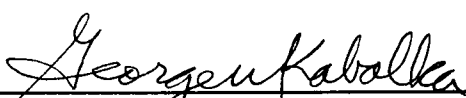
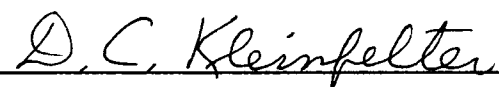


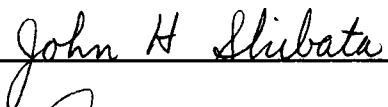
To the Graduate Council:

I am submitting herewith a dissertation written by Elizabeth M. Zippi entitled "Polymer-Based Substrates for Potential Generation of Nitrogen-13 for Positron Emission Tomography." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


George W. Kabalka, Major Professor

We have read this dissertation
and recommend its acceptance:


D. C. Kleinfelter


John H. Shubata


John R. Kennedy

Accepted for the Council:


Vice Provost
and Dean of The Graduate School

POLYMER-BASED SUBSTRATES FOR POTENTIAL GENERATION OF
NITROGEN-13 FOR POSITRON EMISSION TOMOGRAPHY

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Elizabeth M. Zippi

May 1991

DEDICATION

To Mom and Dad,
David, Marisa and Pierre,
and Jerry

ACKNOWLEDGEMENTS

The author wishes to thank Professor Dr. George W. Kabalka for his advise and support during the course of this work. The author would, also, like to express her appreciation to Dr. Ronald Nutt, Vice President for Research and Development, CTI PET Systems, Inc., Bruce W. Wieland, and the staff at CTI Cyclotron Systems, Inc. for the opportunity to perform research at their facility in Berkeley, California. A warm and special thanks is extended to Dr. Gerald T. Bida for his advice, generous help, and friendship.

The author, also, wishes to thank Professor Dr. Spiro D. Alexandratos for his advice on Polymer Chemistry, Professor Dr. Henry Rapoport for providing the author with the opportunity to study at the University of California, Berkeley as a Visiting Scholar, Dr. N. Satyamurthy for the use of the CS-22 Cyclotron at UCLA, Dr. G. Bhat for his assistance with Thermal Gravimetric Analysis, and Mr. Dick Williams for his guidance with Scanning Electron Microscopy.

Finally, the author would like to express her appreciation to her colleagues, especially to Mr. James F. Green for his help during the formative years of the author's graduate studies, and Mrs. Patricia J. Kreke for her assistance with the molecular structures in this document.

ABSTRACT

Nitrogen-13 is a medically useful positron-emitting isotope with applications in Positron Emission Tomography (PET). Target materials currently available for the production of nitrogen-13 possess a number of deficiencies. New polymer-based materials are being evaluated in an effort to improve nitrogen-13 production on medical cyclotrons. A series of microscopic, spherical poly(styrene/divinylbenzene) derivatives have been synthesized via suspension polymerization and then pyrolyzed to form carbonized beads.

Deuteron irradiation studies have been conducted at UCLA using a 22 MeV multi-particle cyclotron on pyrolyzed particles that possess the desired properties (e.g., size, shape, overall yield) . The stability of the beads upon irradiation, and the yields of nitrogen-13 at end of bombardment (EOB) as well as the purity of nitrogen-13 labelled ammonia were investigated.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.....	1
A. Background.....	1
B. Statement of Problem.....	16
II. DEVELOPMENT OF POLYMERIZATION METHOD.....	19
A. Introduction.....	19
B. Experimental.....	21
1. General.....	21
2. Poly(Styrene/2% Divinylbenzene) via Sonication.....	23
3. Poly(Styrene/15% Divinylbenzene) via Suspension Polymerization.....	25
4. Poly(Styrene) via Emulsion Polymeriz- ation.....	31
C. Results and Discussion.....	32
1. Sonication Polymerization.....	32
2. Suspension Polymerization.....	38
3. Emulsion Polymerization.....	39
D. Conclusion.....	40
III. INVESTIGATION OF PYROLYSIS CONDITIONS.....	41
A. Introduction.....	41
B. Experimental.....	45
1. General.....	45
2. Alloy Furnace Pyrolysis.....	45
3. Quartz Furnace Pyrolysis.....	46

CHAPTER	PAGE
4. Determination of Transition Temperature....	50
C. Results and Discussion.....	50
D. Conclusion.....	55
IV. PREPARATION OF POLY(STYRENE/DIVINYLBENZENE) DERIVATIVES.....	56
A. Introduction.....	56
B. Experimental.....	57
1. General.....	57
2. Poly(4-Bromostyrene/15% Divinylbenzene)....	58
3. Poly(4-Chlorostyrene/15% Divinylben- zene).....	62
4. Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).....	66
a. α -Bromo- <i>p</i> -Toluic Acid.....	66
b. <i>p</i> -Carboxybenzyltriphenylphosphonium Bromide.....	70
c. 4-Vinylbenzoic Acid.....	71
d. 4-Vinylbenzoic Acid.....	72
e. Methyl 4-Vinylbenzoate.....	74
f. Methyl 4-Vinylbenzoate.....	76
g. Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).....	77
5. Poly(Styrenesulfonic Acid/4% Divinyl- benzene).....	78
6. Poly(Nitrostyrene/11% Divinylbenzene).....	82

CHAPTER	PAGE
7. Poly(Chloromethylstyrene/11% Divinyl- benzene).....	86
8. Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).....	90
C. Results and Discussion.....	94
1. Polymerization of Monomers.....	94
2. Functionalization of Poly(Styrene/ Divinylbenzene).....	101
D. Conclusion.....	103
V. PYROLYSIS OF POLY(STYRENE/DIVINYLBENZENE) DERIVATIVES.....	104
A. Introduction.....	104
B. Experimental.....	106
1. General.....	106
2. Sulfonated Resin.....	107
3. Methylcarboxylated Resin.....	107
4. Chlorinated Resin.....	110
5. Brominated Resin.....	110
6. Chloromethylated Resin.....	110
7. Methylsulfonated Resin.....	114
8. Nitrated Resin.....	114
C. Results and Discussion.....	114
D. Conclusion.....	118

CHAPTER	PAGE
VI. CYCLOTRON EVALUATION OF SYNTHESIZED	
MATERIALS.....	119
A. Introduction.....	119
B. Experimental.....	120
C. Results and Discussion.....	123
D. Conclusion.....	127
LIST OF REFERENCES.....	130
VITA.....	136

LIST OF TABLES

TABLE	PAGE
1-1. Reactions for the Production of Nitrogen-13.....	3
2-1. Chemicals Used and Manufacturers.....	24
2-2. Sonication Parameters for the Production of Poly(Styrene/Divinylbenzene) Beads.....	36
3-1. Pyrolysis Parameters.....	54
4-1. Chemicals Used and Manufacturers.....	59
6-1. Deuteron Irradiation Experiments on Carbon-12 Polymer Beads.....	124

LIST OF FIGURES

FIGURE	PAGE
1-1. Construction of a Simple Two-Dee Cyclotron.....	4
1-2. Simplified View of a Cyclotron.....	6
1-3. Beam Extraction Schematic.....	7
1-4. Pole Face of an AVF Cyclotron.....	8
1-5. Nitrogen-13 Ammonia Target.....	10
1-6. Graph of N-13 Yield vs. Energy.....	11
1-7. SEM of Current C-13 Slurry Material after Irradiation with Protons.....	12
2-1. Emulsion Polymerization System.....	22
2-2. SEM of Sonication Product.....	26
2-3. SEM of Suspension Polymerization Product.....	28
2-4. FTIR Spectrum of Suspension Polymerization Product.....	29
2-5. C-13 SS NMR Spectrum of Suspension Polymerization Product.....	30
2-6. SEM of Emulsion Polymerization Product.....	33
2-7. FTIR Spectrum of Emulsion Polymerization Product.....	34
2-8. C-13 SS NMR Spectrum of Emulsion Polymerization Product.....	35
2-9. Sonicator Apparatus.....	37
3-1. Gas Composition as a Function of Temperature in Slow Pyrolysis.....	44

FIGURE	PAGE
3-2. SEM of Product from Pyrolysis in Alloy Furnace (800 °C).....	47
3-3. SEM of Product from Quartz Furnace Pyrolysis (800 °C).....	48
3-4. Quartz Furnace.....	49
3-5. SEM of Product from Quartz Furnace Pyrolysis (325 °C).....	51
3-6. SEM of Product from Quartz Furnace Pyrolysis (449 °C).....	52
4-1. Poly(Styrene/Divinylbenzene) Derivatives.....	57
4-2. SEM of Poly(4-Bromostyrene/15% Divinylbenzene).....	63
4-3. FTIR Spectrum of Poly(4-Bromostyrene/15% Divinylbenzene).....	64
4-4. C-13 SS NMR Spectrum of Poly(4-Bromostyrene/15% Divinylbenzene).....	65
4-5. SEM of Poly(4-Chlorostyrene/15% Divinylbenzene)....	67
4-6. FTIR Spectrum of Poly(4-Chlorostyrene/15% Divinylbenzene).....	68
4-7. C-13 SS NMR Spectrum of Poly(4-Chlorostyrene/15% Divinylbenzene).....	69
4-8. SEM of Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).....	79
4-9. FTIR Spectrum of Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).....	80

FIGURE	PAGE
4-10. C-13 SS NMR Spectrum of Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).....	81
4-11. SEM of Poly(Styrenesulfonic Acid/4% Divinylbenzene).....	83
4-12. FTIR Spectrum of Poly(Styrenesulfonic Acid/4% Divinylbenzene).....	84
4-13. C-13 SS NMR Spectrum of Poly(Styrenesulfonic Acid/4% Divinylbenzene).....	85
4-14. SEM of Poly(Nitrostyrene/11% Divinylbenzene).....	87
4-15. FTIR Spectrum of Poly(Nitrostyrene/11% Divinylbenzene).....	88
4-16. C-13 SS NMR Spectrum of Poly(Nitrostyrene/11% Divinylbenzene).....	89
4-17. SEM of Poly(Chloromethylstyrene/11% Divinylbenzene).....	91
4-18. FTIR Spectrum of Poly(Chloromethylstyrene/11% Divinylbenzene).....	92
4-19. C-13 SS NMR Spectrum of Poly(Chloromethylstyrene/11% Divinylbenzene).....	93
4-20. SEM of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).....	95
4-21. FTIR Spectrum of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).....	96
4-22. C-13 SS NMR Spectrum of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).....	97

FIGURE	PAGE
4-23. Diazald Kit Assembly.....	100
5-1. Proposed Chemical Structures for the Pyrolysis of Sulfonated Styrene/Divinylbenzene Copolymer....	105
5-2. SEM of Pyrolyzed Sulfonated Resin.....	108
5-3. SEM of Pyrolyzed Methylcarboxylated Resin.....	109
5-4. SEM of Pyrolyzed Chlorinated Resin.....	111
5-5. SEM of Pyrolyzed Brominated Resin.....	112
5-6. SEM of Pyrolyzed Chloromethylated Resin.....	113
5-7. SEM of Pyrolyzed Methylsulfonated Resin.....	115
5-8. TGA of Methylsulfonated Resin.....	116
5-9. SEM of Pyrolyzed Nitrated Resin.....	117
6-1. N-13 Target System.....	121
6-2. Radio-HPLC Ion Chromatography.....	126
6-3. Decay Curve Analysis.....	128
6-4. SEM of C-12 Polymer Beads after Irradiation with Deuterons.....	129

CHAPTER I

INTRODUCTION

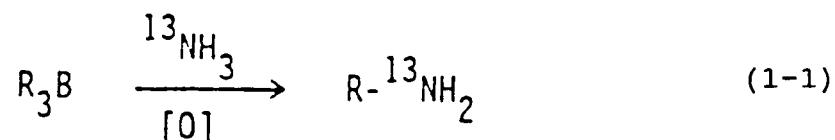
A. Background

Positron Emission Tomography (PET) is a non-invasive medical imaging technique for quantitatively measuring the concentrations of positron-emitting radioisotopes within a three-dimensional object¹. Among the readily prepared positron-emitting radionuclides are isotopes of carbon, nitrogen and oxygen. PET is currently used to study the metabolic fate of compounds containing these isotopes^{2,3}.

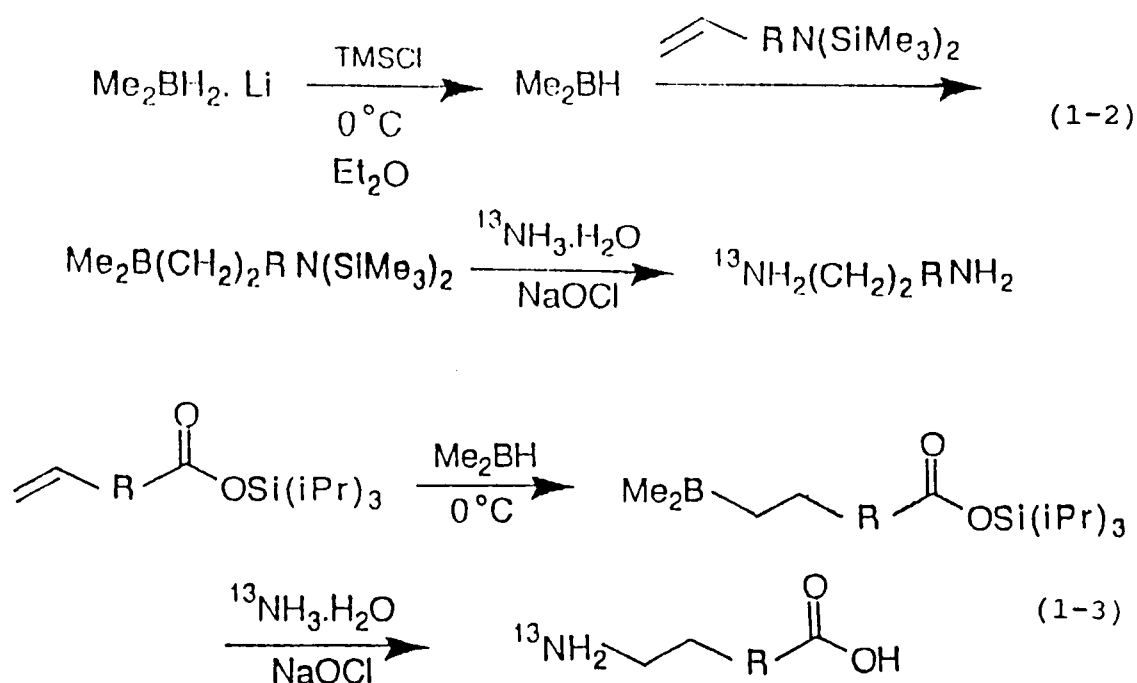
The short-lived positron-emitting isotope of nitrogen [^{13}N ; $t_{1/2} = 9.97$ min.] is important for several reasons: 1) compounds that are radiolabelled with nitrogen are valuable probes of in vivo processes and 2) nitrogen-13 has been used to investigate the uptake, transport and fixation processes in plants. In conjunction with PET, nitrogen-13 is used to image cerebral and myocardial blood flow and amino acid metabolism in both normal and ischemic myocardium⁴⁻¹³. Nitrogen-13 also has utility in detecting disorders of the liver, pancreas, kidneys, lungs, and the central nervous system¹⁴⁻¹⁸.

Synthetic approaches to compounds containing nitrogen-13 for application in PET have been investigated in this laboratory. Organic amines containing nitrogen-13 have

been produced in moderate yields via the direct reaction of nitrogen-13 labelled ammonia with organoborane precursors in the presence of mild oxidants^{19,20,21}:



Polymeric organoboranes have also been utilized for the simple and convenient production of nitrogen-13 labelled amines²⁰. Likewise, nitrogen-13 labelled diamines and amino acids have been prepared in a rapid, convenient, and easy to manipulate one-pot method²²:



These syntheses require nitrogen-13 which is available via several nuclear reactions²³ (Table 1-1).

Table 1-1: Reactions for the Production of Nitrogen-13

$^{13}\text{C}(\text{p}, \text{n})^{13}\text{N}$	$^{14}\text{N}(\text{d}, \text{p}2\text{n})^{13}\text{N}$
$^{14}\text{N}(\text{p}, \text{pn})^{13}\text{N}$	$^{11}\text{B}(^3\text{He}, \text{n})^{13}\text{N}$
$^{16}\text{O}(\text{p}, \alpha)^{13}\text{N}$	$^{10}\text{B}(^4\text{He}, \text{n})^{13}\text{N}$
$^{12}\text{C}(\text{d}, \text{n})^{13}\text{N}$	$^{11}\text{B}(^4\text{He}, 2\text{n})^{13}\text{N}$

All the reactions involve bombardment of an appropriate atom (e.g., ^{13}C) with an energetic charged particle (e.g., p) which results in expulsion of a nuclear particle (e.g., n) and subsequent generation of the desired nuclide (e.g., ^{13}N). The energetic charged particles listed in Table 1-1 are commonly produced by an instrument known as a cyclotron²⁴ (Figure 1-1). The cyclotron was developed in 1929 by E. O. Lawrence, who realized that a single, small accelerating electric field could be used to produce particle beams of high energy. The first cyclotron was constructed in 1931 at the University of California in Berkeley by Lawrence and M. S. Livingston. Since then, ever larger machines capable of accelerating particles to higher energies have been built^{25,26}. Recently, size and space requirements, as well as cost considerations have dictated that smaller, self-shielded cyclotrons be built for use in PET facilities^{26,27,28}.

Basically, the cyclotron consists of two hollow metal accelerating electrodes between which a radiofrequency oscillator generates an oscillating electric field. The

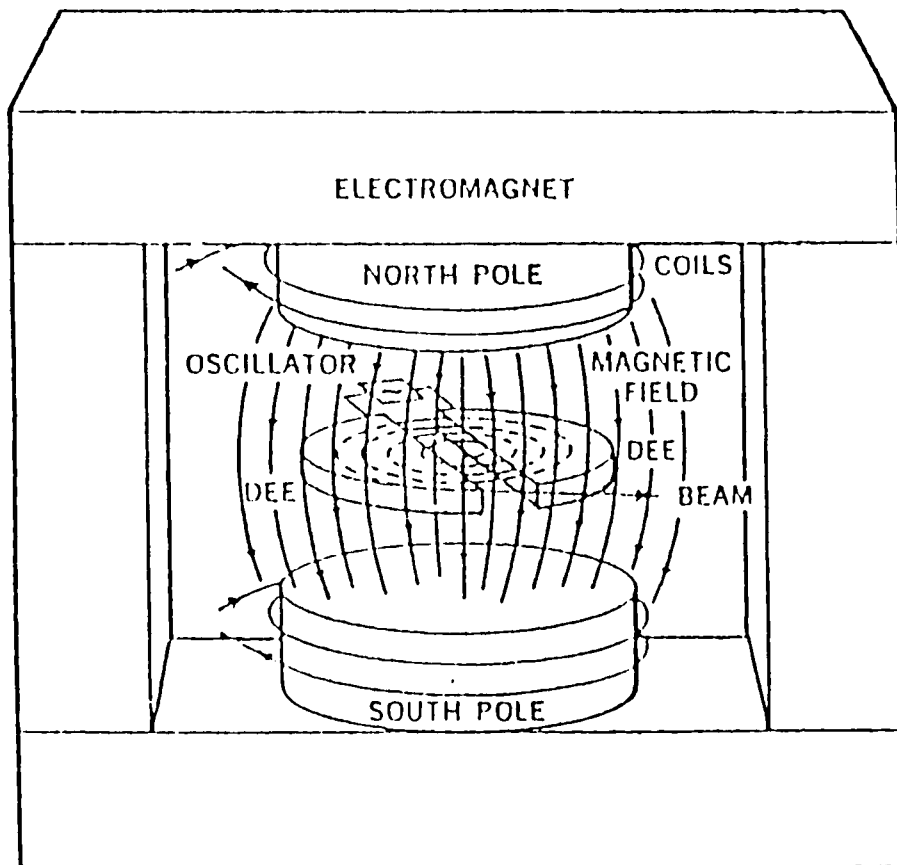


Figure 1-1. Construction of a Simple Two-Dee Cyclotron.

electrodes, or "dees", are located in an approximately uniform magnetic field^{25,28} (Figure 1-2). Charged particles are produced by an ion source which is located at the center of the dees. The magnetic field induces movement of the particles in circular orbits inside and across the dees with increasing acceleration. Eventually, the radius of the orbit increases to where the particles are removed from the edge of the magnet by an electrostatic or magnetic deflector. The particles are then passed through a window (as an external beam) and strike the target. In the target, nuclear reactions take place to yield radioactive nuclides^{25,28}.

The devices for beam extraction may vary. In a conventional positive ion cyclotron, an electrostatic deflector is sometimes used with a magnetic channel to aid in focusing the emergent beam. Extraction efficiencies are on the order of 50%. In a negative ion cyclotron, extraction is accomplished via the passage of hydride ions through an electron stripping foil to produce protons. Here, efficiencies greater than 50% are achieved^{26,29,30} (Figure 1-3).

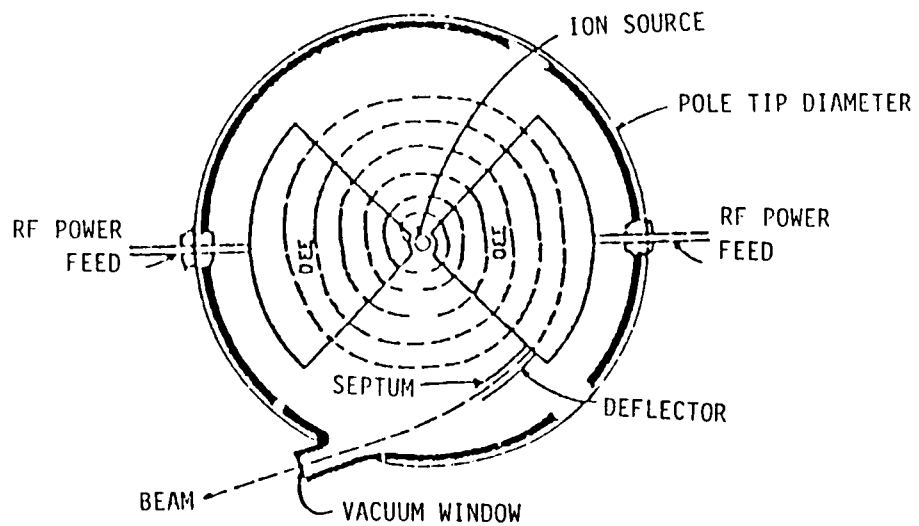
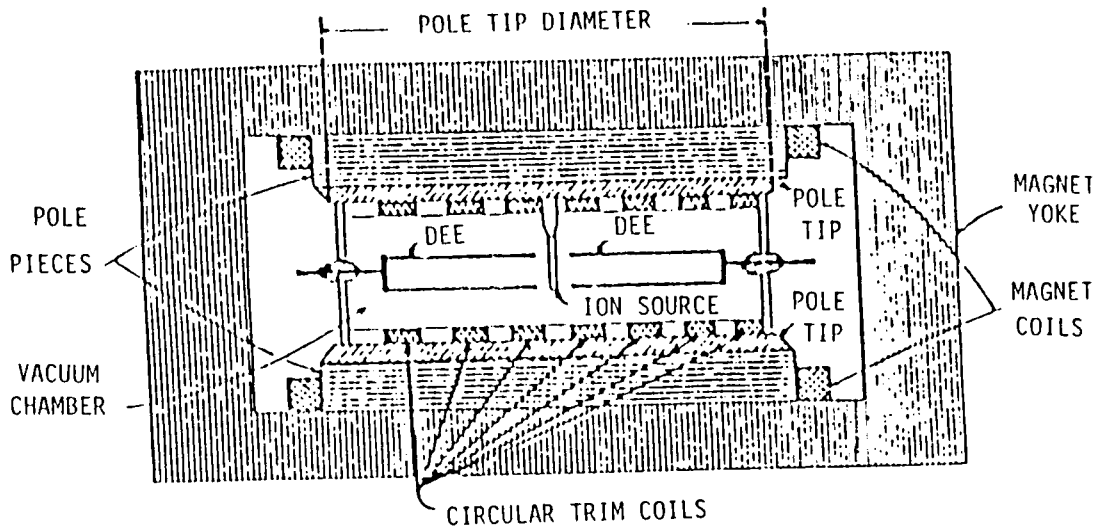


Figure 1-2. Simplified View of a Cyclotron.

