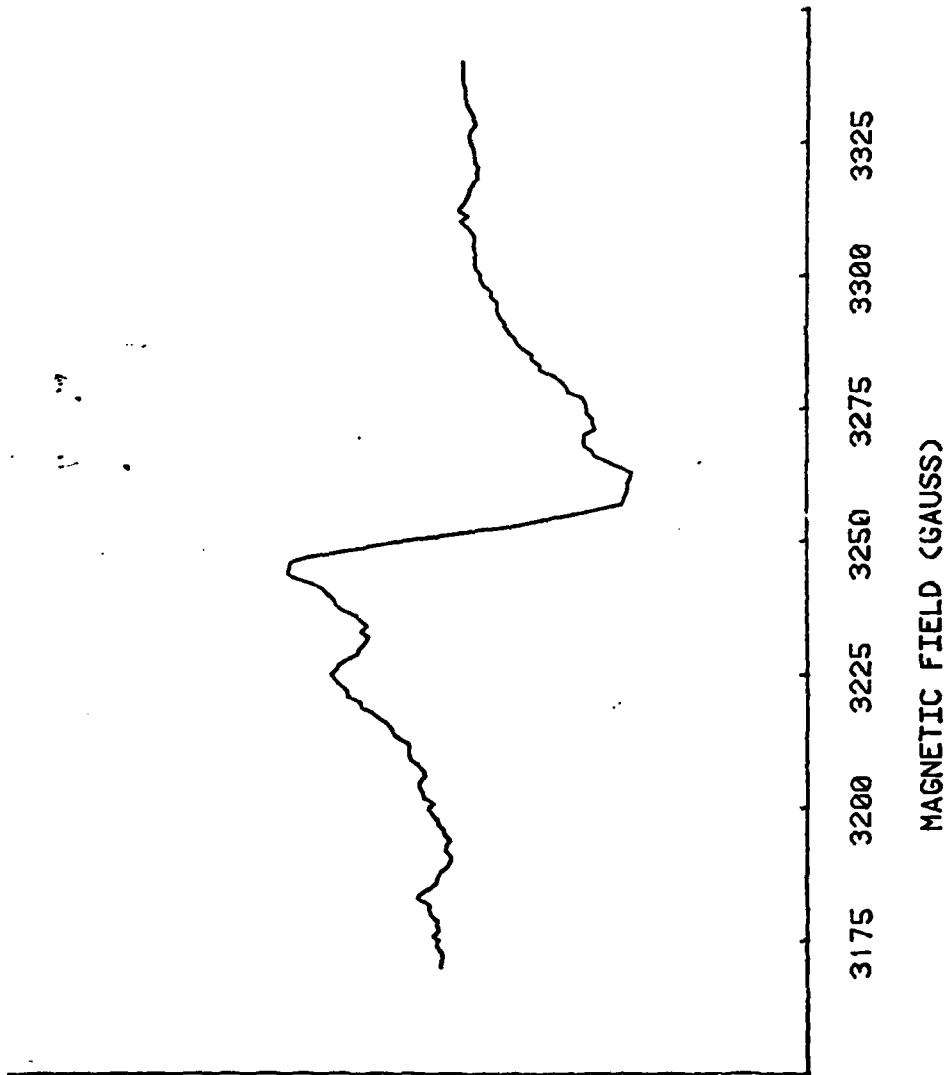
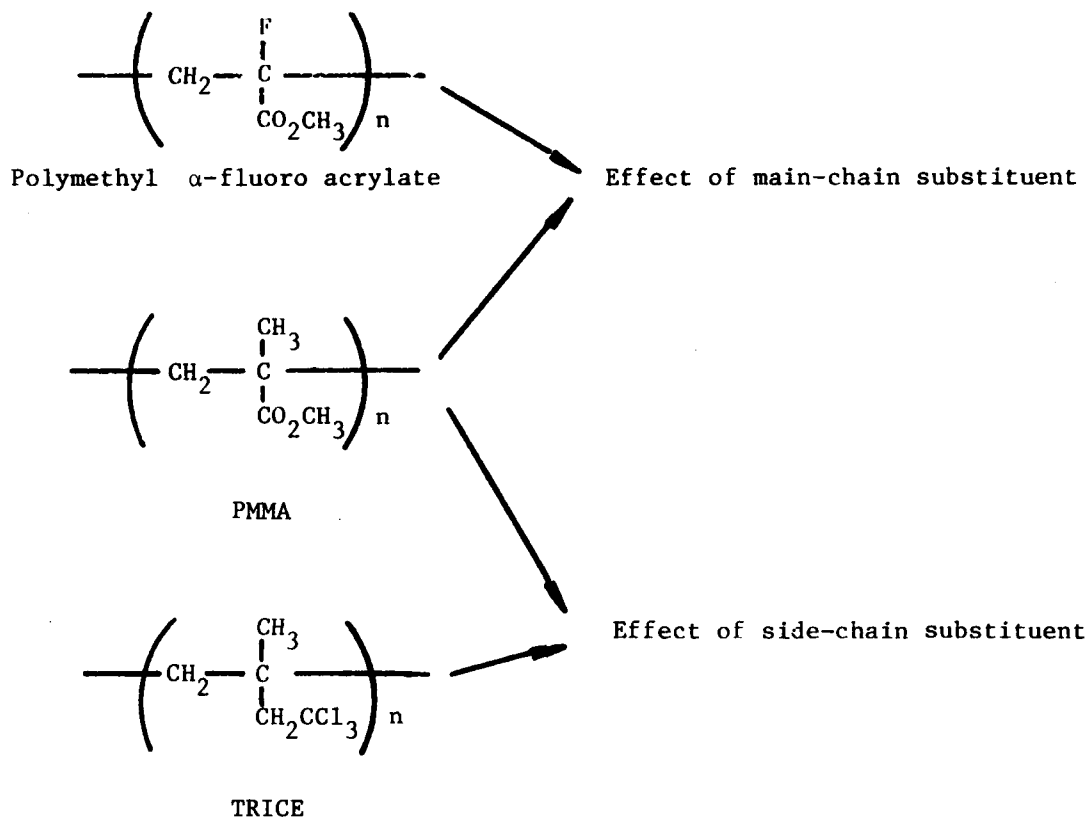