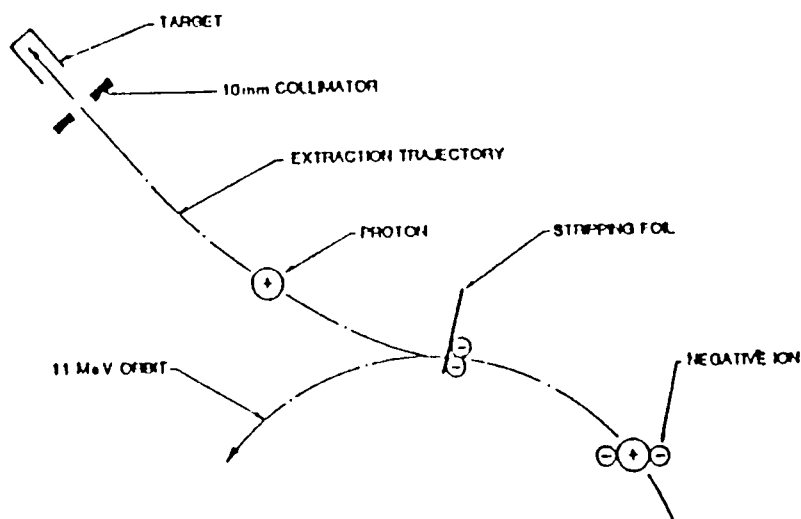


Figure 1-3. Beam Extraction Schematic.

The classical cyclotron, which operated at a fixed frequency of the RF oscillator, possessed a limitation in that protons could only be accelerated to a maximum energy of 25 MeV. To avoid this restriction, azimuthally varying fields (AVF) were studied. Modern cyclotrons are AVF isochronous machines in which ions revolve at a constant frequency. It has been shown that with this type of design, particles can be accelerated to higher energies. Periodic azimuthal field variations are arrived at with the use of pole faces with alternate "hill" and "valley" sectors^{25,26,28,31} (Figure 1-4).

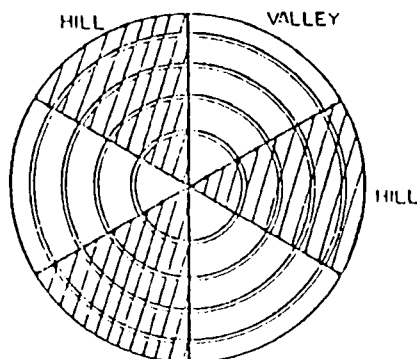
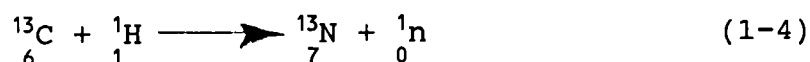


Figure 1-4. Pole Face of an AVF Cyclotron.

Based on the available data for the various reactions that generate nitrogen-13, the proton bombardment of carbon-13 is the most desirable³². This reaction is written as:



where ${}^1_1\text{H}$ represents the proton and ${}^1_0\text{n}$ represents the neutron. It may also be written in the following short-hand notation:



where the target atom appears on the left, the reaction type is in the middle, and the product appears on the right³³.

The methods for the production of nitrogen-13 along with their advantages and disadvantages are outlined as follows:

1. $^{13}\text{C} (p,n) ^{13}\text{N}$ Targets:

Carbon-13 enriched powder³², carbon-13 powder in oxygen-16 water^{24,34} (slurry target) (Figure 1-5), carbon-13 carbon dioxide in oxygen-16 water⁴, carbon-12 carbon dioxide in oxygen-16 water⁴.

Advantages (Carbon-13 enriched powder and slurry targets):

- a. High yields of nitrogen-13 are produced at relatively low beam energies³⁵ (Figure 1-6).
- b. Greater than 99% radiochemical purity is attained³².
- c. On-line separation of the radionuclide from a reusable target is available³⁵.
- d. Convenient solid targets of high purity are available³⁶.
- e. Cost after initial target charge is negligible³⁴.
- f. Production of nitrogen-13 is predominantly in the form of $^{13}\text{NH}_4^{+35}$
- g. Slurry target utilizes both the $^{13}\text{C}(p,n)^{13}\text{N}$ and the $^{16}\text{O}(p,\alpha)^{13}\text{N}$ reactions³⁴.

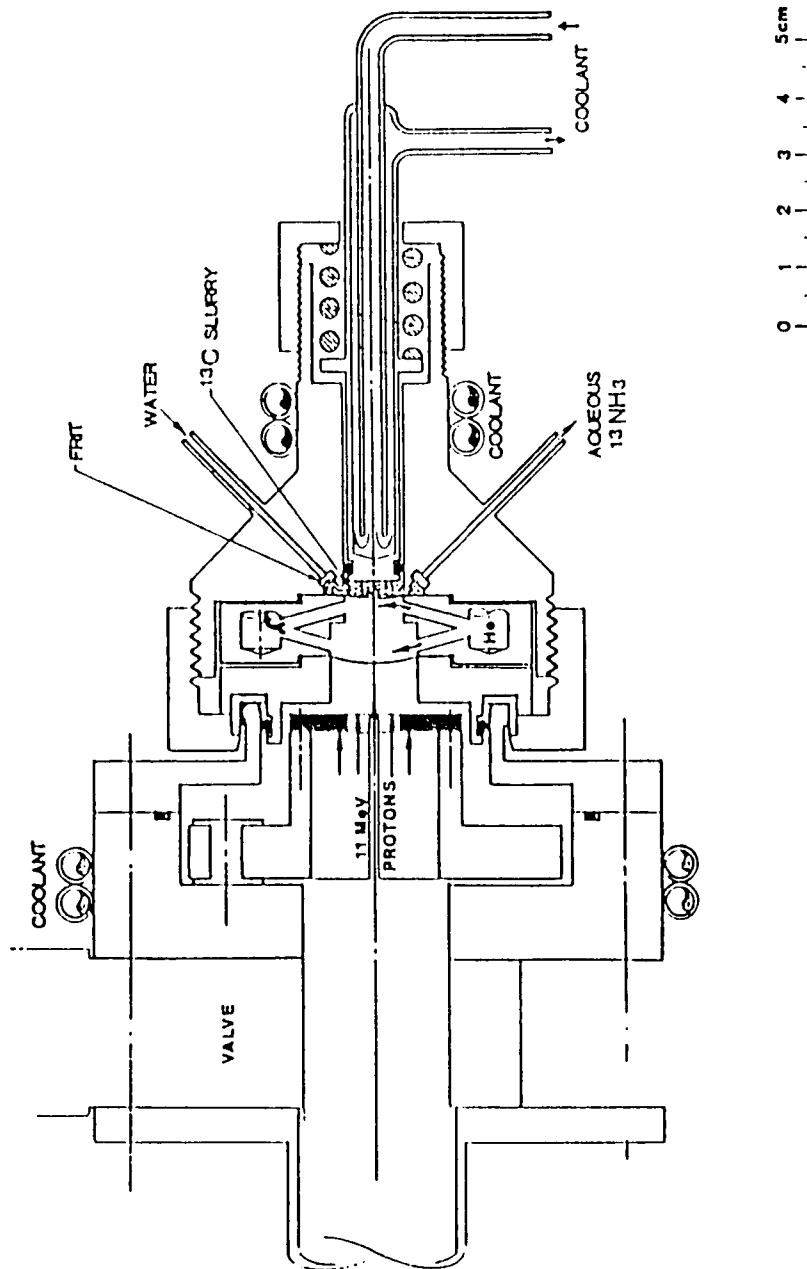


Figure 1-5. Nitrogen-13 Ammonia Target.

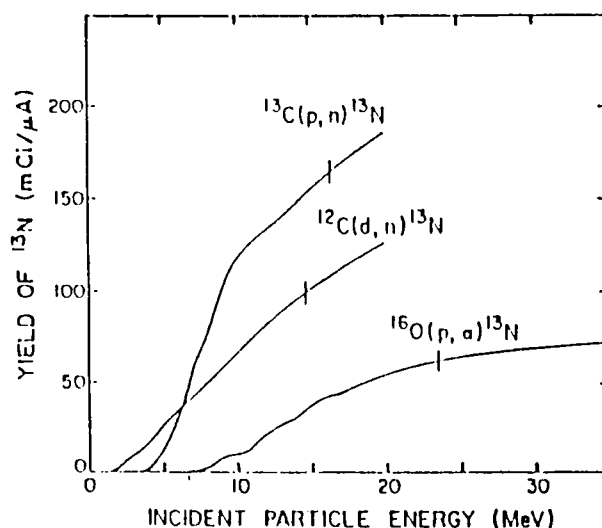
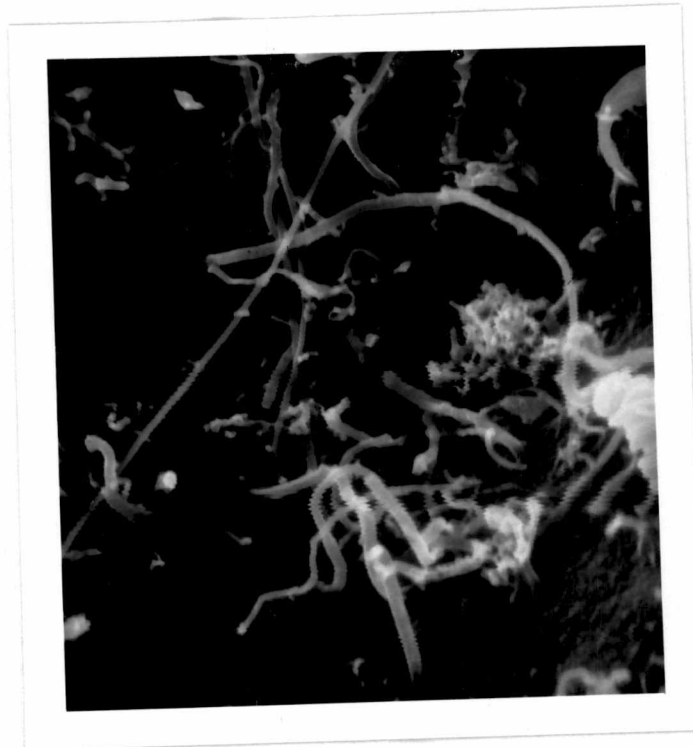


Figure 1-6. Graph of N-13 Yield vs. Energy.

Disadvantages (Carbon-13 enriched powder and slurry targets):

- a. The density of carbon-13 relative to oxygen-16 in the beam strike is low; therefore, less nitrogen-13 from the more favorable $^{13}\text{C}(p, n)^{13}\text{N}$ reaction occurs in the slurry target³⁷.
- b. Nitrogen-13 is also produced in the form of nitrates and nitrites (< 10% of total nitrogen-13), which require column purification³⁵.
- c. In the case of the slurry target, the amorphous carbon, after irradiation, breaks down into tiny, hair-like structures (Figure 1-7) which are responsible for blockage of the stainless steel



5 mm = 1 μ m

Figure 1-7. SEM of Current C-13 Slurry Material after Irradiation with Protons.

frits used to isolate the carbon-13 powder from the aqueous stream of $^{13}\text{NH}_3$ ³⁷.

2. $^{16}\text{O} (p, \alpha) ^{13}\text{N}$

Targets:

Oxygen¹⁶, water³⁸, ethanol/ H_2O ^{16,38-41}, acetic acid/ H_2O ^{39,40,41}.

Advantages:

- a. Ethanol and acetic acid targets give a favorable product distribution of nitrogen-13 containing species^{39,40}.
- b. High yields of nitrogen-13 in the form of ammonia can be achieved using hydrogen as the overpressure gas⁴².
- c. Naturally abundant starting materials are available at a low cost.

Disadvantages:

- a. This reaction normally requires high beam energy and/or high beam current for adequate radionuclide production³².
- b. In the water target, nitrogen-13 is produced in the form of nitrates which must be chemically reduced to ammonia^{36,43-45}.

- c. Trace fluorine-18 contaminants are present from this reaction³⁶.

3. ^{12}C (d,n) ^{13}N

Targets:

Methane^{36,46}, metal carbides^{15,16,36,47}, carbon dioxide^{36,48,49}, graphite/carbon dioxide³⁶, ethanol³⁶, diamond⁴⁶.

Advantages:

- a. High yields of nitrogen-13 labelled ammonia are produced in the methane target³⁶.
- b. Convenient solid target materials of high purity are available³⁶.
- c. Naturally abundant starting materials are available at a low cost.

Disadvantages:

- a. Impurities and radiolytic NH_3 carrier are produced with the methane target³⁶.
- b. In the case of metal carbides, radiation hazards are generated¹⁵.

4. ^{14}N (p,d) ^{13}N Advantage:

- a. Naturally abundant starting materials are available at a low cost.

Disadvantage:

- a. Product is in the form of $^{13}\text{N}_2$ gas which must be converted to ammonia³⁶.

5. ^{14}N (n,2n) ^{13}N Advantage:

- a. Naturally abundant starting materials are available at a low cost.

Disadvantage:

- a. Along with low yields of nitrogen-13, other species (carbon-11, chlorine-38...) are produced which must be separated⁴⁷.

6. $^{12}\text{C} (p, \gamma) ^{13}\text{N}$ Advantage:

- a. Naturally abundant starting materials are available at a low cost.

Disadvantage:

- a. Low yields of nitrogen-13 are produced³⁵.

B. Statement of Problem

The proton irradiation of the carbon-13 powder/oxygen-16 water slurry target is the method of choice for production of nitrogen-13 labelled ammonia^{32,48}. Although this target possesses several important advantages over other targets, serious deficiencies still exist with respect to the carbon-13 labelled target materials; the most significant of these is the instability of the current target material upon irradiation by high energy particles. The focus of this research has been to develop new carbon-13 labelled materials that would produce nitrogen-13 labelled ammonia and obviate the present instability problems. New polymer-based materials composed of poly(styrene/divinylbenzene) derivatives were synthesized

and then pyrolyzed to yield spherical, microscopic, carbonized beads with thermosetting properties. This route to new materials was chosen based on the characteristic properties of glassy polymers⁵⁰. The polymerization procedure produces crosslinked polymers in quantitative yields. The degree of crosslinking can be controlled by the addition of divinylbenzene, as well as by the addition of various reducible functional groups. Crosslinking enhances the percent carbon remaining after the pyrolysis step.

Following pyrolysis, the carbon particles often retain their spherical shape with uniform shrinkage. It was felt that beads with diameters of 3-5 μm would not deteriorate upon irradiation and, therefore, would avoid the problem associated with blockage of the frits. These beads are of a diameter that approaches the recoil range of the nascent recoiling nitrogen-13 atom from the $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$ reaction. It was also felt that glassy carbon beads would possess a higher packing density to allow for a larger fraction of carbon-13 in the proton beam strike. This would take advantage of the higher nitrogen-13 yields obtained from the $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$ reaction. Finally, it was felt that high yields of nitrogen-13 in the form of ammonia (with insignificant, if any, amounts of nitrates/nitrites) could be obtained with this target. The derivatives synthesized in these pilot

studies have all been prepared using isotopically normal carbon reagents due to the high costs of the corresponding carbon-13 labelled reagents.

CHAPTER II

DEVELOPMENT OF POLYMERIZATION METHOD

A. Introduction

As stated in Chapter I, thermal treatment of polymeric resins provides microscopic, spherical particles which have application in the cyclotron production of nitrogen-13. In order to achieve polymeric beads on the order of 3 μm , three polymerization methods (sonication, suspension, and emulsion) were explored. Sonication appeared to be an attractive method of polymerization since small, spherical liposomes are prepared by the sonication of lipid films^{51,52}. It was originally thought that the sonication of organic monomers in aqueous solution might lead to the production of small polymer beads since it is well known that, when two immiscible liquids are sonicated, the liquid becomes emulsified such that microscopic droplets of one liquid are suspended in the other. Upon continued sonication, these droplets will burst into smaller droplets⁵³. Localized heat is generated as the droplets collapse, and this heat should be sufficient to allow for the polymerization of monomer droplets^{53,54}.

Another polymerization method available for the production of beads of small diameters is suspension polymerization. Suspension polymerization (also referred to as bead or pearl polymerization) is a technique which

is carried out by suspending the monomer as droplets (0.001-1 cm) in water. The suspension is maintained by the addition of water-soluble stabilizers, which prevent agglomeration of the droplets by increasing the viscosity of the aqueous phase, and by mechanical agitation. The rate of agitation controls the size of the droplets which, in turn, controls the size of the beads⁵⁵. The final polymer (0.1-1 mm) can be isolated and purified by simple filtration^{55,56}.

Emulsion polymerization is yet another polymerization technique that can be used to provide small, spherical particles. In emulsion polymerization two immiscible liquid phases are present; however, emulsion polymerization differs from suspension polymerization in that emulsion polymerization yields particles of smaller size (inherent of colloidal dispersions) and requires a water-soluble initiator^{55,56}. Rather than employing stabilizers, emulsion polymerization requires an emulsifier, or surfactant, which is used to disperse the two phases. The action of the surfactant is attributed to its possession of both hydrophilic and hydrophobic segments. When the concentration of the surfactant reaches a certain value, excess surfactant molecules cluster together to form colloidal aggregates called micelles. This level of concentration is referred to as the CMC, or the critical micelle concentration.

Figure (2-1) shows the orientation of micelles in an emulsion polymerization. The molecules arrange themselves such that the hydrocarbon (hydrophobic) ends point toward the interior of the micelle while the ionic (hydrophilic) ends point outward toward the water. The monomer, in small concentrations, enters the interior hydrocarbon section of the micelle, while the major portion of the monomer exists as dispersed monomer droplets. The size of the droplets is controlled by the intensity of agitation to yield monomer droplets not less than 1 μm in diameter. Polymerization begins when the initiator decomposes into two free radicals. This process occurs in the aqueous phase. Through the action of the micelles, the initiator radical finds its way to the monomer where chain reactions proceed until a polymer is formed. This process is called particle nucleation. Emulsion polymerizations are carried out with 100% conversion of the monomer to inseparable polymer beads of 0.1 μm in size. However, since no present method for the removal of surfactant exists, the product (known as a latex) cannot be purified⁵⁵.

B. Experimental

1. General

Solid state NMR spectra were recorded on a Nicolet NT-200 MHz pulsed FT-NMR spectrometer.

Infrared spectra were obtained on a Bio-Rad Model FTS-7 FT-IR spectrometer. Elemental analyses were

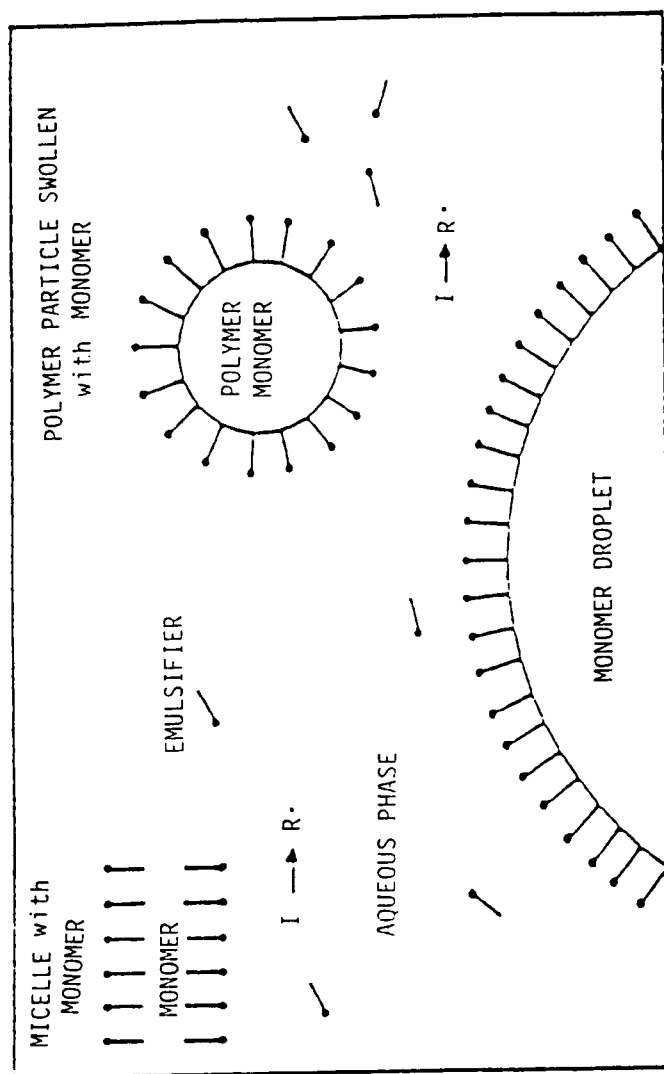


Figure 2-1. Emulsion Polymerization System.

performed by Galbraith Laboratories, Knoxville, Tennessee. Scanning electron micrographs were recorded on Polaroid Type 55 P/N film using an ETEC Autoscan SEM Instrument. Samples were prepared as follows: 12 mm SEM aluminum specimen mounts were coated with double-stick Scotch tape. Samples were placed on glassine paper and the specimen mounts were inverted onto the samples. Standard 2.68 micron latex spheres (size determinations) were then atomized onto the exposed surface. Samples were placed in a Danton DV-515 Vacuum Evaporator where approximately 100 Å Palladium-Gold (60:40) was evaporated onto each sample. The chemicals used and their manufacturers are listed in Table 2-1.

2. Poly(Styrene/2% Divinylbenzene) via Sonication

An adaptation of the procedure reported by Alexandratos was employed⁵⁷. Into a 50-mL beaker was placed an aqueous solution containing pharmagel (0.024 g) dissolved in water (2.5 mL) at 40 °C, and a solution of poly(diallyldimethyl-ammonium chloride) (0.275 g) with boric acid (0.15 g) in water (5.0 mL). The pH of the latter solution was adjusted to 10 by the dropwise addition of NaOH (33%, approximately 12 drops). For the preparation of 2% crosslinked copolymer, the organic phase consisted of

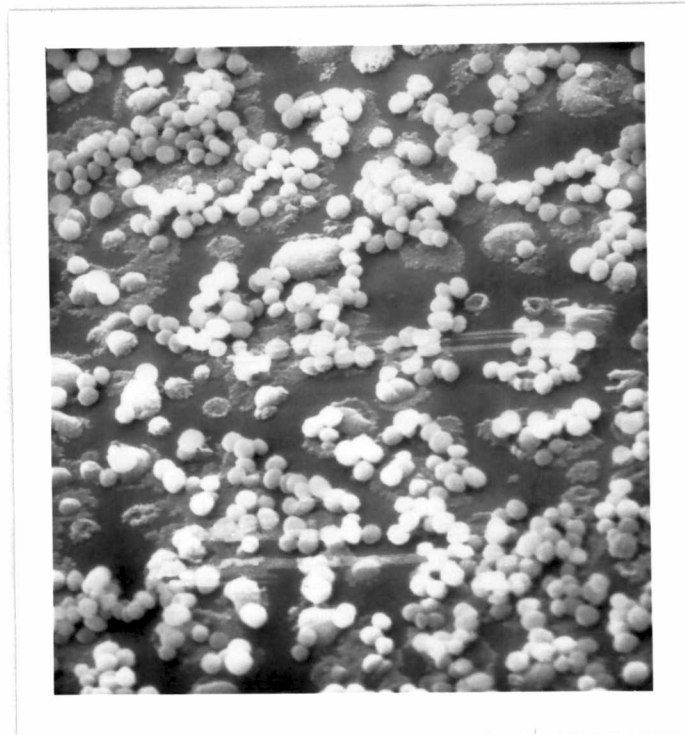
Table 2-1: Chemicals Used and Manufacturers

Reagent	Manufacturer
Aluminum Sulfate	Aldrich
Benzoyl Peroxide	Aldrich
Boric Acid	Aldrich, Mallinckrodt
Divinylbenzene, 55%	Aldrich
Hydrochloric Acid	Fisher, Mallinckrodt
Methanol	Aldrich
Pharmagel	Knox Gelatin Company
Poly(dimethyldiallyl- Ammonium Chloride)	Calgon Corporation
1-Pentanol	Aldrich
Sodium Dodecylsulfate	Aldrich
Sodium Hydroxide	Fluka, Mallinckrodt
Sodium Persulfate	Aldrich
Sodium Phosphate, monobasic	Aldrich
Styrene	Aldrich

styrene (6.7 g; 64 mmol), divinylbenzene (containing 45% ethylvinylbenzene; 0.32 g; 0.14 mmol), and benzoyl peroxide (0.07 g; 0.3 mmol). The aqueous phase, along with an additional 10 mL of water, was purged with argon, and the argon flow was maintained throughout the entire polymerization. The organic phase was added slowly, and the suspension was stirred briefly. The beaker was placed under the sonicator probe and the sonicator was set to full power for 10 min. Unreacted styrene was removed by extraction with 1-pentanol (4 X 10 mL). The copolymer film was stored in 1-pentanol and examined by scanning electron microscopy (Figure 2-2).

3. Poly(Styrene/15% Divinylbenzene) via Suspension Polymerization

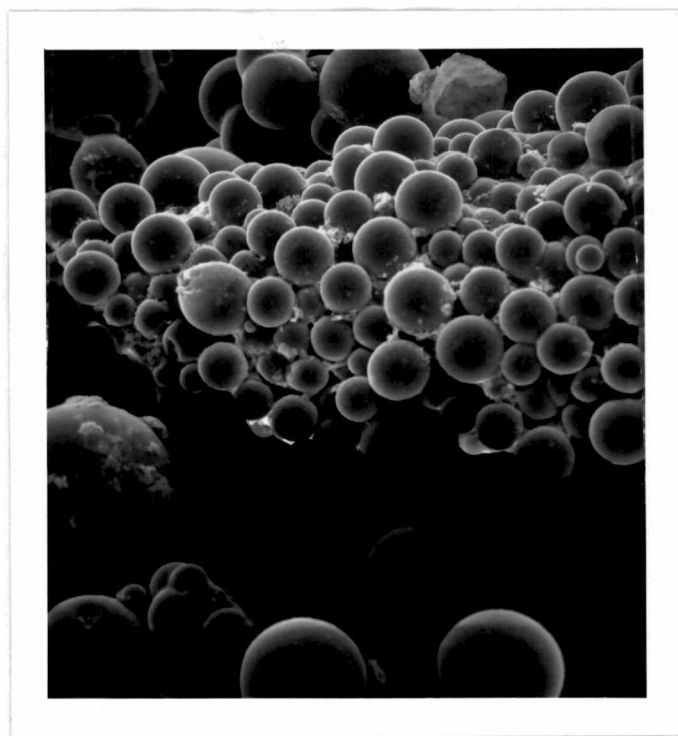
The procedure reported by Alexandratos was used⁵⁷. Into a 50-mL round-bottomed flask equipped with a condenser, a thermometer, and an overhead stirrer were placed an aqueous solution containing pharmagel (0.024 g) dissolved in water (2.5 mL) at 40 °C, and a solution of poly(diallyldimethyl-ammonium chloride) (0.275 g) and boric acid (0.15 g) in water (5.0 mL). The pH of the latter solution was adjusted to 10 by the dropwise addition of NaOH (33%, approximately 12 drops). For the preparation of 15%




6 mm = 2.3 μm

Figure 2-2. SEM of Sonication Product.

crosslinked copolymer, the organic phase consisted of styrene (6.7 g; 64 mmol), divinylbenzene (containing 45% ethylvinylbenzene; 3.05 g; 12.9 mmol), and benzoyl peroxide (0.07 g; 0.3 mmol). The two phases were stirred for 2 min. and then allowed to separate for 1 min. This process was repeated two times for a total of 9 min. Water (10 mL) was added and the reaction mixture was heated from room temperature to 80 °C at a rate of approximately 7 °C/15 min. under an argon atmosphere which was maintained throughout the entire polymerization. The mixture was held at 80 °C for 10 h, and then allowed to cool. To ensure complete polymerization, the mixture was heated to 100 °C for an additional 2 h, cooled, washed with HCl (pH 4, 4 X 20 mL, 15 min.) and then with water (4 X 20 mL, 15 min.). The copolymer was filtered and air-dried to yield 9.65 g (99% yield) of poly(styrene/15% divinylbenzene) beads; ^{13}C SS-NMR: δ 146.28 (ArCH-CH_2), 127.72 (Ar-C), 48.91 (CH), 40.74 (CH_2); FTIR (KBr): 3025 cm^{-1} (CH_2), 2925 cm^{-1} (CH), 1950-1700 cm^{-1} (combinations and overtones), 1600 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1} (C=C), 1050 cm^{-1} , 900 cm^{-1} (C-H), 775 cm^{-1} , 700 cm^{-1} (Ar-H). Anal. Calcd for $\text{C}_8\text{H}_8/\text{C}_{10}\text{H}_{10}/\text{C}_{10}\text{H}_{12}$ copolymer: C, 92.11; H, 7.89. Found C, 90.81; H, 8.07. The SEM photograph and IR and NMR spectra are presented in Figures 2-3 through 2-5.



6 mm = 50 μ m

Figure 2-3. SEM of Suspension Polymerization Product.

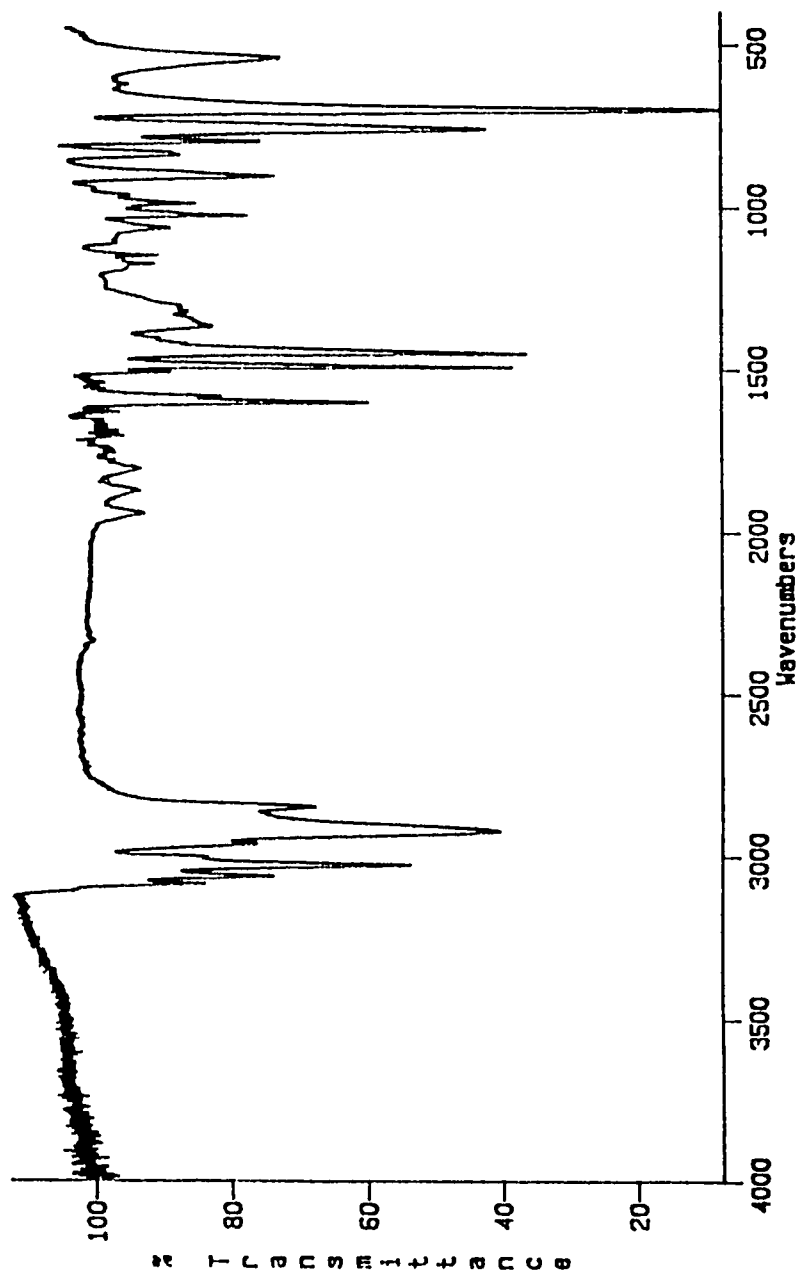


Figure 2-4. FTIR Spectrum of Suspension Polymerization Product.

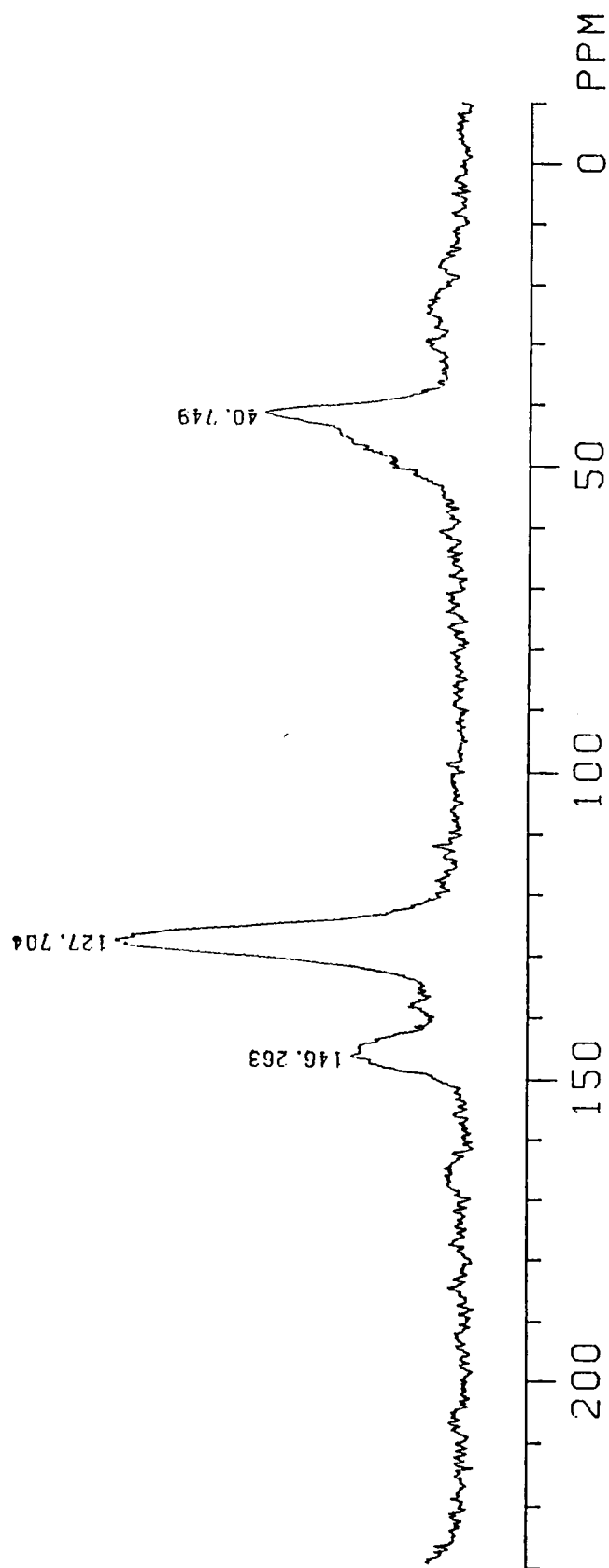


Figure 2-5. C-13 SS NMR Spectrum of Suspension Polymerization Product.

4. Poly(Styrene) via Emulsion Polymerization

The procedure reported by Braun and coworkers was employed⁵⁸. A 250-mL, three-necked round-bottomed flask equipped with an eggbar stirrer (or an overhead stirrer), a thermometer, and a condenser was flushed with nitrogen. The following were then added under nitrogen: sodium persulfate (122 mg; 0.510 mmol), NaH_2PO_4 (50.0 mg; 0.420 mmol), sodium dodecyl sulfate (1.0 g; 3.5 mmol) and water (100 mL) that had been boiled under nitrogen. When everything had dissolved, styrene (50.0 mL; 437 mmol) was added with constant stirring; the resulting oil-in-water emulsion was heated at 60 °C for 6 h with steady stirring under a slow stream of nitrogen. After the polymer latex was cooled, 30 mL was pipetted into a beaker. The polymer was precipitated by the addition of an equal volume of concentrated aluminum sulfate. A further 30 mL sample was precipitated by pouring it into methanol (300 mL). The latex remaining in the flask was coagulated by the addition of concentrated HCl. The samples were washed with water and with methanol until the styrene odor was no longer detectable, filtered and dried via Kugelrohr distillation. The $\text{Al}_2(\text{SO}_4)_3$ fraction yielded 5.46 g after drying for 18 h at 47 °C at 1 mm. The methanol fraction afforded 8.48 g after drying for 1.5 h at 25 °C at 2.1 mm, followed by drying

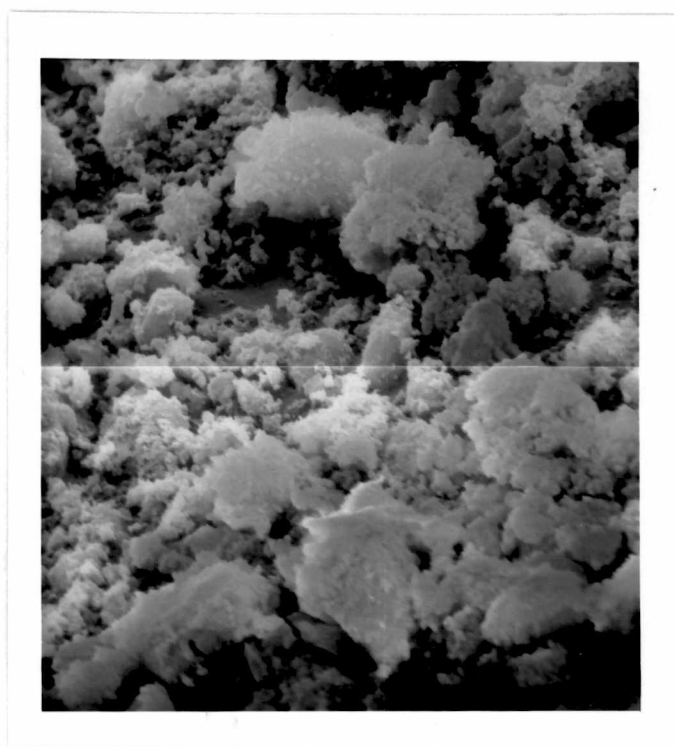
for 19.5 h at 80 °C at 1.2 mm. The HCl fraction yielded 27.96 g after drying for 28 h at 25 °C at 2.1 mm, followed by drying for 0.5 h at 62 °C, at 2.1 mm. The overall yield was 41.90 g (92.2% yield) of a polymer latex; ^{13}C SS-NMR: δ 146.85 (ArCH-CH_2), 128.08 (Ar-C), 46.64 (CH), 40.72 (CH_2); FTIR (KBr): 3025 cm^{-1} (CH_2), 2925 cm^{-1} (CH), 1925-1660 cm^{-1} (combinations and overtones), 1600 cm^{-1} , 1495 cm^{-1} , 1450 cm^{-1} (C=C), 1025 cm^{-1} , 900 cm^{-1} (C-H), 750 cm^{-1} , 700 cm^{-1} (Ar-H). Anal. Calcd for C_8H_8 polymer: C, 92.31; H, 7.69. Found C, 91.99; H, 7.87. The SEM photograph and IR and NMR spectra are presented in Figures 2-6 through 2-8.

C. Results and Discussion

1. Sonication Polymerization

Several experiments were conducted using the sonication method. Various parameters were systematically changed (Table 2-2). An organic layer consisting of styrene, divinylbenzene, ethylvinylbenzene and benzoyl peroxide was suspended in an aqueous layer and polymerized in an ultrasonic medium (Figure 2-9). The heat generated by sonication is sufficient to decompose the organic-soluble initiator, benzoyl peroxide, into two free radicals^{55,56}.

The reaction then proceeds as follows:



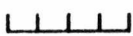

4 mm = 5 μ m

Figure 2-6. SEM of Emulsion Polymerization Product.

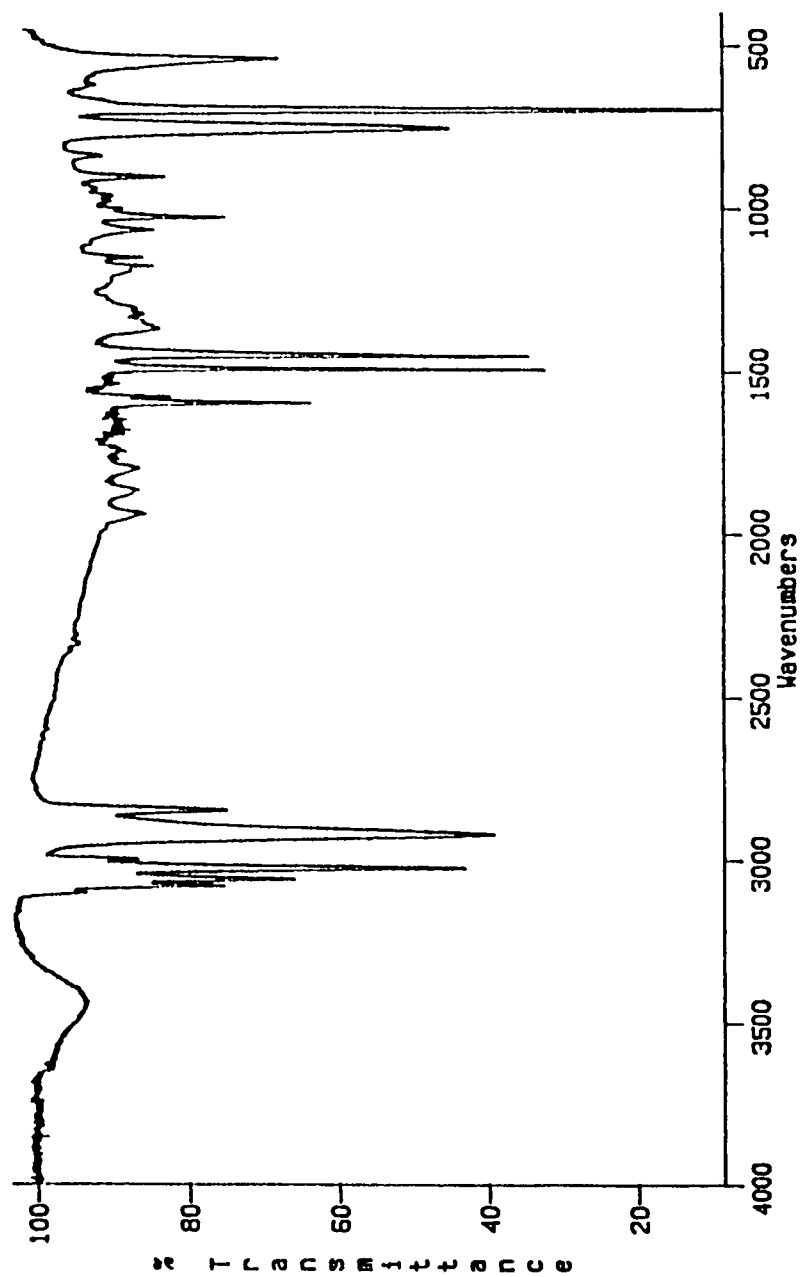


Figure 2-7. FTIR Spectrum of Emulsion Polymerization Product.

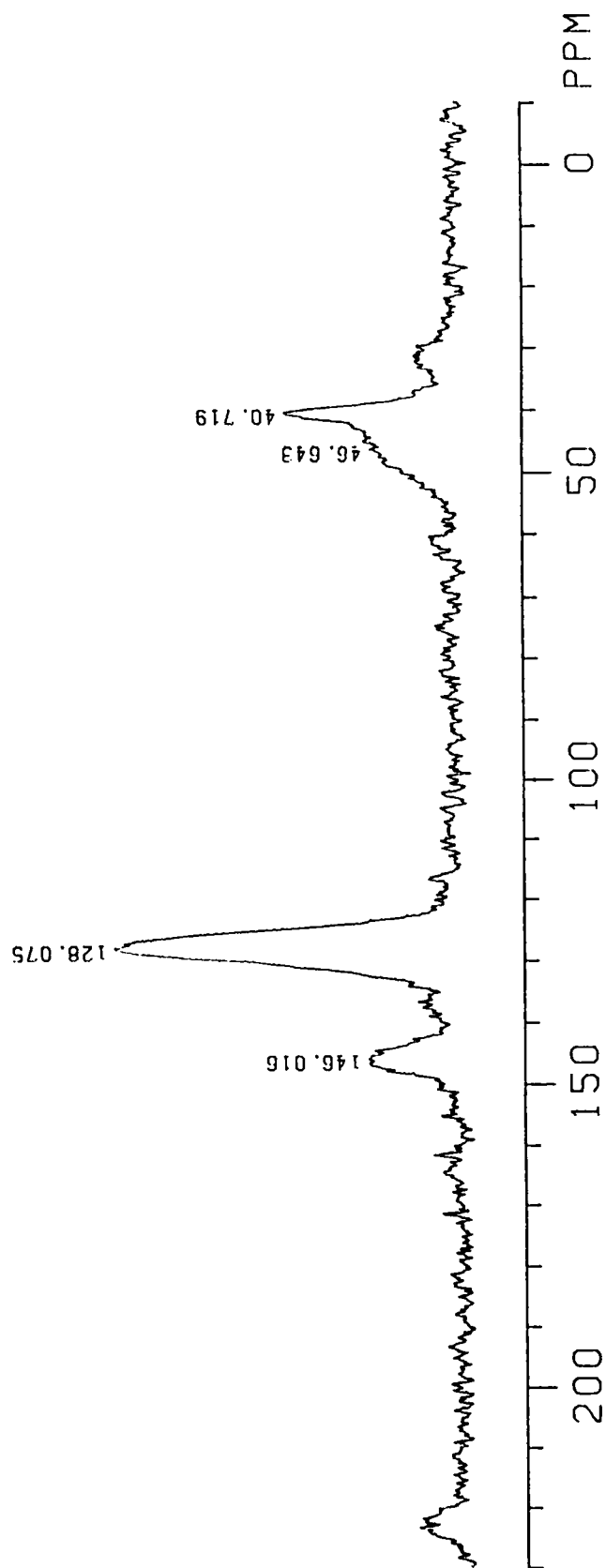


Figure 2-8. ^{13}C SS NMR Spectrum of Emulsion Polymerization Product.

Table 2-2: Sonication Parameters for the Production of Poly(Styrene/Divinylbenzene) Beads

EXPT. #	% POWER	TEMP. (°C)	RXN. TIME (min.)	ADDN TIME (min.)	ADDN METHOD
3-5	100	25	10	1	Poured
3-6	35	25	270	1	Poured
3-7	75	25	70	1	Poured
3-8	45	25	180	1	Poured
3-9	100	25	50	1	Poured
3-10*	100	25	25	1	Poured
3-11	40	25	240	1	Poured
3-12*+	40	25	2	1	Poured
3-13	100	25	30	9	Dropwise
3-14	40	80-140	10	1	Poured
3-15	40	80	1	1	Poured
3-16*	80	25	20	1	Poured
3-17*	100	25	25	10	Dropwise
3-18*	43	80	10	7	Dropwise
3-19*	42	60-80	120	5	Dropwise
3-20*	100	80	45	10	Dropwise
3-21*	100	-1	50	10	Dropwise
3-22*	100	-9- -1	53	7	Dropwise
3-23	100	-1- -10	54	6	Dropwise
3-24*#	45	-6-0	52	8	Dropwise
3-25*	45	80	45	15	Dropwise
3-26*	45	80-65	185	7	Dropwise
3-27*	45	60-80	120	5	Dropwise
3-28*	45	60	120	5	Dropwise
3-29*	42	60-80	120	5	Dropwise
3-30*	42	60	120	5	Dropwise
3-31*	60	25	120	5	Dropwise
3-32*	45	60-80	75	5	Dropwise
3-37*	42	60-55-70	120	5	Dropwise
3-40*	42	60	120	5	Dropwise
3-41*	42	60	120	5	Dropwise
3-42*	42	60	300	5	Dropwise
3-43*	42	72-60	120	5	Dropwise

* = Sample stored in pentanol

+ = Aqueous concentration was doubled

= Syringe needle at solution interface during the addition

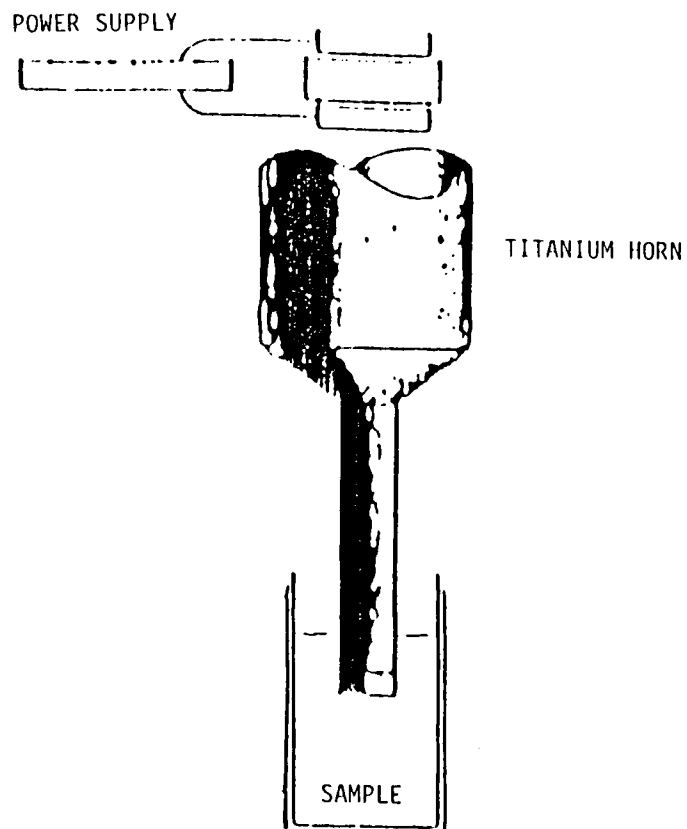
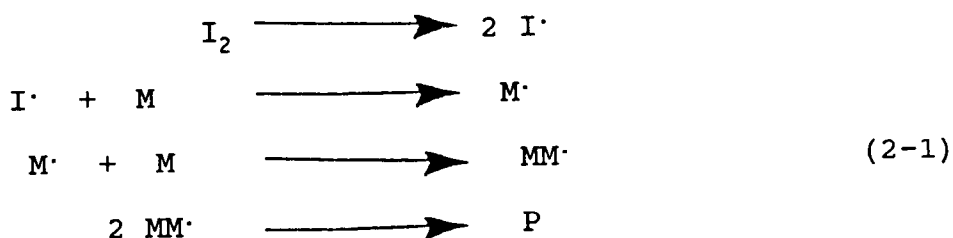


Figure 2-9. Sonicator Apparatus.



where: I = Initiator

M = Monomer

P = Polymer

Eventually microscopic beads on the order of 1-2 μm were obtained (see Figure 2-2 on p. 26). Due to the difficulty in attaining the exact parameters (sonication power was difficult to control), reproducibility became a problem. Another drawback to this method lies in the conversion of only a small percentage of monomer to polymer beads. Longer reaction times led to polymerization of the interfacial layer in the form of a disk. Therefore, it was concluded that other polymerization methods should be studied.