Figure 13. UV- IRRAD PMMA 7/17/18/19 min.



- 5) To study the effect of polymer heterogeneity, and the effect of cross-radical reactions, copolymers of trifluoromethyl methyl methacrylate (100-n%) with methylmethacrylate (n%); ( $0 \leq n \leq 100$  in 20% stages) could be degraded. Due to the large esr splitting expected in fluoropolymers, the relative contributions of the two components can probably be disentangled. Nitrogen-containing polymer fractions also give rise to characteristic esr signals.
- 6) Finally, a systematic basic research program on chemical effects in polymer degradation and polymer dissolution should be carried out.

Polymers required for these studies already seem to be available (or will be available shortly) as a result of outside research contracts. Again, staffing limitations may prevent the performance of these studies.

#### ACKNOWLEDGEMENTS

The author would like to express his deep appreciation for the faithful experimental assistance of Mr. A. J. Montedoro, the technical advice of Mr. J. Kwiatkowski, and the general guidelines for this project delineated by Dr. E. H. Poindexter. The hospitality of the ET&D Laboratory personnel in general is also appreciated.

APPENDIX A  
Polymer Dissolution Plots

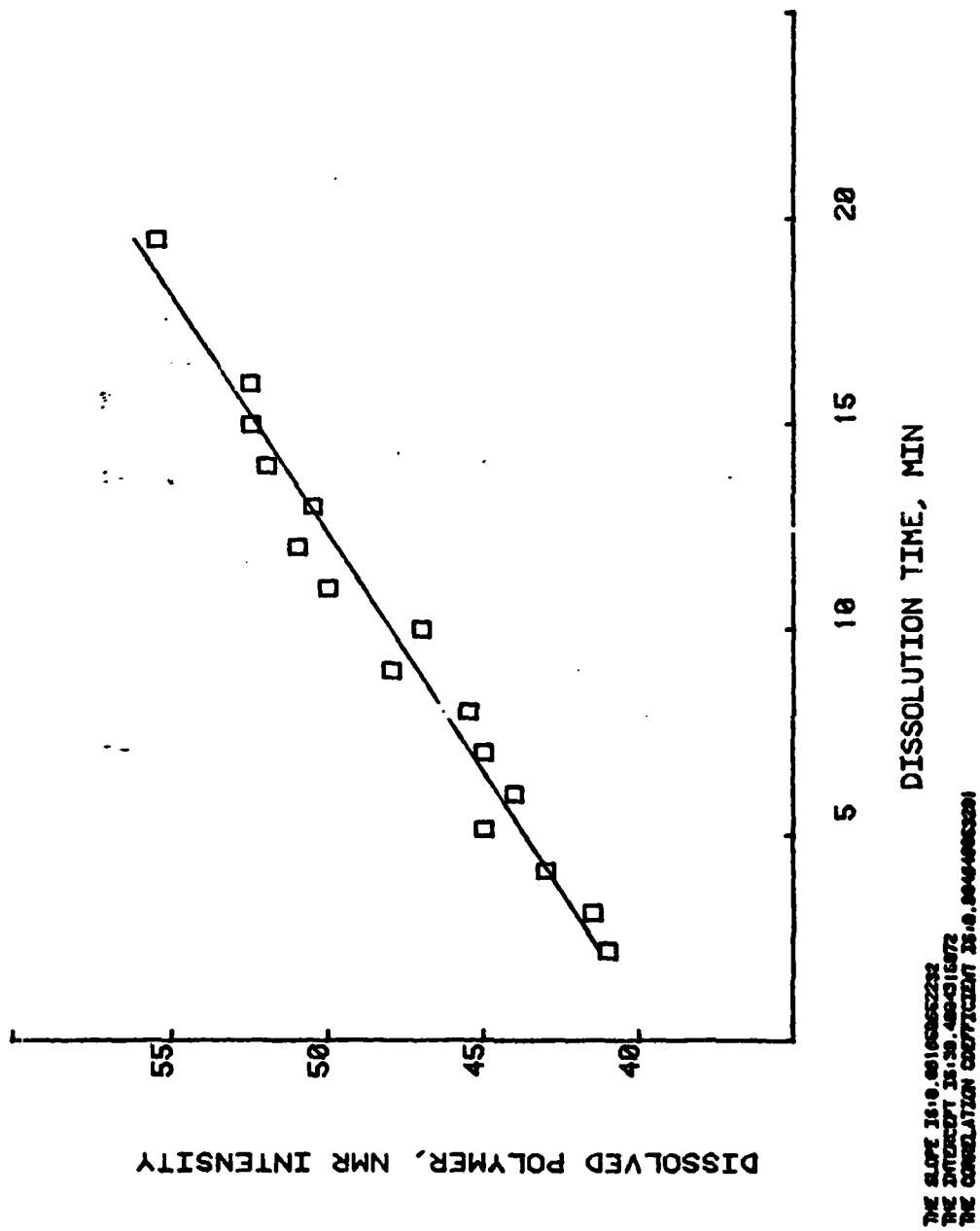


Figure A-1. Dissolution rate of TRICE, unirradiated.