2. Suspension Polymerization

In order to improve the yield of polymer beads, suspension polymerization was investigated. Polymerizations were carried out using four different concentrations of divinylbenzene (4, 8, 11, and 15 mole percent) for the purpose of altering the crosslinking

and, hence, the thermal stability of the polymers. In most cases, the size of the beads decreased with an increased concentration of divinylbenzene with the average size varying from 2-200 μm (see Figure 2-3 on p. 28). Production of smaller sized beads was limited by a maximum stirring rate of 300 rpm. At this rate, the smaller sizes are not reproducible. High speed stirrers capable of achieving 1000 rpm are necessary to reproducibly achieve 3-5 μm particles⁵⁹.

Suspension polymerization proceeds via the free radical mechanism shown earlier. The reaction is quantitative, which makes the suspension method favorable due to the high costs of carbon-13 labelled monomers to be used eventually.

3. Emulsion Polymerization

Emulsion polymerization was then studied because of its ability to produce microscopic beads. Styrene was polymerized in an aqueous mixture of potassium persulfate (initiator) and sodium dodecyl sulfate (emulsifier). The final polymer beads were aggregated in clusters (see Figure 2-6 on p. 33).

Styrene latex is not suitable for the production of carbon via pyrolysis because linear polymers like poly(styrene) possess no crosslinkable moiety. Crosslinking is responsible for providing polymers with

greater thermal stability. Because of this, pyrolyses of linear polymers afford extremely low yields of carbon residue. Functionalization of the styrene monomer ($-\text{SO}_3\text{H}$) can provide the polymer with the prerequisite crosslinking property and enhance the pyrolysis yields of carbon. During attempts to functionalize the monomer, it was decided that suspension polymerization would provide beads of the desired size if conducted with high speed stirring. While this was being investigated, the suspension polymerization products were simultaneously pyrolyzed in order to produce the carbonized beads.

D. Conclusion

Suspension polymerization was chosen as the method for production of microscopic, spherical beads due to the advantages it has over sonication and emulsion polymerizations. In order to produce target materials for the cyclotron production of nitrogen-13, the polymer beads were converted to carbon in a pyrolysis procedure which is the subject of the next chapter.

CHAPTER III

INVESTIGATION OF PYROLYSIS CONDITIONS

A. Introduction

Pyrolyses were conducted on the poly(styrene/divinylbenzene) resins in order to convert the polymers into carbonized beads for the cyclotron production of nitrogen-13. Pyrolysis can be defined as the destructive distillation of material heated well above ordinary laboratory temperatures without the addition of oxygen^{60,61}. Pyrolysis reactions can fall into one of three categories: flow pyrolysis (slow heating; <1 °C/s), rapid pyrolysis ($500-10^5$ °C/s), and flash pyrolysis ($>10^6$ °C/s)^{61,62}. Flow pyrolysis is the classical procedure in the carbonization industry for the production of steel from coke. The other two pyrolysis methods are used in the petroleum industry for the production of hydrocarbons⁶². The nature and proportions of pyrolysis products are determined by factors such as the rate of heating, the residence time at a particular temperature (soak time), the reaction temperature, the carrier gas, and the chemical composition of the material^{60,62-64}. Slow heating rates and high temperatures favor the formation of increasingly stable molecules that are rich in carbon^{60,62,63,65}.

Three stages of decomposition occur during the pyrolysis of organic molecules. Organic molecules are

rapidly converted to semi-coke and "primary" volatiles (tar, C_2 , C_2H_6 , CH_4 , and H_2O). The "primary" volatiles are then converted into "secondary" volatiles (C_2H_6 , CH_4 , H_2O , and "secondary" tar). The semi-coke is slowly transformed into carbon and "tertiary" volatiles (H_2 with saturated and unsaturated gaseous hydrocarbons)^{62,63}. Tar formation is attributed to the distillation and decomposition of weakly bonded rings in the structure of the molecule, while methane and ethane result from dealkylation processes. Hydrogen gas is generated from the ring rupture of aromatic C-H bonds⁶².

In terms of chemical reactions, three simultaneous reactions occur during slow pyrolysis in an inert atmosphere: devolatilization (the organic material is converted to tar and char), cracking (tar is converted to gas), and deposition (tar is converted to char)⁶². At low temperatures, gases and moisture are released; most of the water is driven off below 150 °C and is completely gone at 300 °C⁶². When heated to approximately 350 °C, the organic compound melts to form a highly viscous, non-Newtonian liquid or melt⁶³. The high temperatures disrupt the secondary bonds and permit the dissociation of covalent bonds which induce melting and fluid behavior⁶³. Around 500-550 °C aromatic compounds, such as benzene, decompose to form biphenyl (radical recombination), carbon, and hydrogen gas^{63,65}. Aromatic rings maintain their integrity when heated as high as 700 °C. Gasification occurs from 600-1000 °C

where vapors and gaseous compounds fragment further and react with the carbonaceous residues to form CO, H₂, CH₄, and CO₂⁶⁰ (Figure 3-1). The processes which occur during pyrolysis are not completely understood. For example, very little is known regarding the effects of particle size on the yield of carbon, but it is believed that smaller particles (<100 μm) produce higher carbon yields^{62,63}. Both mass and heat transfer affect the pyrolysis of a single organic particle; thus small sample sizes are essential for uniform sample temperatures^{62,63}. Pyrolyses of polymers, such as poly(styrene), have been studied^{66,67,68}. Linear poly(styrene) produces essentially no carbonaceous residue as it is completely volatilized by 440 °C. However, incorporation of small amounts of a difunctional monomer, such as divinylbenzene, increase the carbon yields by providing a thermosetting crosslinking mechanism for the polymer chains, thereby increasing the thermal stability of the polymer. The styrene/divinylbenzene copolymer was studied over the temperature range of 300-1200 °C. Carbonaceous residues are produced between 300-500 °C, but volatile products (consisting of mainly styrene, methane, ethane, benzene, toluene, and hydrogen) are produced at higher temperatures. The yields of solid residue increase as the crosslinking levels are increased⁶⁶.

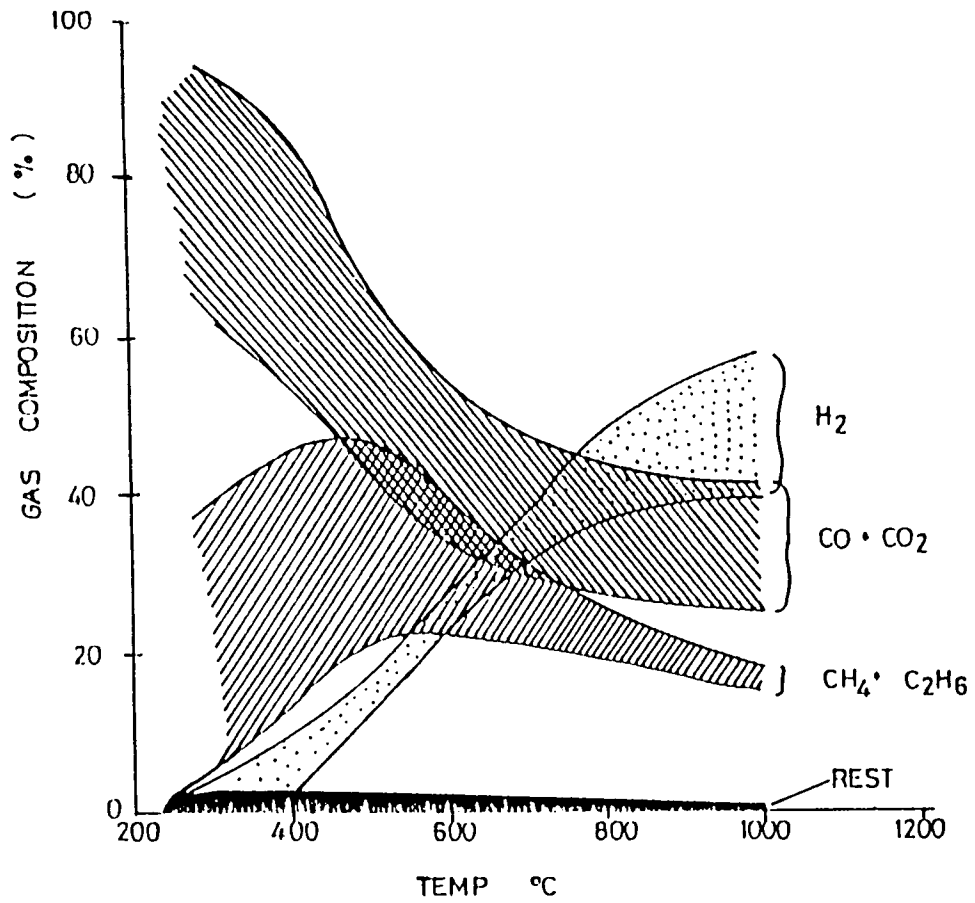


Figure 3-1. Gas Composition as a Function of Temperature in Slow Pyrolysis.

B. Experimental

1. General

All pyrolysis experiments were conducted in either an Electric Multiple Unit Furnace Model #M-3024 33" alloy furnace or in a Trans-Temp 6" quartz furnace. The temperature was controlled with an ECS Brand temperature controller for the alloy furnace experiments and programmed with a Therm-X LFE #2010 temperature controller for the quartz furnace experiments. The temperature profile was monitored with a Kipp and Zonen Model #BD41 strip chart recorder. For both furnaces, a Chromel-Alumel thermocouple was utilized to convey heat readings from the furnace to the temperature controllers. Argon flow rates were measured with a Gasmet gas chromatography flow meter and were found to be <30 cc/min.

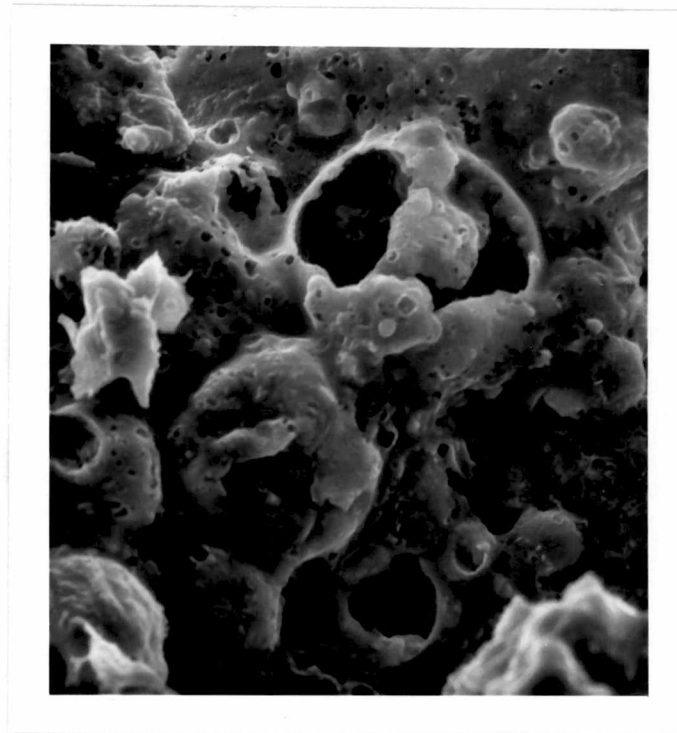
2. Alloy Furnace Pyrolysis

Poly(styrene/2% divinylbenzene) beads (3.00 g) were placed between two ceramic boats, wrapped with copper wire, and placed in the alloy tube. The furnace was purged with argon to maintain a slight positive pressure, and the argon was released into a mineral oil bubbler where the flow was measured. The temperature was set to 200 °C and was incremented by 200 °C every hour until 800 °C was attained. The temperature was

then held at 800 °C for 1 h, after which the sample was cooled to room temperature under an argon flow. This afforded 0.03 g (1% yield based on carbon in the polymer sample) of carbon. The SEM photograph is presented in Figure 3-2.

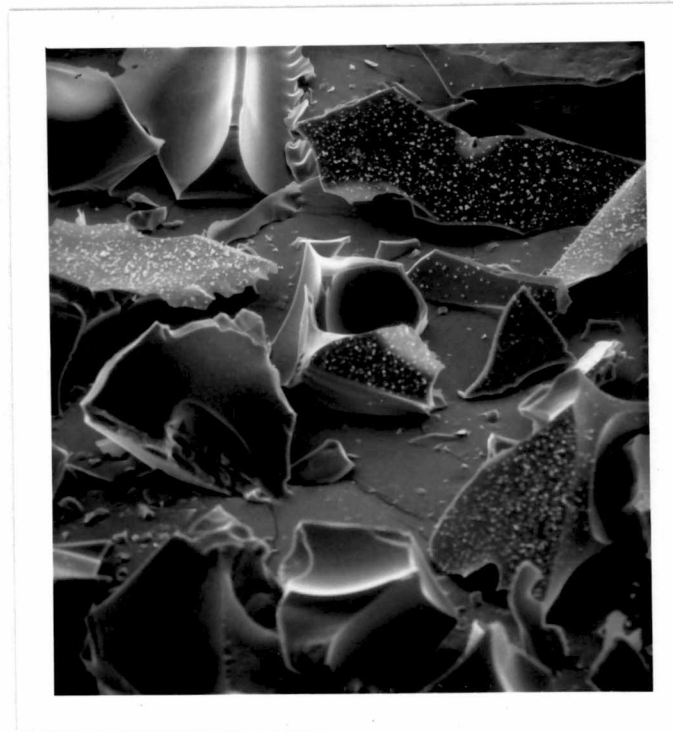
3. Quartz Furnace Pyrolysis

Poly(styrene/10% divinylbenzene) beads (2.79 g) were placed between two ceramic boats, wrapped with copper wire, and placed in the quartz tube. The furnace was purged with argon to maintain a slight positive pressure, and the argon was released into a mineral oil bubbler where the flow was measured. The temperature controller was programmed to increase the furnace temperature from room temperature to about 800 °C at a rate of 0.5 °C/min. After 25 h, 50 min., the controller turned off automatically and the furnace was allowed to cool to room temperature under an argon flow. This afforded 0.14 g (5.0% yield based on carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 91.80; H, 0.77. The remaining fraction is attributed to absorbed gases. (9.6% polymer remains). The SEM photograph and a diagram of the quartz furnace are presented in Figures 3-3 and 3-4.




5 mm = 5 μ m

Figure 3-2. SEM of Product from Pyrolysis in Alloy Furnace (800 °C).



4 mm = 50 μ m

Figure 3-3. SEM of Product from Quartz Furnace Pyrolysis (800 °C).

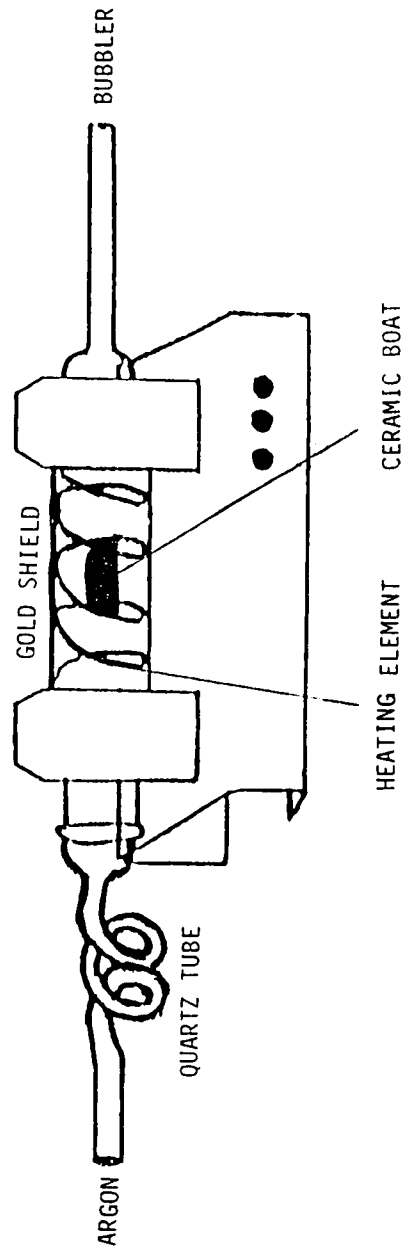


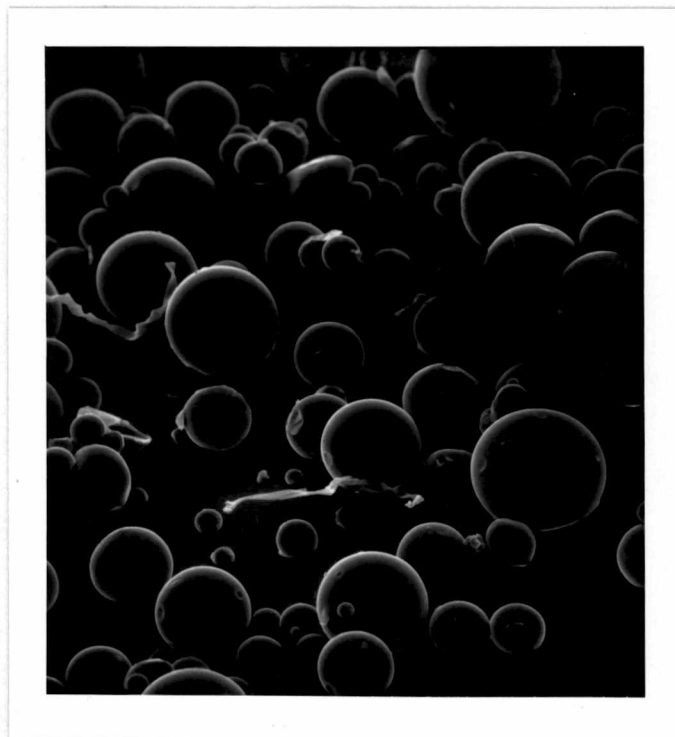
Figure 3-4. Quartz Furnace.

4. Determination of Transition Temperature

Poly(styrene/10% divinylbenzene) beads (2.12 g) were placed between two ceramic boats, wrapped with copper wire, and placed in the furnace tube. The furnace was purged with argon to maintain a slight positive pressure, and the argon was released into a mineral oil bubbler where the flow was measured. The copolymer beads were heated to 320 °C at a rate of 5.0 °C/min., held at 320 °C for 1 h, and allowed to cool under an argon flow to give 1.97 g (93.0%) of slightly discolored beads. These beads (1.18 g) were reheated to 320 °C at 5.0 °C/min., brought to 325 °C at 0.8 °C/min., and then held at 325 °C for 4 h to afford 0.43 g (24% over the two pyrolyses) of a black-brown resin. Final pyrolysis of the beads from room temperature to 449 °C at 1 °C/min. yielded 0.02 g (4% overall) of carbon. Anal. found $C_8H_8/C_{10}H_{10}/C_{10}H_{12}$ copolymer at 325 °C: C, 92.78; H, 7.03. (91% polymer remains at 325 °C.) The SEM photographs are shown in Figures 3-5 and 3-6.

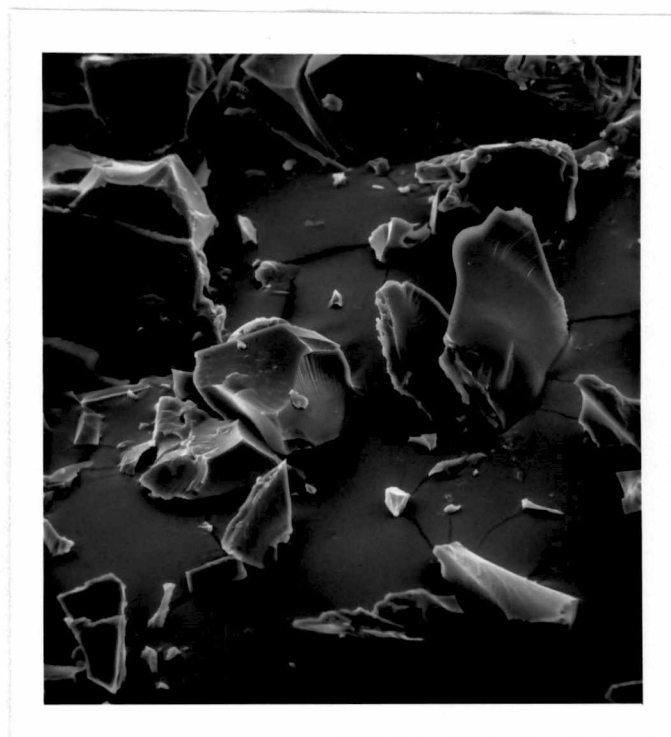
C. Results and Discussion

Several parameters were investigated to determine the ideal pyrolysis conditions for the production of carbon from microscopic, spherical poly(styrene/divinylbenzene) beads. Ideal conditions would lead to high conversion yields of polymer to carbon with retention of the bead-like shape.




6 mm = 50 μ m

Figure 3-5. SEM of Product from Quartz Furnace Pyrolysis (325 °C).




6 mm = 50 μ m

Figure 3-6. SEM of Product from Quartz Furnace Pyrolysis (449 °C).

Table 3-1 presents experimental data which describe the parameters that were examined.

It was determined that the method of polymerization did not have a significant effect on the pyrolysis yields. Suspension polymerization products were studied more thoroughly than products from sonication and emulsion simply because the high-yielding suspension products possess bead-like shapes prior to pyrolysis.

The rate of heating did have an effect on the carbon yields. Slower heating rates (0.5 °C/min.) provided the most satisfactory yields. However, soak time seemed to have no drastic effect.

Studies were conducted to determine the transition temperature of polymer to carbon, and thus the maximum required reaction temperature. Several pyrolyses were interrupted at various times and temperatures, and the products were weighed and analyzed for percent composition. It was concluded that at 325 °C, 91% of the polymer remains with only 8% loss of starting material, whereas at 449 °C, 95% of the material is lost. (This conclusion was based on the percent of hydrogen left in the sample after pyrolysis relative to the percent of hydrogen in the original polymer). It was decided that heating the samples to 800 °C, where >80-90% of the recovered sample consisted of carbon (determined via elemental analyses), would be appropriate.

Table 3-1: Pyrolysis Parameters

Polymerization Method	%DVB	Furnace Type	Pyrolysis Rate(°C/min.)	Soak Time(h)/Temp. (°C)	%Yield
Sonication	2	Alloy	2.5	1/800	1
Sonication	2	Alloy	1.7, 0.6		1
Suspension	2	Alloy	2.2		1
Suspension	2	Alloy	1.9	1/845	1
Sonication	2	Alloy	2.2	1/800	4
Suspension	10	Alloy	2.2	1/800	5
Suspension	10	Alloy	2.2	1/800	6
Suspension	10	Quartz	2.3	1/800	7
Suspension	10	Quartz	3.2	1/800	7
Suspension	10	Quartz	4.7		4
Suspension	10	Quartz	11.7		5
Suspension	10	Quartz	0.5		6
Suspension	5	Quartz	0.5		4
Suspension	15	Quartz	3.3		6
Suspension	15	Quartz	0.5		5
Suspension	20	Quartz	0.5		8
Suspension	50	Quartz	3.7		14
Suspension	50	Quartz	FAST		10
Suspension	50	Quartz	0.5		15
Suspension	100	Quartz	0.6		20
Suspension	100	Quartz	0.5		25
Emulsion	0	Quartz	0.5		2

Originally, it was thought that loss of product was due to combustion. Therefore, the pyrolyses were conducted in an inert atmosphere using either nitrogen or argon as the carrier gas. Successful leak tests were performed on the furnace system, but low yields still plagued the reactions.