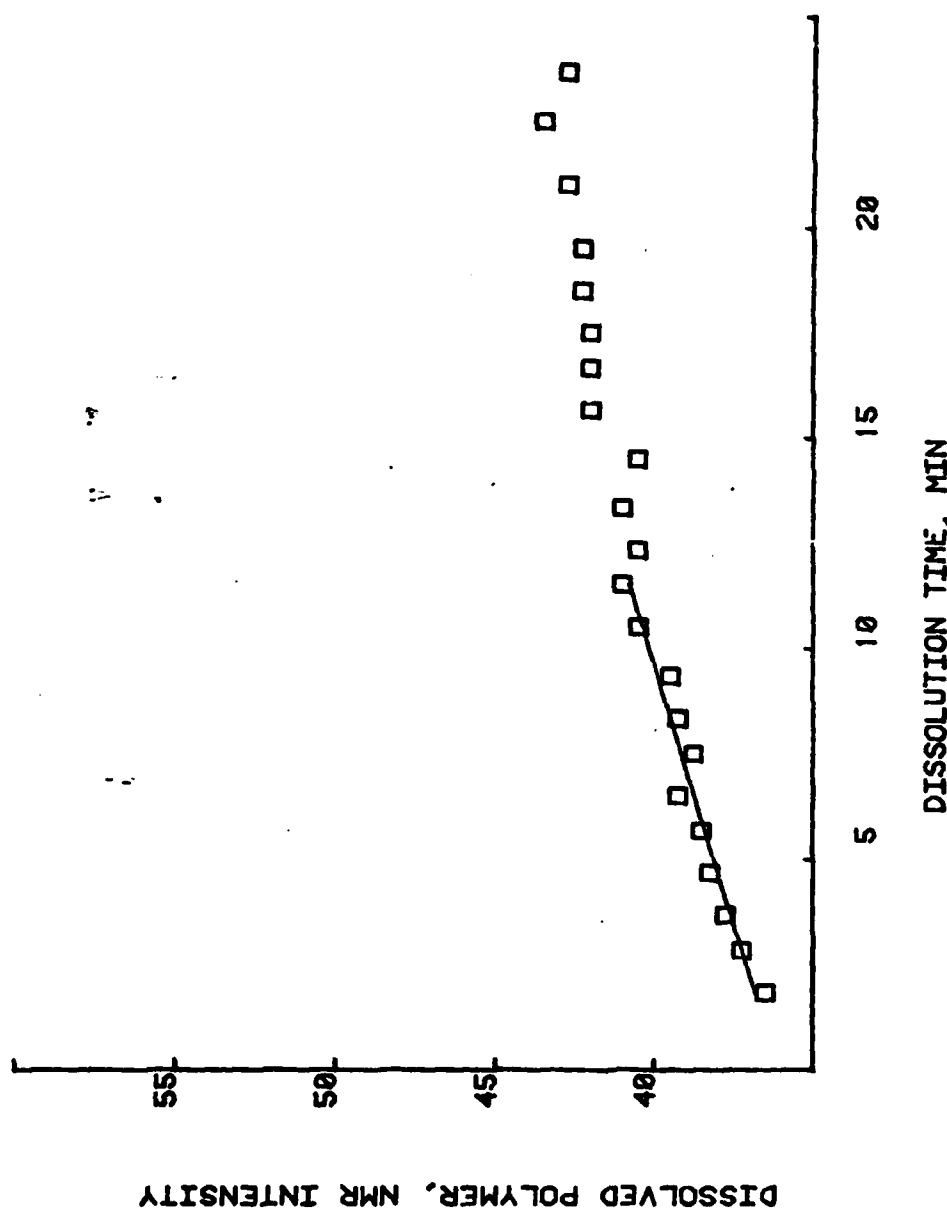
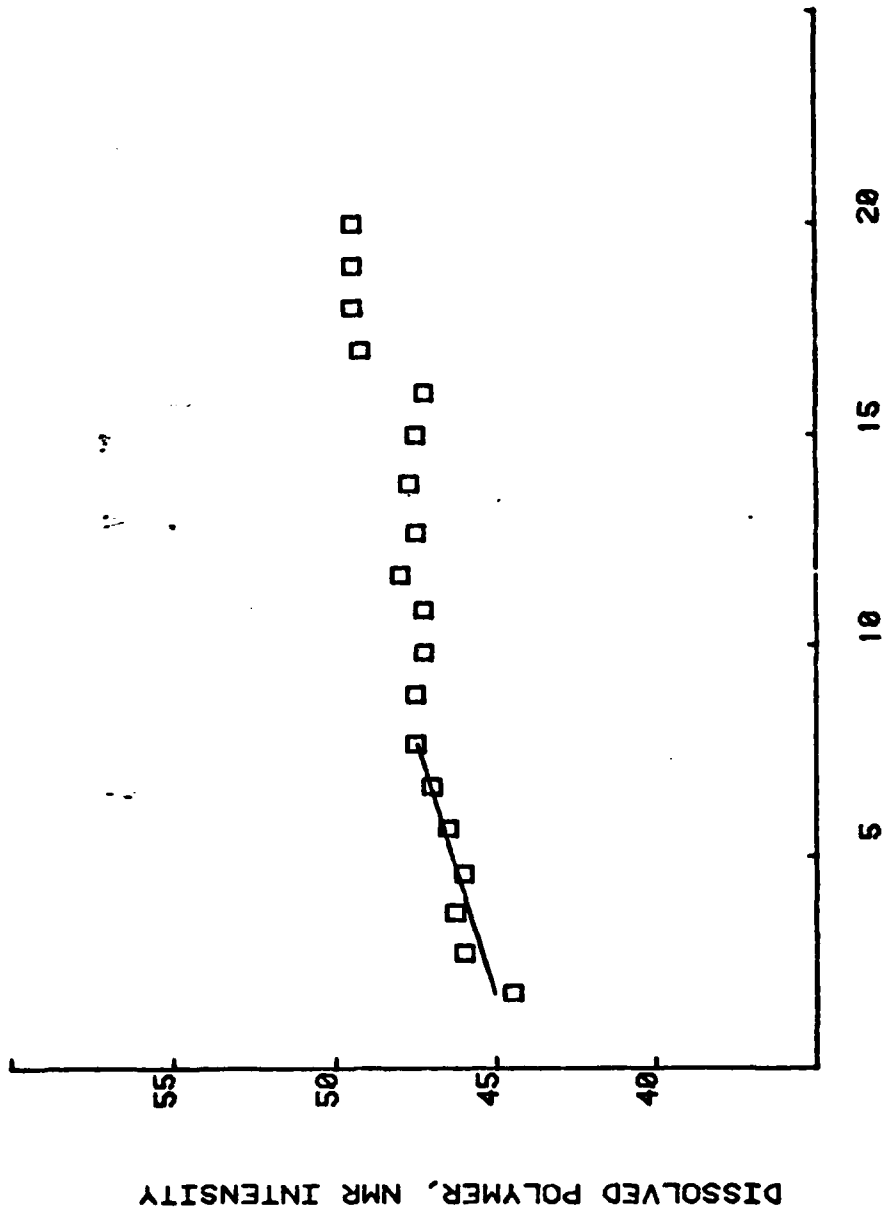