The incorporation of larger amounts of divinylbenzene into the polymer affected the carbon yields in a positive manner at divinylbenzene percentages of $\geq 20\%$. Unfortunately, the 100% divinylbenzene polymer afforded only 25% carbon after pyrolysis.

D. Conclusion

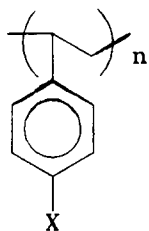
The pyrolysis of a variety of styrene/divinylbenzene copolymers developed from different polymerization procedures was investigated. Since none of the pyrolyses produced high yields of carbon beads, several functionalized styrene/divinylbenzene copolymers were synthesized and then pyrolyzed. They are the subject of the next chapter.

CHAPTER IV

PREPARATION OF POLY(STYRENE/DIVINYLBENZENE) DERIVATIVES

A. Introduction

Increased levels of crosslinking (attributed to higher percentages of divinylbenzene) are responsible for increased yields of carbon in pyrolysis reactions⁶⁶. However, when the incorporation of up to 100% divinylbenzene into the polymer structure provided unsatisfactory pyrolysis results, a series of poly(styrene/divinylbenzene) derivatives were investigated. It has been reported that reactions of poly(styrene) with oxidants afford products which provide increased yields of carbon residue upon pyrolysis⁶⁶. Most commonly, sulfonations have been investigated, but chlorinations have also been reported⁶⁶. During the pyrolysis, these polymer derivatives are chemically reduced via expulsion of a small stable molecule. This induces new carbon-carbon bond formations in the macrostructures of the polymers. The thermal stability of the polymers increases, which then increases the pyrolysis yields⁶⁶. Seven derivatives were studied (Figure 4-1), and were synthesized four times with varying concentrations of divinylbenzene (4, 8, 11, and 15 mole percent), for a total of 28 copolymer samples.



X = Br, Cl, CO₂CH₃, SO₃H, NO₂, CH₂Cl, CH₂SO₃H

Figure 4-1. Poly(Styrene/Divinylbenzene) Derivatives.

The following sections describe the details pertaining to these poly(styrene/divinylbenzene) derivatives.

B. Experimental

1. General

When required, all glassware, syringes, and syringe needles were oven-dried and then flame-dried prior to use. All solid state NMR spectra were recorded on a Nicolet NT-200 MHz pulsed FT-NMR spectrometer. All other NMR spectra were recorded on either a Bruker 500 MHz, a Bruker 400 MHz or a Nicolet NT-200 MHz pulsed FT-NMR spectrometer in deuteriodimethylsulfide ((CD₃)₂S=O) or deuteriochloroform (CDCl₃). The ¹H-NMR and the ¹³C-NMR spectra were referenced using either deuteriodimethylsulfide (δ_H = 2.50 ppm; δ_C = 39.5 ppm) or tetramethylsilane (TMS) (δ = 0.00 ppm) as internal standards⁶⁹. ¹³C-Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra were obtained and are reported with

the ^{13}C -NMR data. Infrared spectra were obtained on a Bio-Rad Model FTS-7 FT-IR spectrometer. Melting points were recorded using a Fisher-Johns melting point apparatus and are uncorrected. Thin layer chromatographic analyses were performed on E M Science brand Kieselgel 60F 254 μm TLC plates using uv detection as an indicator. Column chromatographic separations were accomplished using E M Science 400-230 mesh silica gel. Elemental analyses were performed by either Galbraith Laboratories, Knoxville, TN or by Berkeley Microlabs, Berkeley, CA. Scanning electron micrographs were recorded on Polaroid Type 55 P/N film using an ETEC Autoscan SEM Instrument. Samples were prepared as described on p. 23. The chemicals used and their manufacturers are listed in Table 4-1.

2. Poly(4-Bromostyrene/15% Divinylbenzene)

The procedure reported by Alexandratos was utilized⁵⁷. Into a 50-mL round-bottomed flask equipped with a condenser, a thermometer, and an overhead stirrer were placed an aqueous solution containing pharmagel (0.024 g) dissolved in water (2.5 mL) at 40 °C, and a solution of poly(diallyl-dimethyl-ammonium chloride) (0.275 g) and boric acid (0.15 g) in water (5.0 mL). The pH of the latter solution was adjusted to 10 by the dropwise addition of

Table 4-1: Chemicals Used and Manufacturers

Reagent	Manufacturer
Acetic Acid	Fisher
Acetone, reagent grade	Fisher
Benzoyl Peroxide	Aldrich
Boric Acid	Aldrich, Mallinckrodt
4-Bromostyrene	Aldrich
N-Bromosuccinimide	Aldrich
Calcium Hydride	Sigma
Carbon Dioxide	University of CA
Carbon Tetrachloride	Fisher
Chloroform, anhydrous*	Fisher
Chloromethyl Methyl Ether	Aldrich
4-Chlorostyrene	Aldrich
Diazald	Aldrich
Diethyl Ether	Aldrich, Fisher
Dimethylsulfide	Aldrich
Dioxane	Fisher
Divinylbenzene, 55%	Aldrich
Ethanol, 95%	Aldrich, Fisher
Ethyl Acetate	E M Science
Ethyl Bromide	Aldrich
Formalin	Fisher
Hexanes	Fisher
Hydrochloric Acid	Fisher, Mallinckrodt

Table 4-1 (continued)

Reagent	Manufacturer
Magnesium Sulfate, anhydrous	Fisher
Magnesium Turnings	Aldrich
Methanol	Aldrich, Fisher
O-Methyl-N,N'- Diisopropylisourea	Aldrich
Nitric Acid, fuming	Aldrich
Pharmagel	Knox Gelatin Company
Poly(diallyldimethyl- Ammonium Chloride	Calgon Corporation
Potassium, metal	Aldrich
Potassium Hydroxide, pellets	Aldrich, Fisher
Silica Gel, gravity	E M Science
Silver Sulfate	Aldrich
Sodium, metal	Aldrich
Sodium Carbonate	Fisher
Sodium Chloride	Morton
Sodium Hydroxide	Fisher, Fluka
Sodium Sulfite	Fisher
Sulfuric Acid, concentrated	E M Science, Fisher
Tetrahydrofuran, anhydrous*	Fisher
Tin (IV) Chloride	Aldrich
p-Toluic Acid	Fluka
Triphenylphosphine	Aldrich

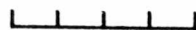
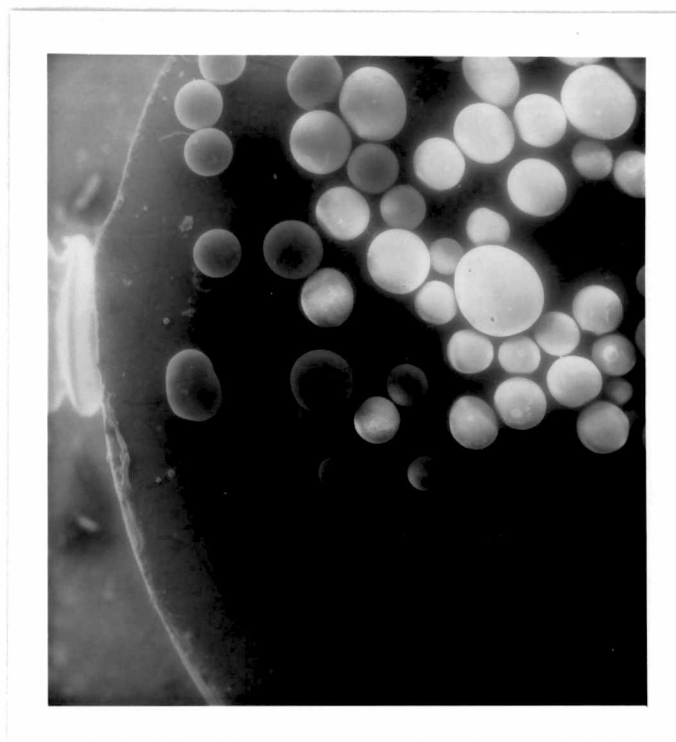
* Chloroform was dried over CaH_2 ; THF was dried over potassium.

NaOH (33%, approximately 12 drops). For the preparation of 15% crosslinked copolymer, the organic phase consisted of 4-bromostyrene (11.8 g; 64.5 mmol), divinylbenzene (containing 45% ethylvinylbenzene; 3.12 g; 13.2 mmol), and benzoyl peroxide (0.07 g; 0.3 mmol). The two phases were stirred for 2 min. then allowed to separate for 1 min. This process was repeated twice for a total of 9 min. Water (10 mL) was added and the reaction mixture was heated from room temperature to 80 °C at a rate of approximately 7 °C/15 min. under an argon atmosphere which was maintained throughout the entire polymerization. The mixture was held at 80 °C for 10 h, and then allowed to cool. To ensure complete polymerization, the mixture was heated to 100 °C for an additional 2 h, cooled, washed with HCl (pH 4, 4 X 20 mL, 15 min.) and then with water (4 X 20 mL, 15 min.). The copolymer was filtered and air-dried to yield 13.35 g (90.0% yield) of poly(4-bromostyrene/15% divinylbenzene) beads; ^{13}C SS-NMR: δ 144.70 (Ar-CH-CH₂), 139.26 (Ar-Br), 131.68 (aromatic C), 46.64 (CH), 40.30 (CH₂); FT-IR (KBr): 3005 cm⁻¹ (CH₂), 2925 cm⁻¹ (CH), 1910-1650 cm⁻¹ (combinations and overtones), 1600 cm⁻¹, 1480 cm⁻¹, 1440 cm⁻¹ (C=C), 1075 cm⁻¹, 1005 cm⁻¹, 900 cm⁻¹ (CH), 825 cm⁻¹, 700 cm⁻¹ (Ar-H). Anal. Calcd for C₈H₇Br/C₁₀H₁₀/C₁₀H₁₂ copolymer: C, 60.52; H, 4.75. Found: C, 60.67; H, 4.86. The SEM photo-

graph and IR and NMR spectra are presented in Figures 4-2 through 4-4.

3. Poly(4-Chlorostyrene/15% Divinylbenzene)

The procedure reported by Alexandratos was followed⁵⁷. Into a 50-mL round-bottomed flask equipped with a condenser, a thermometer, and an overhead stirrer were placed an aqueous solution containing pharmagel (0.024 g) dissolved in water (2.5 mL) at 40 °C, and a solution of poly(diallyldimethyl-ammonium chloride) (0.275 g) and boric acid (0.15 g) in water (5.0 mL). The pH of the latter solution was adjusted to 10 by the dropwise addition of NaOH (33%, approximately 12 drops). For the preparation of 15% crosslinked copolymer, the organic phase consisted of 4-chlorostyrene (8.91 g; 64.3 mmol), divinylbenzene (containing 45% ethylvinylbenzene; 3.35 g; 14.2 mmol), and benzoyl peroxide (0.07 g; 0.3 mmol). The two phases were stirred for 2 min. then allowed to separate for 1 min. This process was repeated twice for a total of 9 min. Water (10 mL) was added and the reaction mixture was heated from room temperature to 80 °C at a rate of approximately 7 °C/15 min. under an argon atmosphere which was maintained throughout the entire polymerization. The mixture was held at 80 °C for 10 h, and then allowed to cool. To ensure complete



6 mm = 500 μm

Figure 4-2. SEM of Poly(4-Bromostyrene/15% Divinylbenzene).

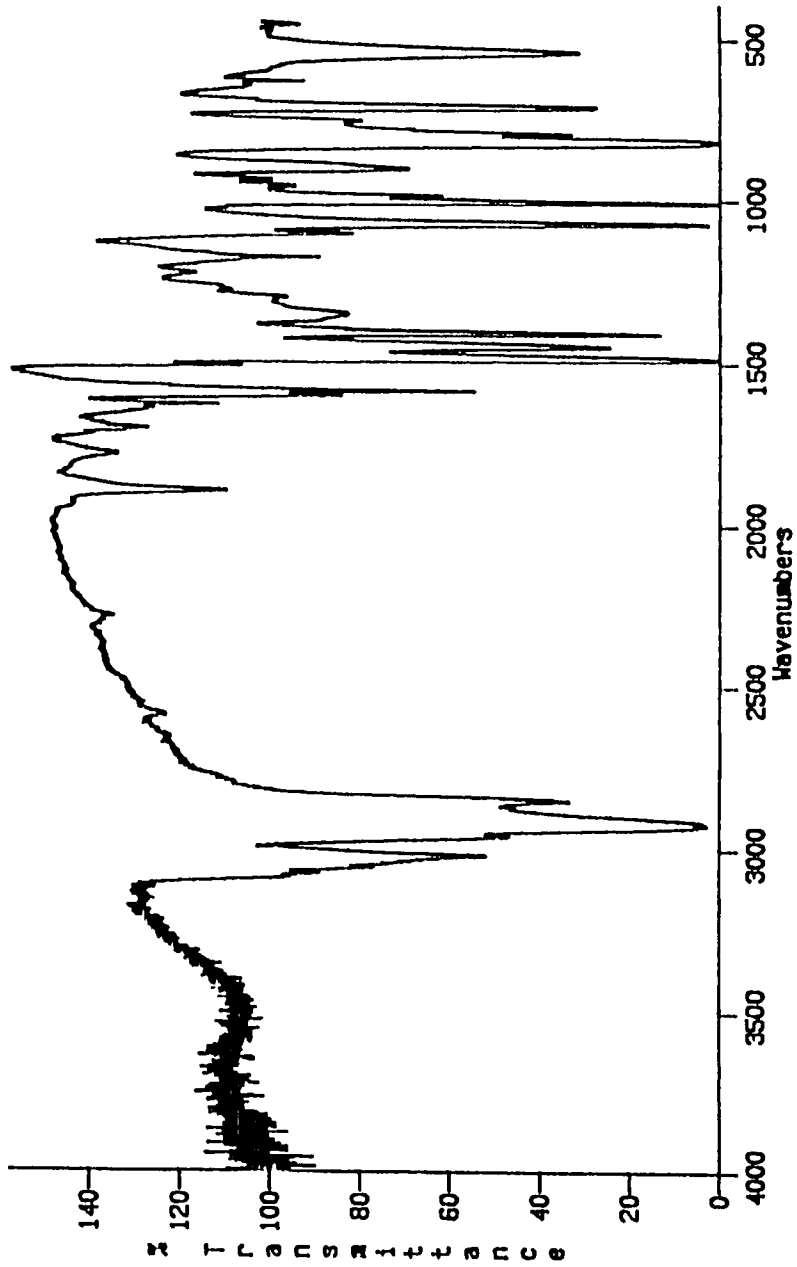


Figure 4-3. FTIR Spectrum of Poly(4-Bromostyrene/15% Divinylbenzene).

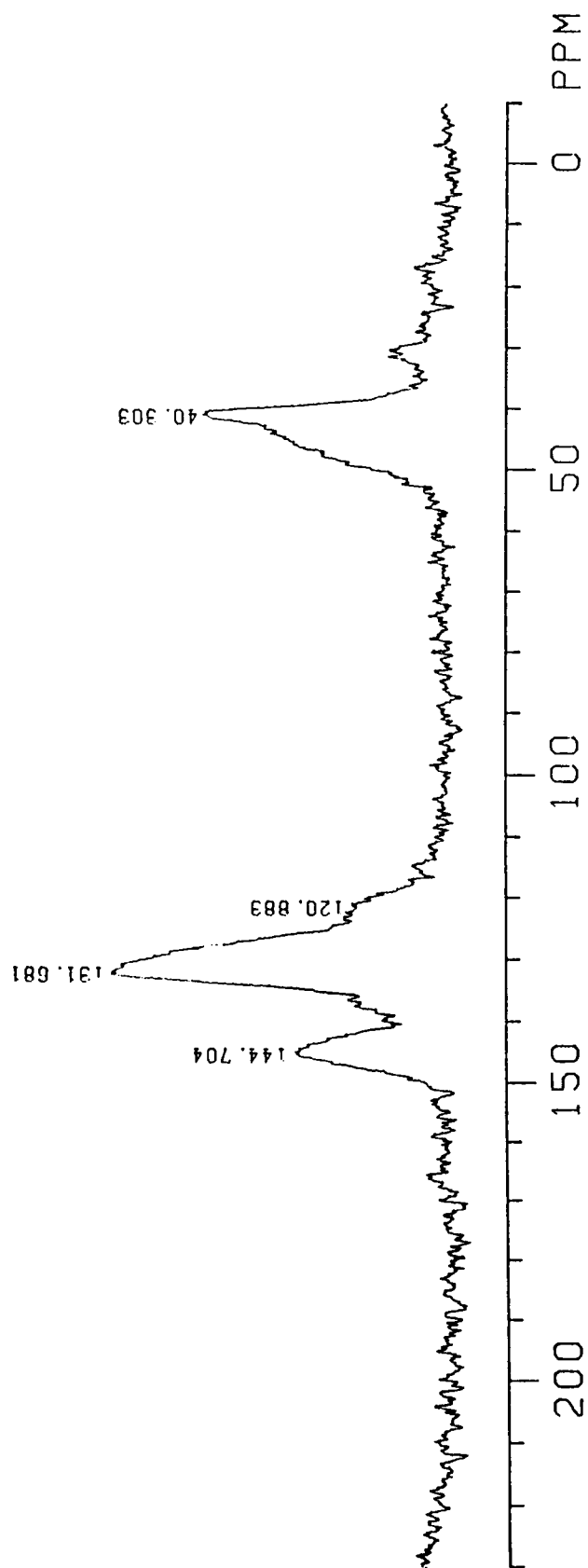


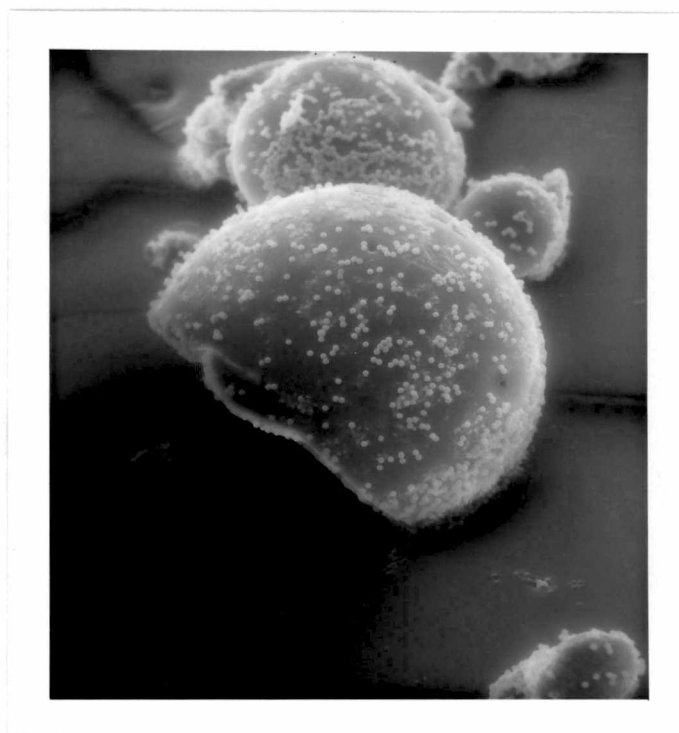
Figure 4-4. C-13 SS NMR Spectrum of Poly(4-Bromostyrene/15% Divinylbenzene).

polymerization, the mixture was heated to 100 °C for an additional 2 h, cooled, washed with HCl (pH 4, 4X 20 mL, 15 min.) and then with water (4 X 20 mL, 15 min.). The copolymer was filtered and air-dried to yield 10.56 g (86.0% yield) of poly(4-chlorostyrene/15% divinylbenzene) beads; ^{13}C SS-NMR: δ 144.66 (Ar-CH-CH₂), 137.00 (Ar-Cl), 128.82 (aromatic C), 45.44 (CH), 40.34 (CH₂); FT-IR (KBr): 3005 cm⁻¹ (CH₂), 2905 cm⁻¹ (CH), 1905-1660 cm⁻¹ (combinations and overtones), 1600 cm⁻¹, 1490 cm⁻¹, 1450 cm⁻¹ (C=C), 1090 cm⁻¹, 1000 cm⁻¹, 900 cm⁻¹ (CH), 830 cm⁻¹, 750 cm⁻¹ (Ar-H). Anal. Calcd for C₈H₇Cl/C₁₀H₁₀/C₁₀H₁₂ copolymer: C, 73.43; H, 5.95. Found: C, 75.26; H, 5.98. The SEM photograph and the IR and NMR spectra are shown in Figures 4-5 through 4-7.

4. Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene)

a. α -Bromo-p-Toluic Acid

The procedure of Tuleen and Hess was used⁷⁰. p-Toluic acid (27.23 g; 200.0 mmol), N-bromosuccinimide (35.95 g; 202.0 mmol), benzoyl peroxide (2.01 g; 80.0 mmol), and carbon tetrachloride (400 mL) were placed in a 1 L flask and refluxed for 1 h. The reaction was complete when evolution of bromine ceased. The contents were filtered, washed with hexanes (3 X 100 mL),



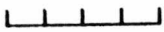

5 mm = 20 μ m

Figure 4-5. SEM of Poly(4-Chlorostyrene/15% Divinylbenzene).

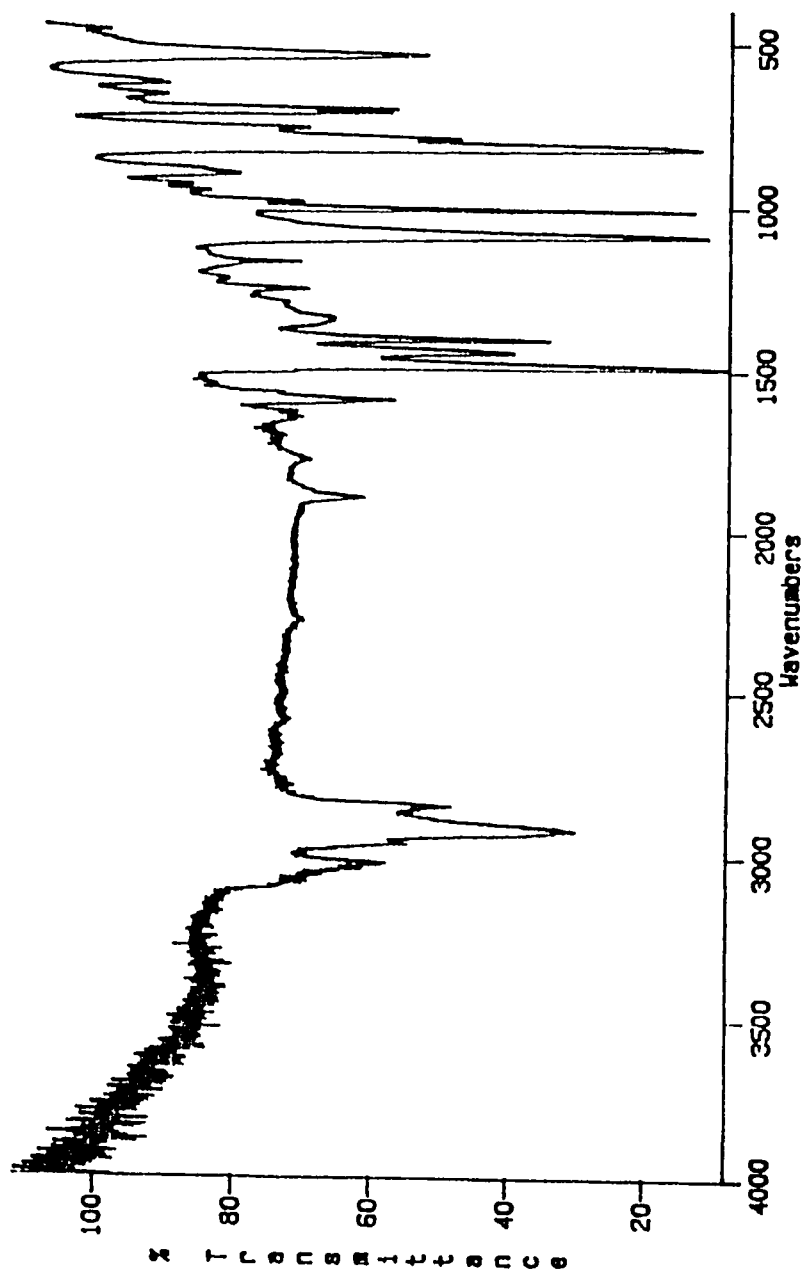


Figure 4-6. FTIR Spectrum of Poly(4-Chlorostyrene/15% Divinylbenzene).