Figure A-2. Dissolution rate of TRICE, 1.13 MRAD irradiation.



DISSOLUTION TIME, MIN

THE SLOPE IS 0.487542811001  
 THE INTERCEPT IS 44.3421807234  
 THE CORRELATION COEFFICIENT IS 0.912802897828

Figure A-3. Dissolution rate of TRICE, 2.34 MRAD irradiation.

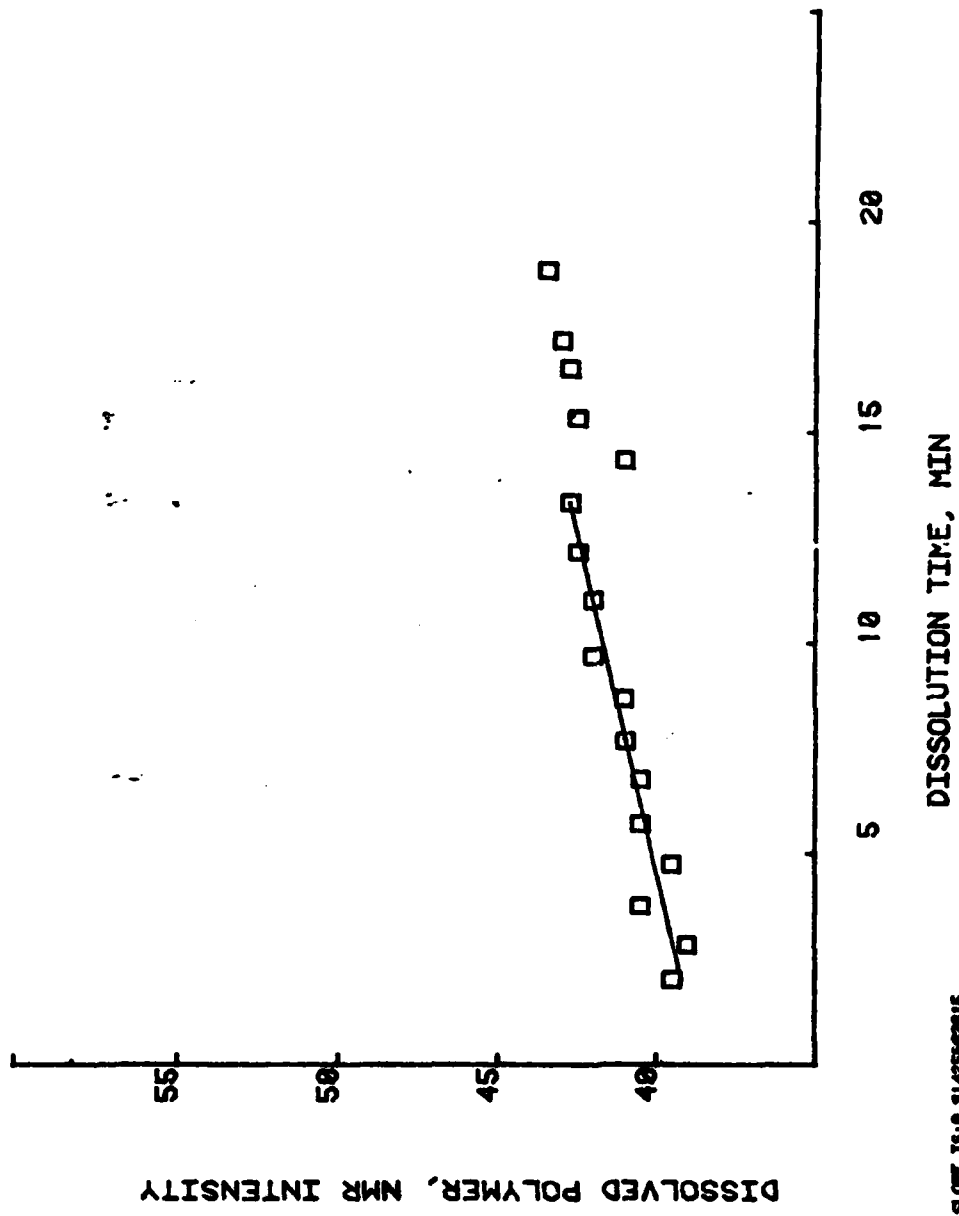
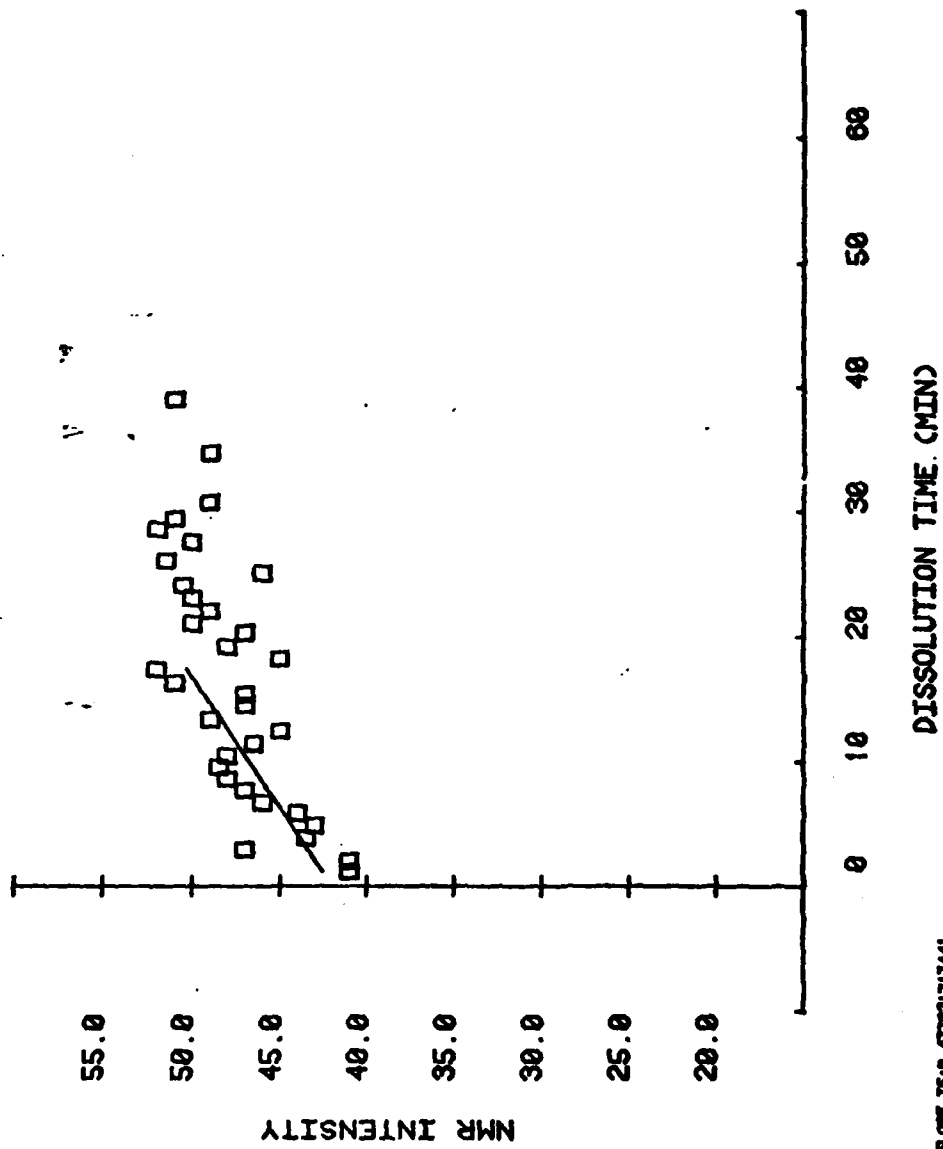


Figure A-4. Dissolution rate of TRICE, 4.8 MRAD irradiation.



THE SLOPE IS 0.47702171741  
 THE INTERCEPT IS 40.0000000000  
 THE CORRELATION COEFFICIENT IS 0.9999999999

Figure A-5. 2010 PMMA new ACE., 7/15.

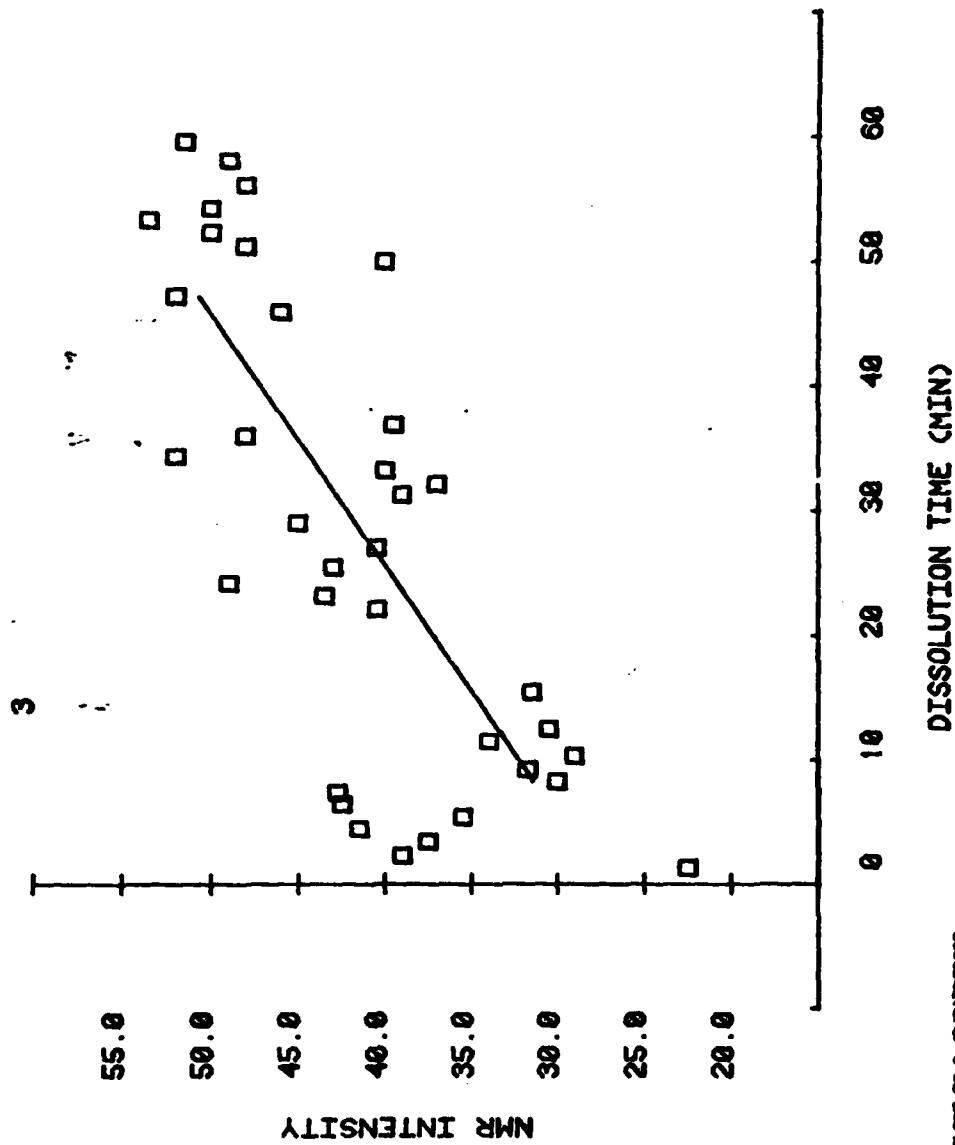


Figure A-6. PMMA 2041/CCl<sub>3</sub>D/0.1 SENS/2x MULT. 7/16.