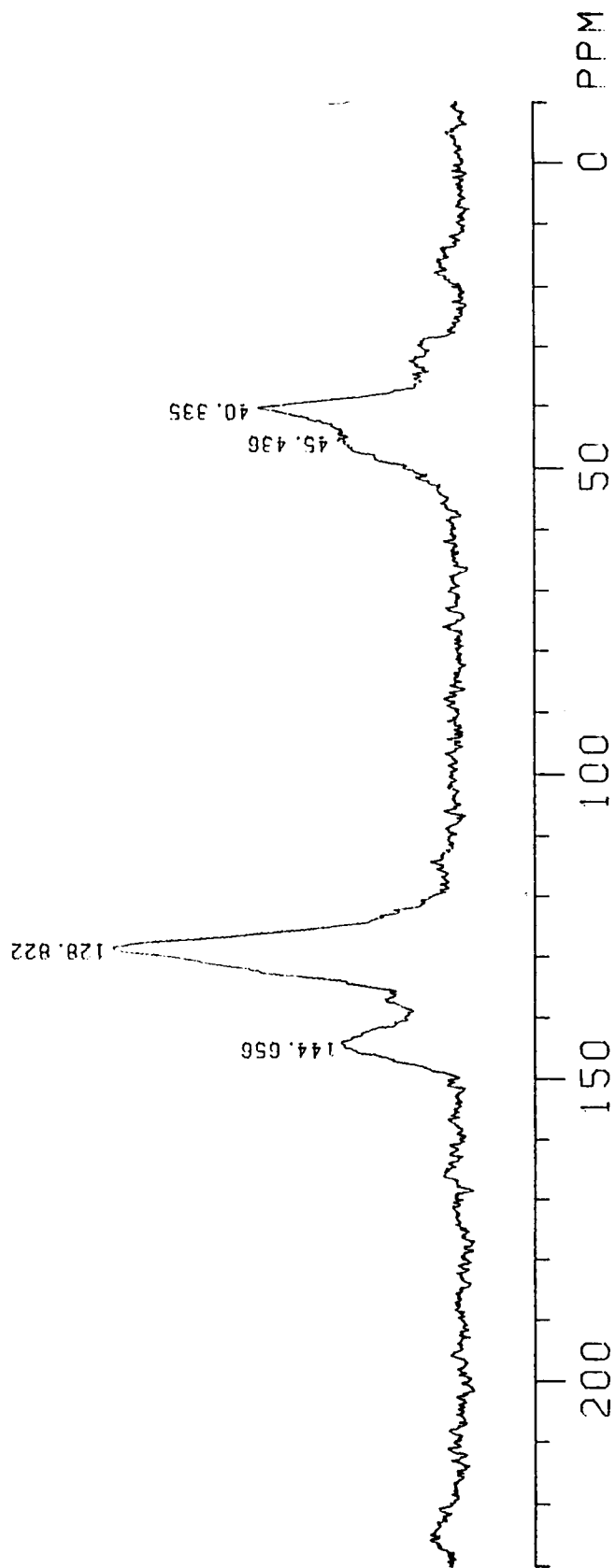


Figure 4-7. C-13 SS NMR Spectrum of Poly(4-Chlorostyrene/15% Divinylbenzene).

and the product was transferred to a conical flask. Water (500 mL) was added, and the mixture was refluxed briefly to dissolve any remaining succinimide. The remaining solid material was filtered while hot. This procedure was repeated, and the remaining solid was dissolved in THF (300 mL) and dried (MgSO_4). Filtration, followed by evaporation of the solvent, gave 13.45 g (69.00% yield) of α -bromo-*p*-toluic acid as a white solid; ^1H -NMR ($\text{DMSO}-d_6$): δ 7.92-7.54 (dd, 4H, AA'BB', aromatic H), 4.74 (s, 2H, CH_2Br); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 166.86 (COOH), 142.84 (aromatic $\text{C}-\text{COOH}$), 130.51 (aromatic $\text{C}-\text{CH}_2\text{Br}$), 129.67 (aromatic), 129.44 (aromatic), 32.28 (CH_2Br).

b. *p*-Carboxybenzyltriphenylphosphonium Bromide

The procedure of Broos, Tavernier, and Anteunis was used⁷¹. To a 500-mL round-bottomed flask containing *p*-carboxybenzyl bromide (10.78 g; 50.00 mmol) and acetone (300 mL) was added a solution of triphenylphosphine (13.12 g; 50.00 mmol) dissolved in acetone (50 mL). The flask was equipped with a magnetic stir bar and a reflux condenser. The mixture was refluxed for 1 h, and after cooling to 0 °C, the precipitated salt was filtered and washed with ether (2 X 50 mL) to

give after air-drying 30.28 g (72.00% yield) of p-carboxytriphenylphosphonium bromide as a powder; ^1H -NMR ($\text{DMSO}-d_6$): δ 7.93-7.66 (m, 17H, aromatic), 7.10-7.07 (m, 2H, aromatic), 5.30 (d, CH_2P); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 166.70 (COOH), 166.69, 135.20, 134.04, 133.96, 131.02, 130.21, 130.11, 129.56, 117.87, 117.19 (aromatic), 28.50, 28.00 (CH_2P).

c. 4-Vinylbenzoic Acid

The procedure described by Broos, Tavernier, and Anteunis was employed⁷¹. To a 250-mL round-bottomed flask equipped with a magnetic stir bar and an addition funnel were added 4-carboxybenzyltriphenylphosphonium bromide (9.41 g; 20.0 mmol) and aqueous formaldehyde (37%, 80 mL). Aqueous sodium hydroxide (6 g in 30 mL of water) was added with stirring over a 15 min. period. On initial addition of the sodium hydroxide solution the phosphonium salt dissolved, but on continued addition of base a white precipitate (triphenylphosphine oxide) formed. The contents were stirred for an additional hour, and the precipitate was filtered and washed with water. Acidification of the filtrate (HCl , pH 1) gave a

white precipitate, which was filtered and recrystallized from a 70:30 mixture of water and ethanol (500 mL) to afford 2.89 g (99.0% yield) of 4-vinylbenzoic acid as white plates; mp 139-141 °C (lit⁷² 142-143 °C); ¹H-NMR (DMSO-d₆): δ 7.91-7.57 (dd, 4H, AA'BB', aromatic H), 6.82-6.77 (m, 1H, H₂C=CHPh), 5.97 (d, 1H, J_{trans} = 17.50 Hz, HH'C=CHPh), 5.40 (d, 1H, J_{cis} = 10.50 Hz, HH'C=CHPh); ¹³C-NMR (DMSO-d₆): δ 167.05 (COOH), 141.31 (aromatic C-CH=CH₂), 135.86 (PhCH=CH₂), 129.93 (aromatic C-COOH), 129.68 (aromatic carbon ortho to COOH), 126.23 (aromatic carbon ortho to CH=CH₂), 117.00 (PhCH=CH₂); ¹³C-DEPT NMR (DMSO-d₆): positive peaks δ 135.86, 129.68, 126.23, negative peaks δ 117.00.

d. 4-Vinylbenzoic Acid

The procedure reported by Leebrick and Ramsden was followed⁷³. Magnesium (4.85 g) was charged under nitrogen to a flame-dried, 500-mL three-necked round-bottomed flask equipped with a condenser, a thermometer, and an addition funnel. Bromoethane (1.5 mL) in THF (25 mL) was added via cannula in order to activate the metal. The temperature rose to 42 °C. A solution of

4-chlorostyrene (12 mL) in THF (250 mL) was introduced through the addition funnel and then added dropwise over a 220 min. period. The reaction mixture was refluxed for 1 h and left to stir without heat overnight. The contents of the flask were then poured onto crushed dry ice and the carbonated mixture was acidified (10% H_2SO_4 , pH 2). The mixture was extracted with ether (3 X 350 mL), and the organic layer was added to a solution of potassium hydroxide (200 mL, 0.10 M). The layers were separated and the aqueous layer was extracted with ether (1 X 100 mL). To the aqueous layer was added H_2SO_4 (10%, 200 mL, pH 1-2). The precipitated product was filtered and the filtrate was extracted with chloroform (2 X 100 mL). The organic layer was concentrated in vacuo. The filtrate was then extracted with a 25:75 mixture of THF and ether (2 X 100 mL), and dried via rotary evaporation. Only the chloroform extractions gave a solid product, whereas the others afforded an oily, yellow compound. The acid/water/ CO_2 layer was extracted with chloroform (1 X 500 mL) and concentrated in vacuo. The solid contents were combined to afford 1.43 g (9.3% yield) of 4-vinylbenzoic acid as a white oligomer; mp 149-155 °C (lit⁷² 142-143 °C); $^1\text{H-NMR}$ (DMSO-d_6):

δ 7.91-7.57 (dd, 4H, AA'BB', aromatic H), 6.82-6.77 (m, 1H, $\text{H}_2\text{C}=\text{CHPh}$), 5.97 (d, 1H, $J_{\text{trans}} = 17.50$ Hz, $\text{HH}'\text{C}=\text{CHPh}$), 5.40 (d, 1H, $J_{\text{cis}} = 10.50$ Hz, $\text{HH}'\text{C}=\text{CHPh}$); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 167.05 (COOH), 141.31 (aromatic $\text{C}-\text{CH}=\text{CH}_2$), 135.86 ($\text{PhCH}=\text{CH}_2$), 129.93 (aromatic $\text{C}-\text{COOH}$), 129.68 (aromatic carbon ortho to COOH), 126.23 (aromatic carbon ortho to $\text{CH}=\text{CH}_2$), 117.00 ($\text{PhCH}=\text{CH}_2$).

e. Methyl 4-Vinylbenzoate

The procedure reported by Black was employed⁷⁴. Into a 100-mL Clear-Seal round-bottomed flask containing a solution of potassium hydroxide (11.22 g) in water (18.0 mL) was added ethanol (95%, 23.0 mL). A 500-mL Clear-Seal receiving flask containing 4-vinylbenzoic acid (5.52 g; 37.3 mmol) in ether was cooled in an ice water/salt bath with stirring. An ice cooled ether trap containing acetic acid (2.24 g; 100 mmol) was connected to the sidearm in order to trap any escaping diazomethane. A Clear-Seal separatory funnel was placed over the reaction vessel and charged with a solution of Diazald (11.23 g; 51.70 mmol) in ether (100 mL). The reaction vessel was warmed to 65 °C with a water

bath, and the Diazald solution was added dropwise over a 4.5 h period. (The rate of distillation should approximate the rate of addition). When all of the Diazald had been consumed, ether (23.0 mL) was slowly added and the distillation was continued. The yellow color persisted in both the reaction vessel and in the receiving flask but had disappeared from the condenser and from all the remaining glassware. The system was disassembled and acetic acid was slowly pipetted into both of the yellow solutions until they became clear. The ether, along with any methyl acetate that had formed, was removed via rotary evaporation. The crude product was dissolved in chloroform and washed with sodium carbonate (10%, 3 X 100 mL). The organic layer was dried (MgSO_4) and then concentrated in vacuo. The product was purified via column chromatography (5:95 ethyl acetate/hexanes eluant) to give 2.56 g (42% yield) of the ester as white needles; mp 35-36 °C; $^1\text{H-NMR}$ (CDCl_3): δ 8.00-7.45 (dd, 4H, AA'BB', aromatic H), 6.78-6.71 (dd, 1H, $\text{CH}_2\text{-CHPh}$), 5.86 (d, 1H, $J_{\text{trans}} = 17.58$ Hz, $\text{HH}'\text{C=CHPh}$), 5.34 (d, 1H, $J_{\text{cis}} = 10.50$ Hz, $\text{HH}'\text{C=CHPh}$), 3.91 (CH_3); $^{13}\text{CNMR}$ (CDCl_3): δ 166.84 (COOCH_3), 141.88 (aromatic C-CH=CH_2), 135.98 (PhCH=CH_2), 129.84 (aromatic carbon ortho to

COOCH₃), 129.23 (aromatic C-COOCH₃), 126.07 (aromatic carbon ortho to CH=CH₂), 116.41 (PhCH=CH₂), 52.03 (CH₃); ¹³C-DEPT NMR (CDCl₃): positive peaks δ 135.98, 129.84, 126.07, 52.03, negative peak δ 116.41.

f. Methyl 4-Vinylbenzoate

The procedure described by Vowinkel was followed⁷⁵. Into a 100-mL round-bottomed flask, under a nitrogen atmosphere, 4-vinylbenzoic acid (10.0 g; 67.6 mmol) was dissolved in dry THF (67.0 mL). To the flask was added O-methyl-N,N'-diisopropylisourea (11.76 g; 74.30 mmol, 110.0 mol%). The mixture was stirred at room temperature and was monitored by TLC. The reaction was complete within 18 h after which the solution was filtered and the THF was removed. The crude product was purified via column chromatography (5:95 ethyl acetate/hexanes eluant) to give 9.09 g (83.0% yield) of the ester as white needles; mp 35-36 °C; ¹H-NMR (CDCl₃): δ 8.00-7.45 (dd, 4H, AA'BB', aromatic H), 6.78-6.71 (dd, 1H, CH₂-CHPh), 5.86 (d, 1H, J_{trans} = 17.58 Hz, HH'C=CHPh), 5.34 (d, 1H, J_{cis} = 10.50 Hz, HH'C=CHPh), 3.91 (CH₃); ¹³C-NMR (CDCl₃): δ 166.84 (COOCH₃), 141.88 (aromatic C-CH=CH₂), 135.98 (PhCH=CH₂), 129.84 (aromatic

carbon ortho to COOCH_3), 129.23 (aromatic $\underline{\text{C}}$ - COOCH_3), 126.07 (aromatic carbon ortho to $\text{CH}=\text{CH}_2$), 116.41 ($\text{PhCH}=\underline{\text{CH}}_2$), 52.03 (CH_3); ^{13}C -DEPT NMR (CDCl_3): positive peaks δ 135.98, 129.84, 126.07, 52.03, negative peak δ 116.41.

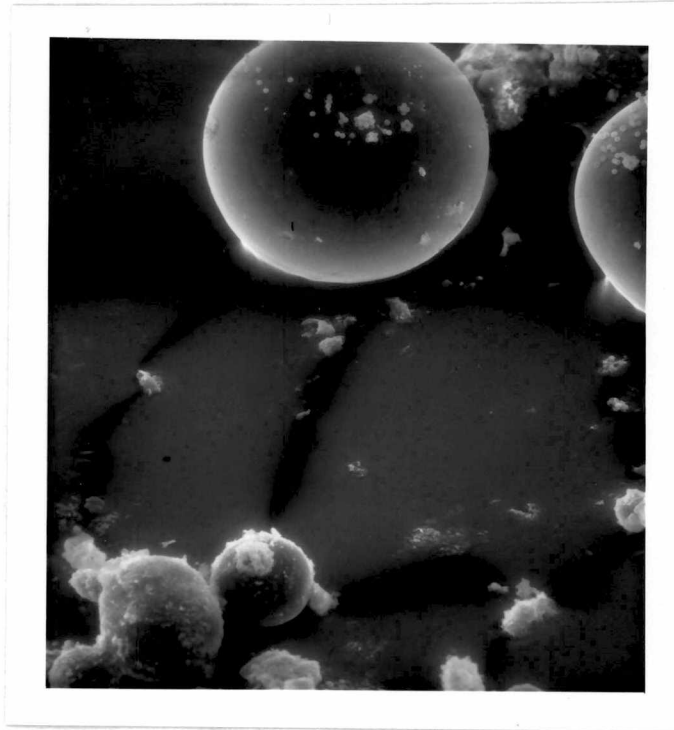
g. Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene)

The procedure reported by Alexandratos was followed⁵⁷. Into a 50-mL round-bottomed flask equipped with a condenser, a thermometer, and an overhead stirrer were placed an aqueous solution containing pharmagel (0.024 g) dissolved in water (2.5 mL) at 40 °C, and a solution of poly(diallyldimethyl-ammonium chloride) (0.275 g) and boric acid (0.15 g) in water (5.0 mL). The pH of the latter solution was adjusted to 10 by the dropwise addition of NaOH (33%, approximately 12 drops). For the preparation of 15% crosslinked copolymer, the organic phase consisted of methyl 4-vinylbenzoate (10.44 g; 64.40 mmol), divinylbenzene (containing 45% ethylvinylbenzene; 3.20 g; 13.5 mmol), and benzoyl peroxide (0.07 g; 0.3 mmol). The two phases were stirred for 2 min. then allowed to separate for 1 min. This process was repeated twice for a total of 9 min. Water

(10 mL) was added and the reaction mixture was heated from room temperature to 80 °C at a rate of approximately 7 °C/15 min. under an argon atmosphere which was maintained throughout the entire polymerization. The mixture was held at 80 °C for 10 h, and then allowed to cool. To ensure complete polymerization, the mixture was heated to 100 °C for an additional 2 h, cooled, washed with HCl (pH 4, 4X 20 mL, 15 min.) and then with water (4 X 20 mL, 15 min.). The copolymer was filtered and air-dried to yield 12.28 g (90.00% yield) of poly(methyl 4-vinylbenzoate/15% divinylbenzene) beads; ^{13}C SS-NMR: δ 166.54 (C=O), 151.00 (Ar-CH-CH₂), 137.00 (Ar-COOR), 129.20 (aromatic C), 47.00 (CH), 40.80 (CH₂); FT-IR (KBr): 3000 cm⁻¹ (CH₂), 2925 cm⁻¹ (CH), 1900-1660 cm⁻¹ (combinations and overtones), 1720 cm⁻¹ (C=O), 1600 cm⁻¹, 1500 cm⁻¹, 1425 cm⁻¹ (C=C), 1280 cm⁻¹, 1180 cm⁻¹ (C-O-C), 1100 cm⁻¹ (ArCOOR), 1100 cm⁻¹, 1025 cm⁻¹, 900 cm⁻¹ (CH), 825 cm⁻¹, 710 cm⁻¹ (Ar-H). Anal. Calcd for C₁₀H₁₀O₂/C₁₀H₁₀/C₁₀H₁₂ copolymer: C, 77.20; H, 6.53. Found: C, 76.04; H, 6.68. The SEM photograph and IR and NMR spectra are presented in Figures 4-8 through 4-10.

5. Poly(Styrenesulfonic Acid/4% Divinylbenzene)

The procedure of Pepper was followed here⁷⁶.



5 mm = 25 μm

Figure 4-8. SEM of Poly(Methyl 4-Vinylbenzoate/15% Divinylbenzene).

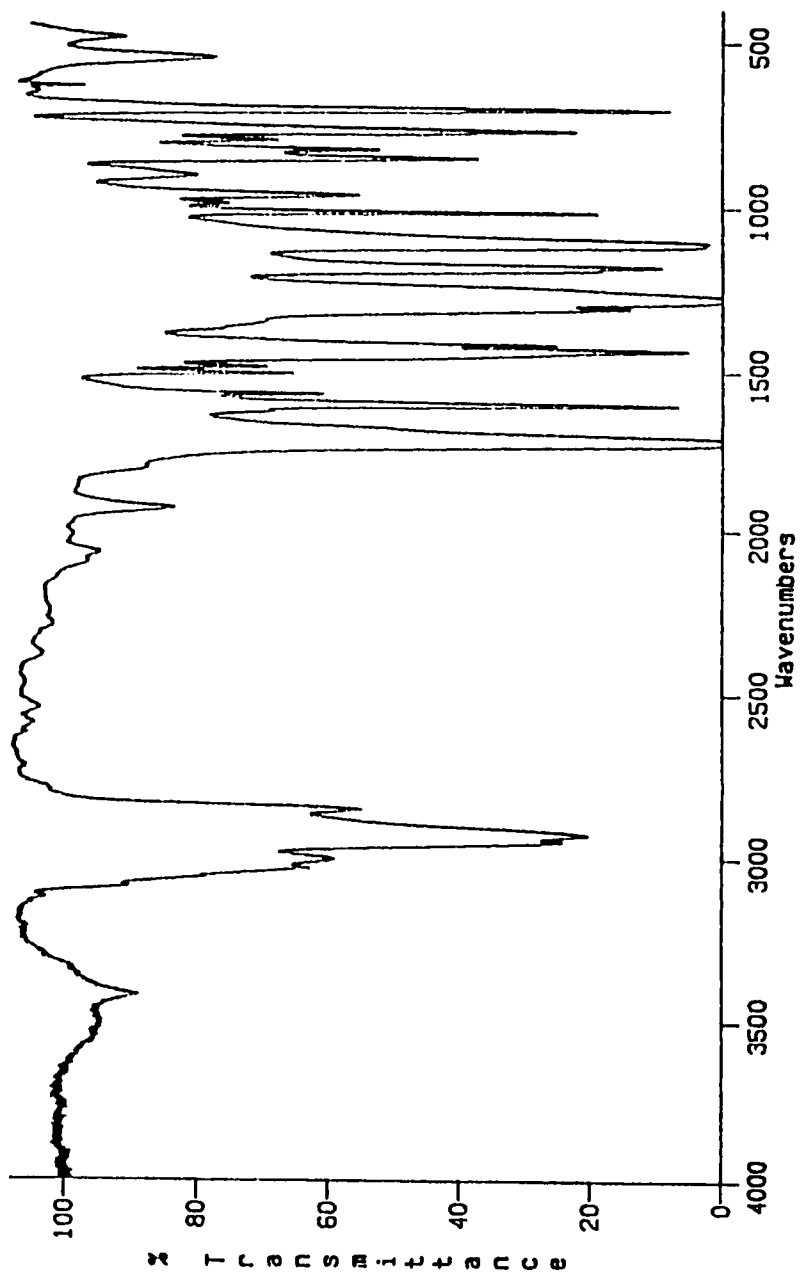


Figure 4-9. FTIR Spectrum of Poly(Methyl 4-Vinylbenzoate/ 15% Divinylbenzene).

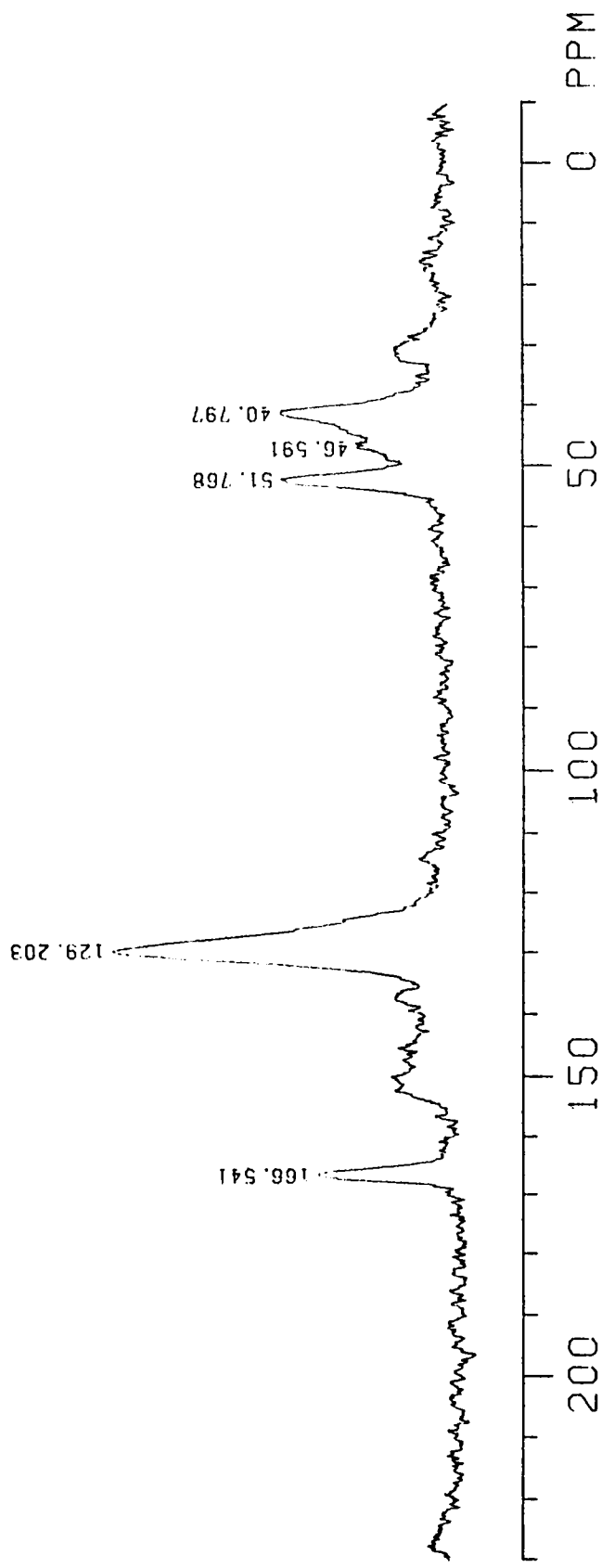
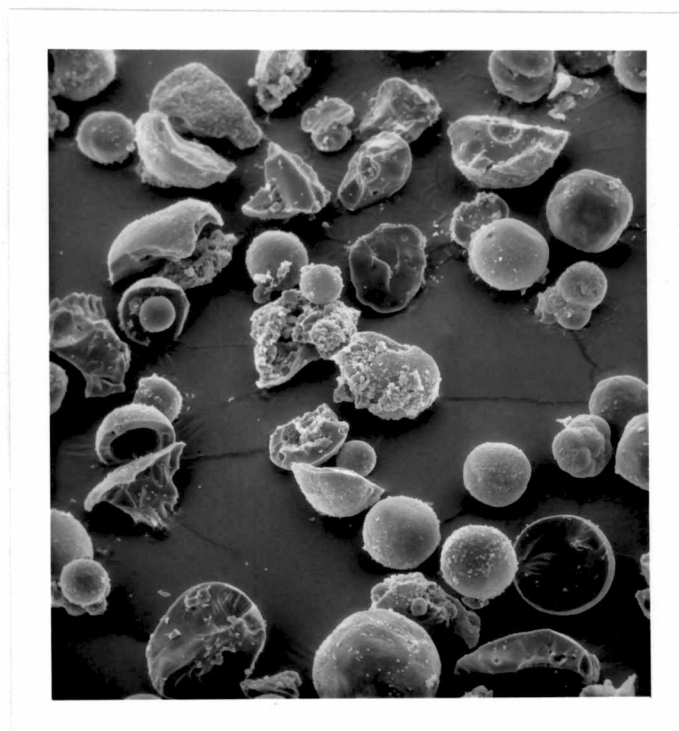


Figure 4-10. C-13 SS NMR Spectrum of Poly(Methyl 4-vinylbenzoate/15% Divinylbenzene).

Sulfuric acid (conc.; 40.0 mL) with silver sulfate (catalytic amount) was heated between 80-90 °C with stirring in a three-necked round-bottomed flask to which the styrene/4% divinylbenzene copolymer (5.00 g) was added. Owing to an exothermic reaction, the temperature rose to 100 °C, at which the temperature of the reactants was maintained for 6 h. The mixture was cooled, then slowly poured into a solution of sulfuric acid (50%; 50 mL), and further cooled via slow dilution with water. The resin was filtered and washed [water, NaCl (2 M), HCl (2 N), water]. After Kugelrohr distillation (0.6 mm, 25 °C, 1h; 0.5 mm, 45 °C, 24 h; 3mm, 80 °C, 12 h) a light brown, gummy resin remained (7.86 g; S content = 12.01%); ^{13}C SS-NMR: δ 149.90 (Ar-CH-CH₂), 139.26 (Ar-S), 127.60 (aromatic C), 45.78 (CH), 40.81 (CH₂); FT-IR (KBr): 3400 cm⁻¹ (OH), 3025 cm⁻¹ (CH₂), 2925 cm⁻¹ (CH), 1940-1650 cm⁻¹ (combinations and overtones), 1600 cm⁻¹, 1500 cm⁻¹, 1450 cm⁻¹ (C=C), 1400 cm⁻¹ (OH), 1175 cm⁻¹ (S=O), 1030 cm⁻¹, 900 cm⁻¹ (CH), 850 cm⁻¹, 775 cm⁻¹, 690 cm⁻¹ (Ar-H), 660 cm⁻¹ (C-S). The SEM photograph and IR and NMR spectra are shown in Figures 4-11 through 4-13.

6. Poly(Nitrostyrene/11% Divinylbenzene)

The procedure reported by Ergozhin and coworkers was employed⁷⁷. To a 250-mL three-necked




4 mm = 50 μ m

Figure 4-11. SEM of Poly(Styrenesulfonic Acid/4% Divinylbenzene).

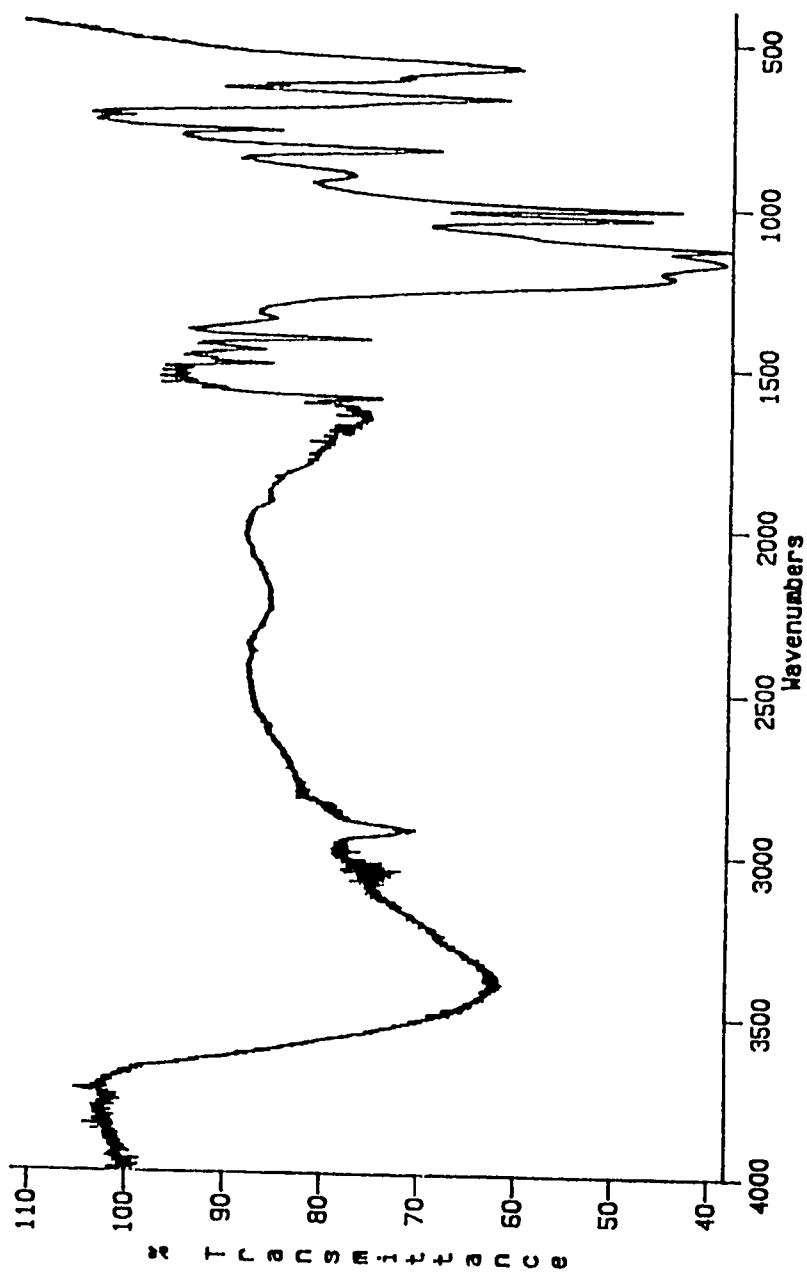


Figure 4-12. FTIR Spectrum of Poly(Styrenesulfonic Acid/4% Divinylbenzene).

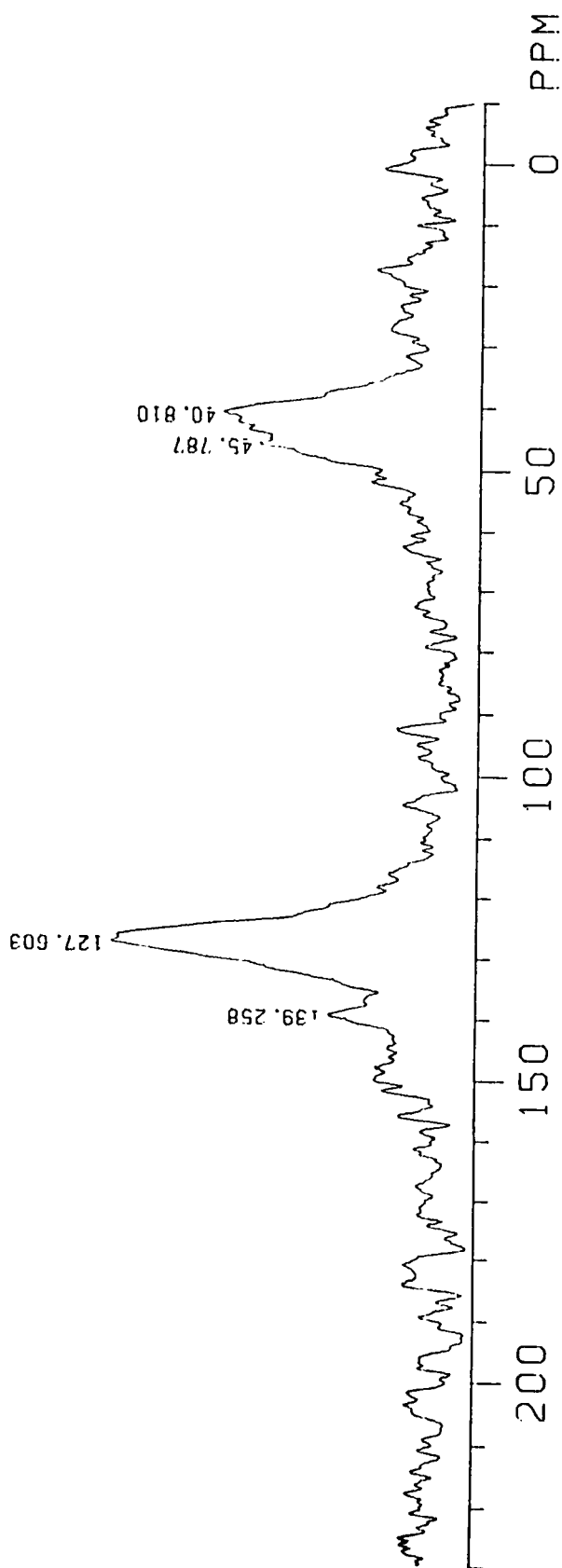
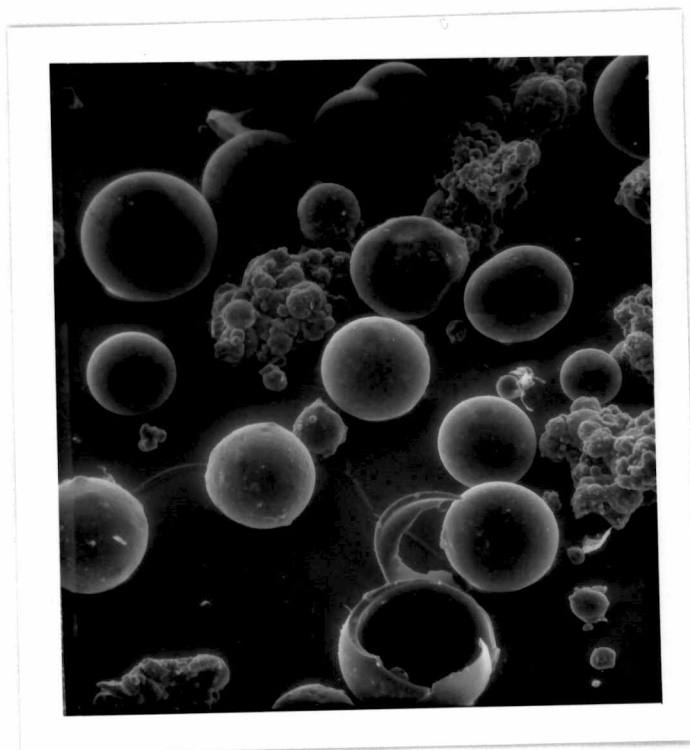


Figure 4-13. ^{13}C NMR Spectrum of Poly(styrenesulfonic Acid/4% Divinylbenzene).

round-bottomed flask containing the styrene/11% divinylbenzene copolymer (2.38 g) and equipped with a thermometer, a condenser, and an addition funnel was added dropwise a mixture of fuming nitric acid (27.0 mL) in concentrated sulfuric acid (30.0 mL) over a 1 h period at 5 °C. The mixture was stirred at 5 °C for 1 h, then washed with distilled water until a neutral pH was attained. The product was air-dried to give a light yellow resin (3.02 g; DF = 0.50); ^{13}C SS-NMR: δ 145.50 (Ar-CH-CH_2), 142.00 (Ar-N), 128.04 (aromatic C), 48.11 (CH), 40.95 (CH_2); FT-IR (KBr): 3025 cm^{-1} (CH_2), 2930 cm^{-1} (CH), 1940-1725 cm^{-1} (combinations and overtones), 1600 cm^{-1} , 1500 cm^{-1} , 1390 cm^{-1} (C=C), 1525 cm^{-1} (N-O), 1350 cm^{-1} (N-O), 900 cm^{-1} (CH), 850 cm^{-1} , 750 cm^{-1} , 700 cm^{-1} (Ar-H). Anal. Calcd for the nitrated copolymer: C, 76.44; H, 6.14; N, 5.31. Found: C, 73.07; H, 6.10; N, 5.45. The SEM photograph and IR and NMR spectra are presented in Figures 4-14 through 4-16.

7. Poly(Chloromethylstyrene/11% Divinylbenzene)

The procedure of Ranganathan and coworkers was followed⁷⁸. The styrene/11% divinylbenzene copolymer (6.00 g) was suspended under nitrogen in a solution of chloromethyl methyl ether (12.0 mL; 158 mmol) and dry chloroform (45 mL) in an oven-dried flask and allowed to stir at room temperature for 2 h. Tin




4 mm = 50 μ m

Figure 4-14. SEM of Poly(Nitrostyrene/11% Divinylbenzene).

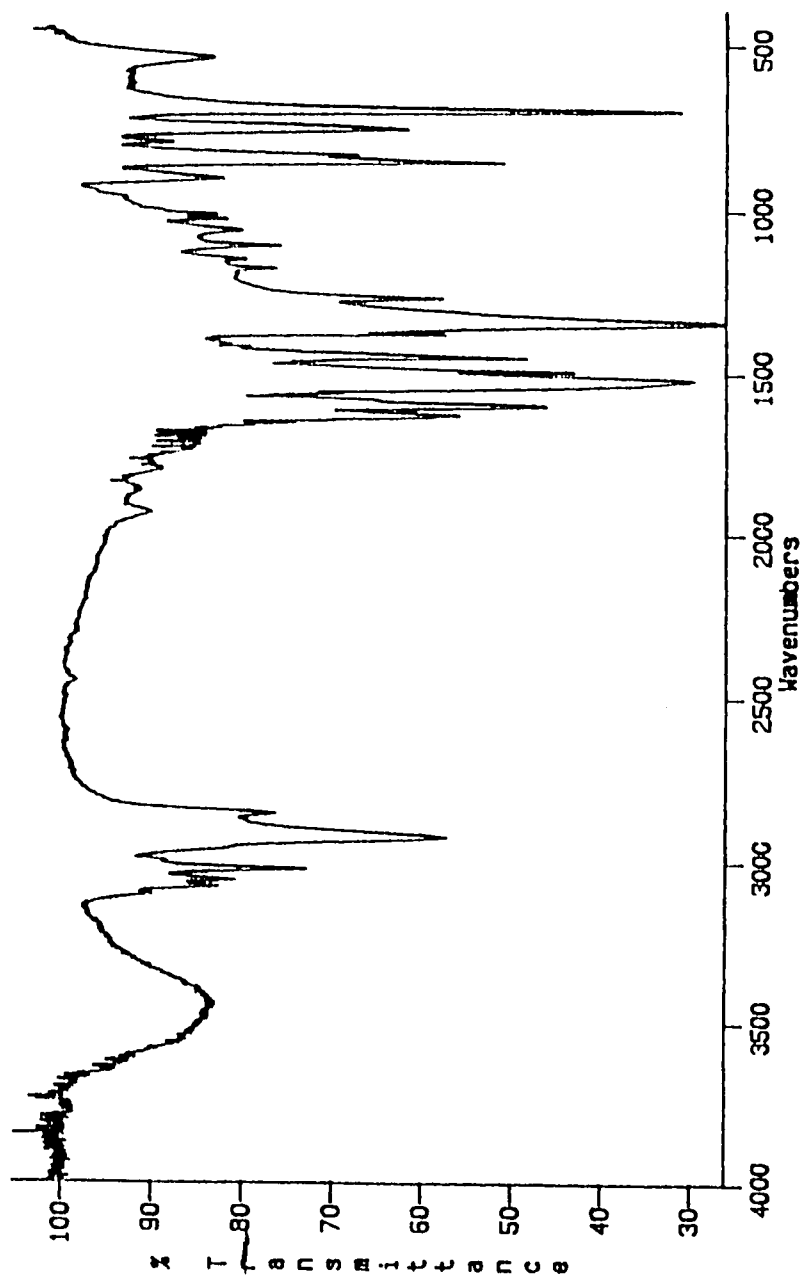


Figure 4-15. FTIR Spectrum of Poly(Nitrostyrene/11% Divinylbenzene).

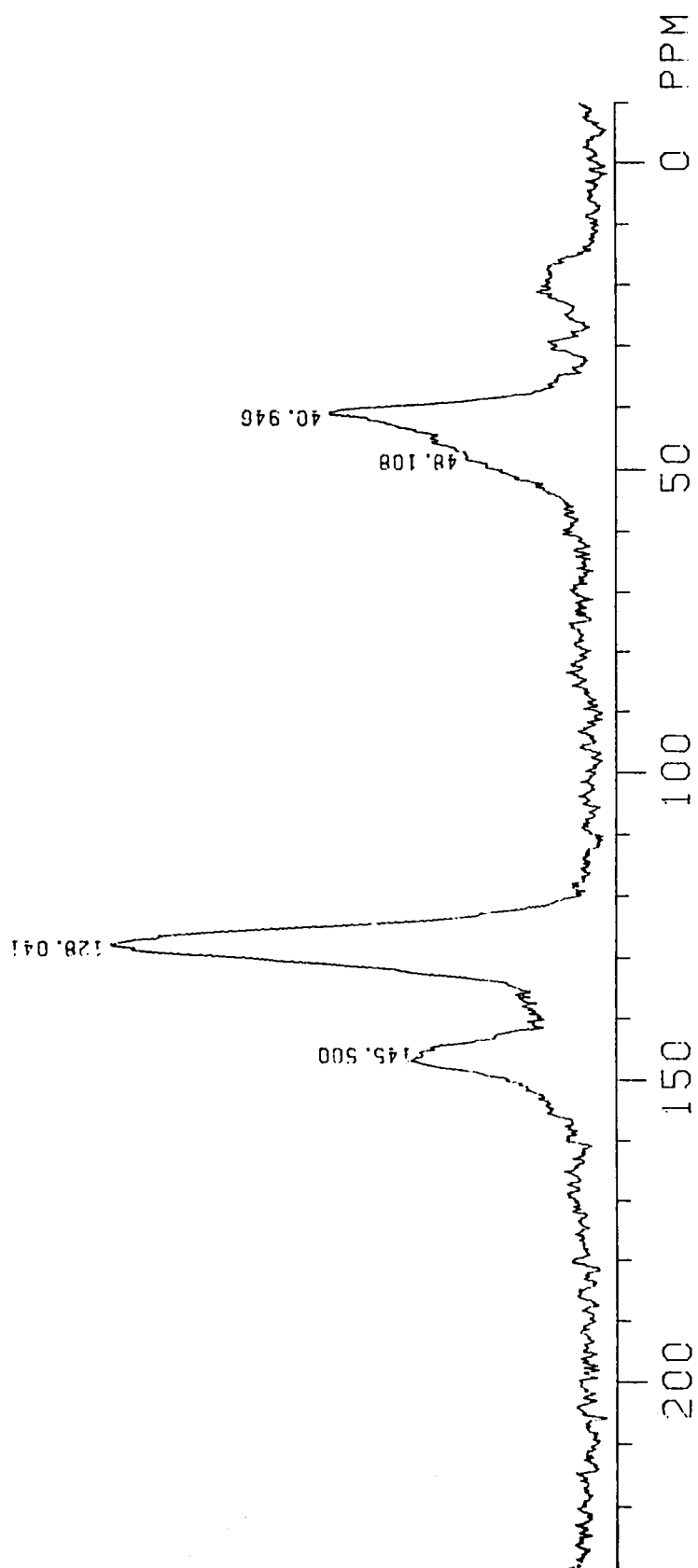
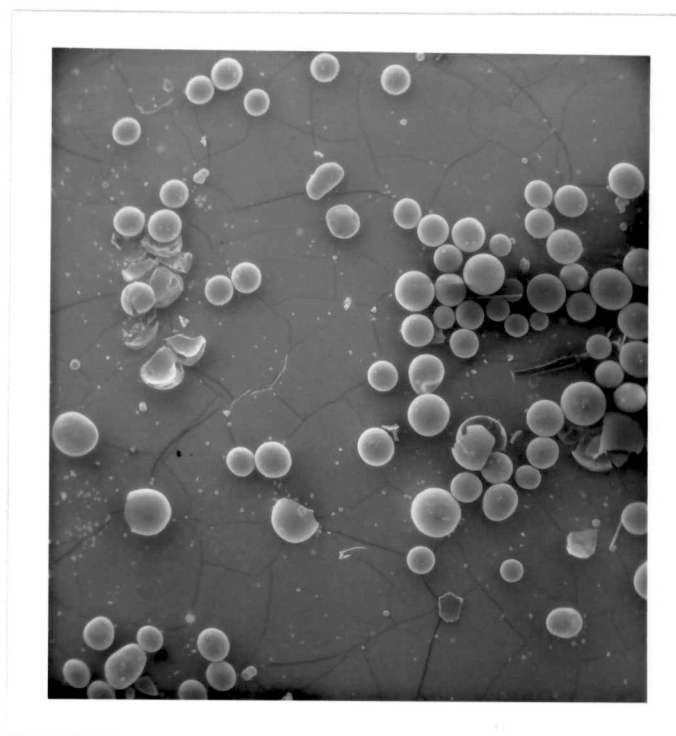


Figure 4-16. C-13 SS NMR Spectrum of Poly(Nitrostyrene/11% Divinylbenzene).

(IV) chloride (2 mL) was added dropwise, followed by an additional lot of chloromethyl methyl ether (6.0 mL; 79 mmol). The reaction mixture was stirred for an additional 4 h, filtered, and then washed repeatedly with methanol, chloroform, dioxane-water (3:1), dioxane-3 N HCl (3:1), dioxane, dioxane-water (3:1), water, and methanol (2 X 100 mL each). The product was dried via Kugelrohr distillation (1 mm, 60 °C, 5 h) to afford a yellow resin (7.20 g; DF = 0.44); ^{13}C SS-NMR: δ 146.0 (Ar-CH-CH_2), 136.00 ($\text{Ar-CH}_2\text{Cl}$), 128.8 (aromatic C), 46.6 (CH), 41.0 (CH_2); FT-IR (KBr): 3010 cm^{-1} (CH_2), 2905 cm^{-1} (CH), 1930-1675 cm^{-1} (combinations and overtones), 1600 cm^{-1} , 1480 cm^{-1} , 1440 cm^{-1} (C=C), 1260 cm^{-1} (CH_2Cl), 1100 cm^{-1} (CH), 870 cm^{-1} , 810 cm^{-1} , 700 cm^{-1} (Ar-H), 750 cm^{-1} (CH_2Cl). Anal. Calcd for chloromethylated copolymer: C, 81.20; H, 6.91; Cl, 11.88. Found: C, 78.14; H, 6.87; Cl, 11.81. The SEM photograph and IR and NMR spectra are presented in Figures 4-17 through 4-19.

8. Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene)

The procedure reported by Doscher and coworkers was used⁷⁹. A suspension of the chloromethylated matrix (3.00 g; 11% divinylbenzene) in methanol (30.0 mL) and dimethylsulfide (22.5 mL) was stirred for



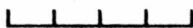

6 mm = 500 μ m

Figure 4-17. SEM of Poly(Chloromethylstyrene/11% Divinylbenzene).