APPENDIX B  
NMR Signals from Dissolution of TRICE

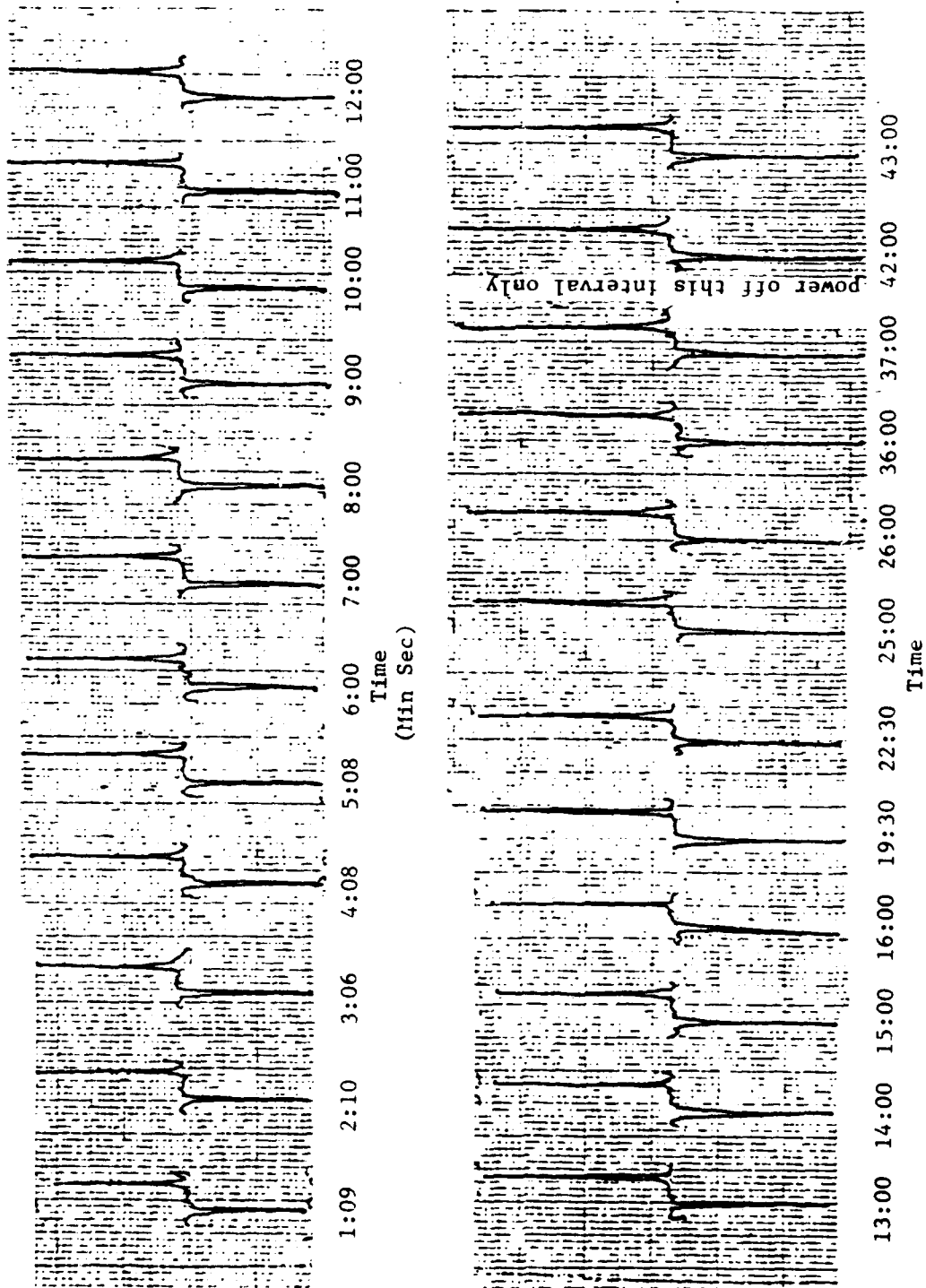


Figure B-1. Dissolution of TRICE, 190 mg in 3cm<sup>3</sup> acetone-d<sub>6</sub>, powder spectrometer conditions: H<sub>1e</sub> 8w, sens 0.5, mod 50 Hz, 75.4 mA.