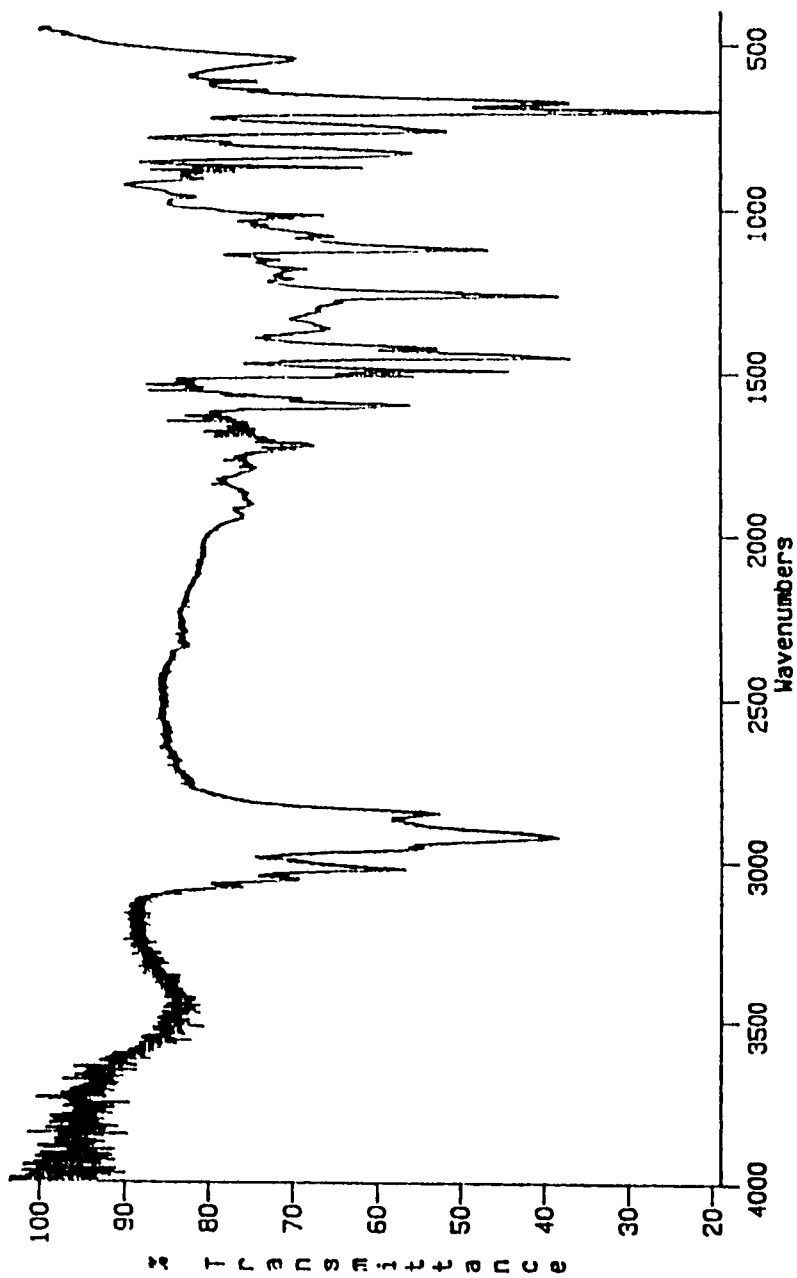


Figure 4-18. FTIR Spectrum of Poly(Chloromethylstyrene/11% Divinylbenzene).

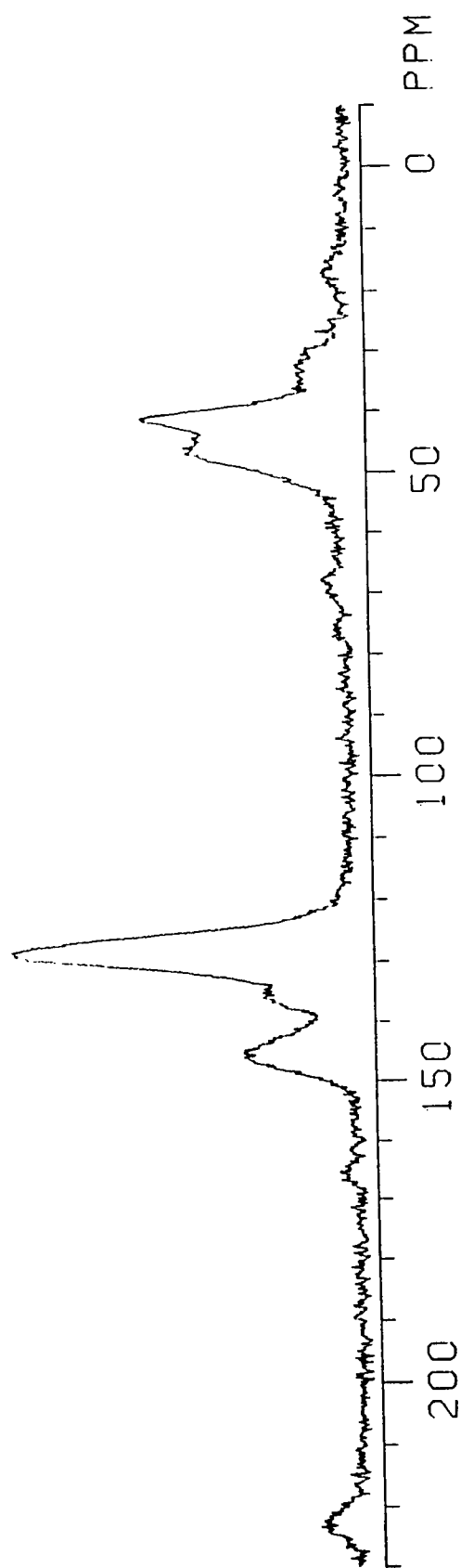


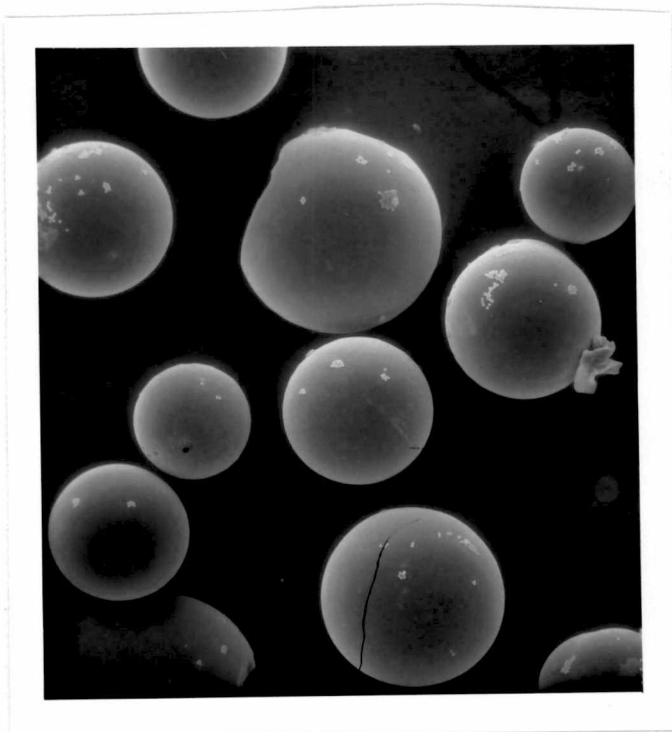
Figure 4-19. C-13 SS NMR Spectrum of Poly(Chloromethylstyrene/11% Divinylbenzene).

96 h at room temperature, after which the product was filtered and washed with methanol (3 x 100 mL). A saturated solution of sodium sulfite (1.40 M, 100 mL, 10 X excess) was added to the resin. The solution was stirred at room temperature for 5 h. Over the next 48 h the reaction temperature was increased to 80 °C. The resin was filtered and then suspended overnight in a solution of HCl (2.4 M, 200 mL), filtered, and washed with deionized water (3 X 100 mL), and then dried in a vacuum dessicator (<1 mm, 1.5 h) to give the methylsulfonated resin (2.50 g; DF = 0.88; S content = 7.08%); ^{13}C SS-NMR: δ 146.0 (Ar-CH-CH_2), 136.0 ($\text{Ar-CH}_2\text{SO}_3\text{H}$), 128.8 (aromatic C), 47.0 (CH), 40.8 (CH_2); FT-IR (KBr): 3400 cm^{-1} (OH), 3025 cm^{-1} (CH_2), 2910 cm^{-1} (CH), 1930-1690 cm^{-1} (combinations and overtones), 1600 cm^{-1} , 1500 cm^{-1} (C=C), 1400 cm^{-1} (S=O), 1175 cm^{-1} (S=O anhydrous), 1100 cm^{-1} (CH), 825 cm^{-1} , 750 cm^{-1} , 700 cm^{-1} (Ar-H), 700 cm^{-1} (C-S). The SEM photograph and IR and NMR spectra are presented in Figures 4-20 through 4-22.

C. Results and Discussion

1. Polymerization of Monomers

Three derivatives were synthesized by the polymerizations of their monomers. 4-Bromostyrene and 4-chlorostyrene, which were commercially




6 mm = 50 μ m

Figure 4-20. SEM of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).

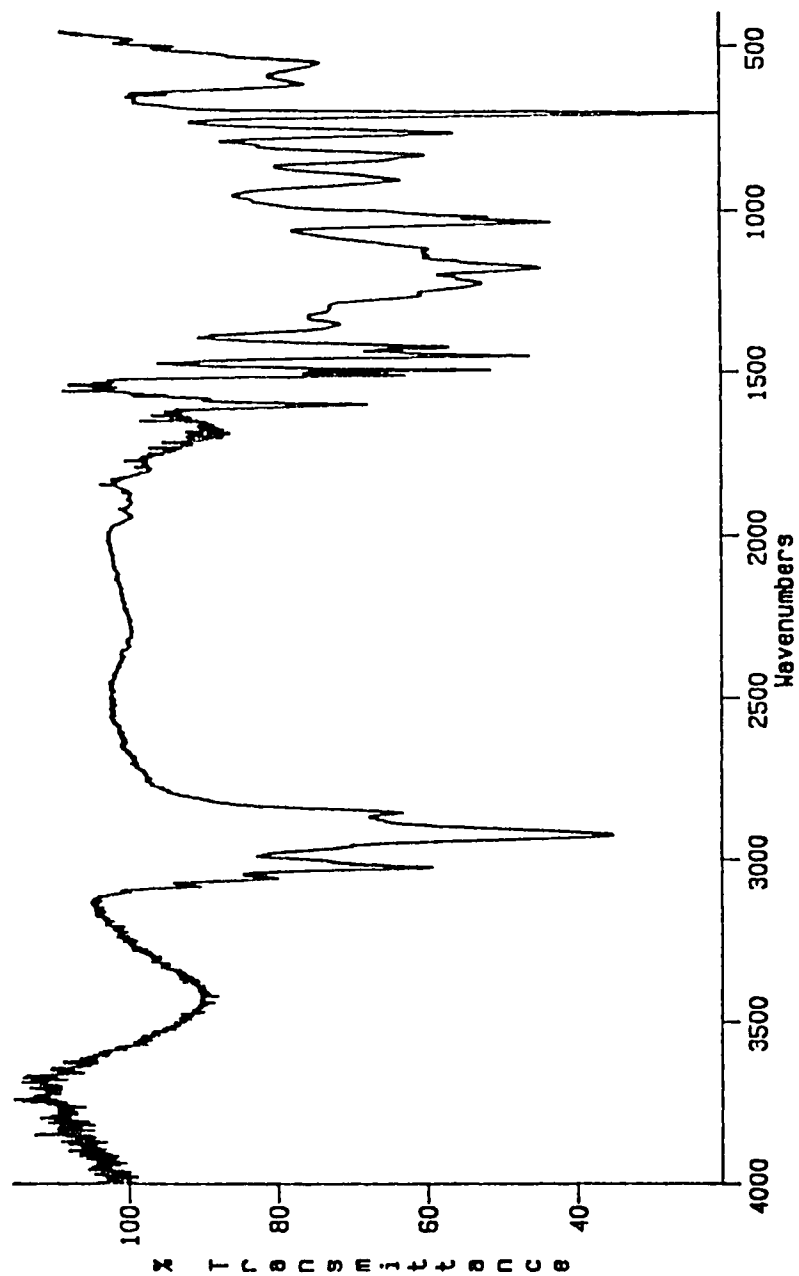


Figure 4-21. FTIR Spectrum of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).

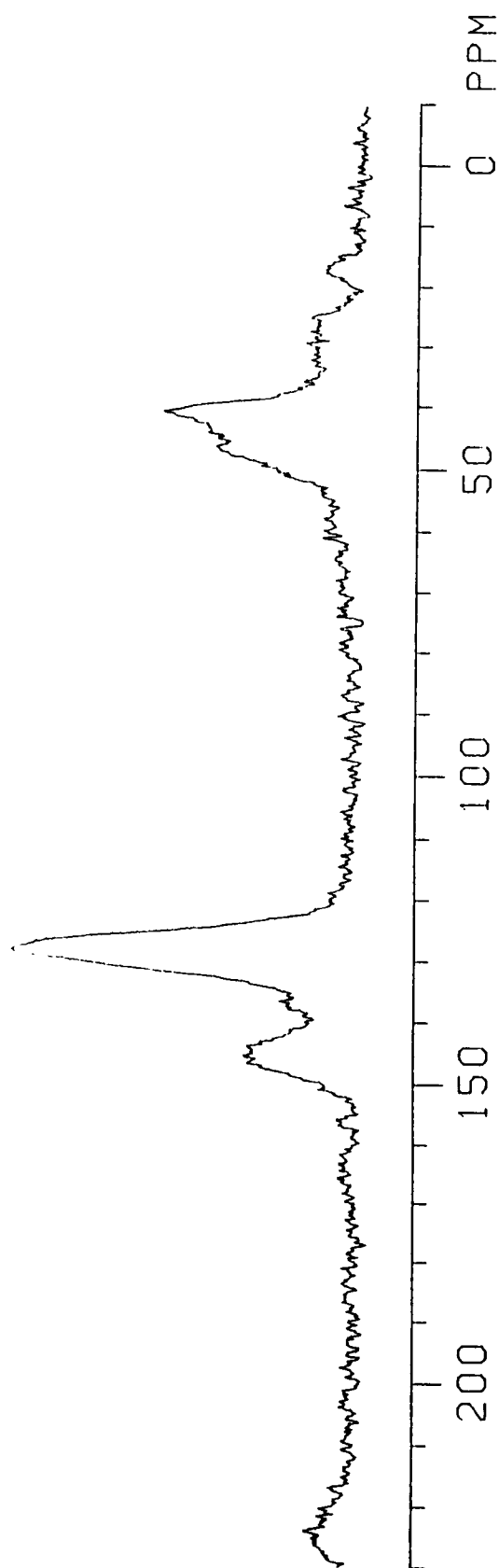
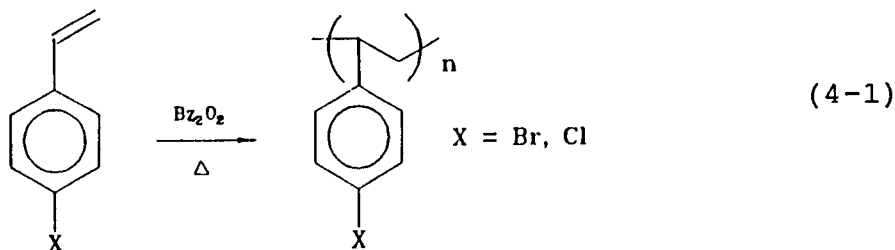
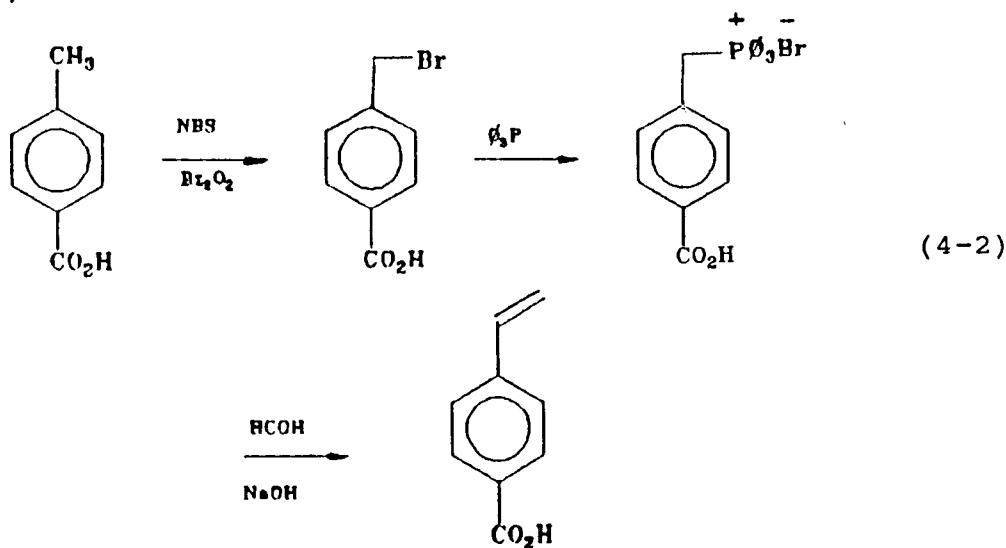


Figure 4-22. C-13 SS NMR Spectrum of Poly(Styrenemethylsulfonic Acid/11% Divinylbenzene).

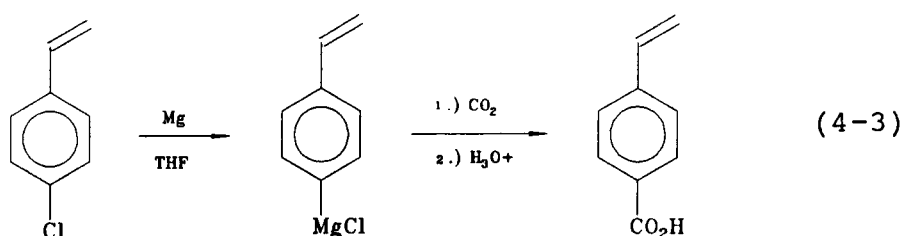
available, were simply polymerized to their corresponding polymers⁵⁷ (Eqn. 4-1).



Another monomer, methyl 4-vinylbenzoate, was not commercially available, and was prepared in the following manner. Beginning with p-toluic acid, bromination of the methyl group was accomplished using N-bromosuccinimide and benzoyl peroxide⁷⁰. The double bond functionality was introduced via the Wittig reaction of α -bromo-p-toluic acid with triphenylphosphine, formaldehyde, and sodium hydroxide⁷¹ (Eqn. 4-2).



This procedure gave yields in close agreement to the literature values. Another method chosen to prepare this monomer utilized the reaction between the Grignard reagent of 4-chlorostyrene and carbon dioxide⁷³ (Eqn. 4-3).



Because this procedure was largely unsuccessful, the former method using the Wittig reaction was employed. Esterification of the acid became a necessity due to its insolubility in divinylbenzene. This was accomplished by two routes. The first employed diazomethane as the methylating agent (which required the use of a Diazald kit) (Figure 4-23)⁷⁴ (Eqn. 4-4), while the second method utilized O-methyl-N,N'-diisopropyl-isourea for the methylation⁷⁵ (Eqn. 4-5).

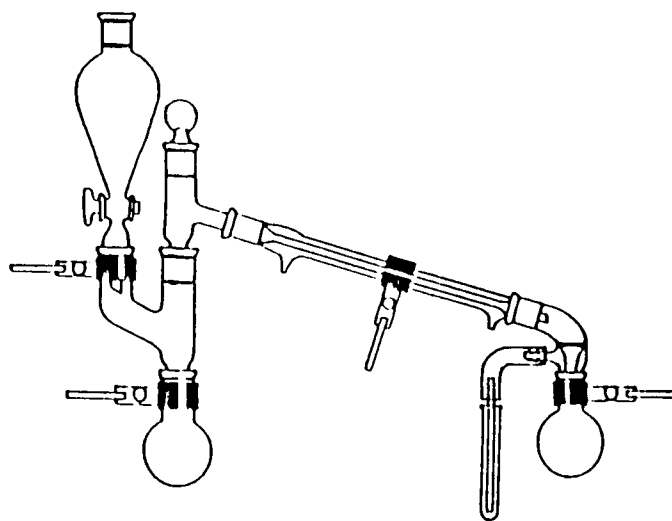
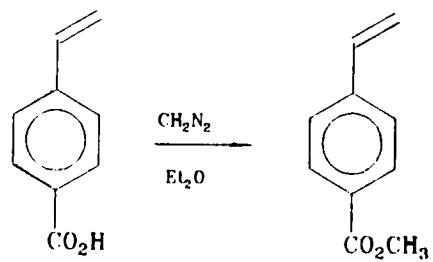
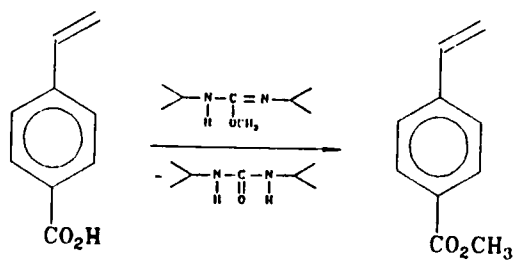


Figure 4-23. Diazald Kit Assembly.



(4-4)

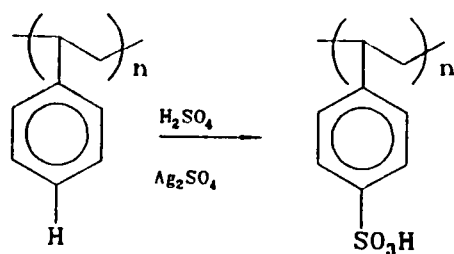


(4-5)

Because the solubility of methyl 4-vinylbenzoate in divinylbenzene was low, careful heating of the monomer with a heat-gun was required to induce dissolution. Once this was accomplished, the polymerization of the monomer was attempted via the suspension technique. Due to the low solubility of the ester, the polymerization was unsuccessful, and the reactions were stopped prematurely due to agglomeration of the early formed polymer.

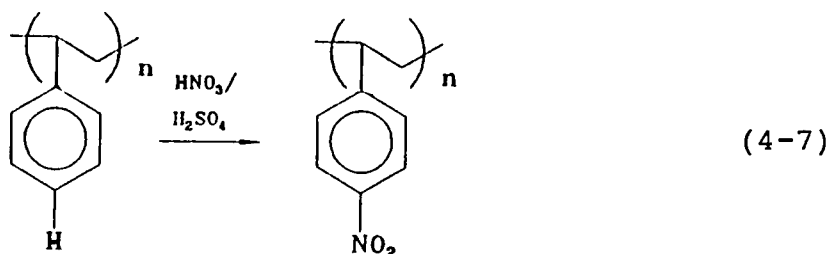
2. Functionalization of Poly(Styrene/Divinylbenzene)

Four derivatives were prepared by the functionalization of the poly(styrene/divinylbenzene) resins. Sulfonated copolymers were prepared by the treatment of the resins with concentrated sulfuric acid and silver sulfate⁷⁶ (Eqn. 4-6).

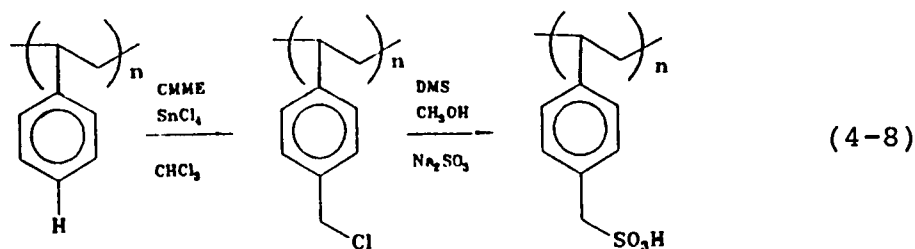


(4-6)

Nitration of the resins with fuming nitric acid in sulfuric acid gave the analogous nitrated copolymers⁷⁷ (Eqn. 4-7).



The direct nitration reaction was performed because pilot studies involving nitrostyrene monomers were largely unsuccessful. The polymerization of 3-nitrostyrene was investigated. Due to the strong electron withdrawing ability of the nitro group, no reaction occurred. The final two derivatives were synthesized by subjecting the resins to treatment with chloromethyl methyl ether and tin (IV) chloride to yield the chloromethylated copolymers⁷⁸. These were subsequently converted to the methylsulfonated copolymers by reaction with dimethylsulfide in methanol followed by the addition of sodium sulfite⁷⁹ (Eqn. 4-8).



D. Conclusion

A variety of functionalized poly(styrene/divinylbenzene) derivatives were prepared and characterized. These were then subjected to pyrolysis in the belief that they would generate higher yields of carbonized beads than the unsubstituted materials discussed in Chapters II and III. The pyrolysis of these derivatives is the subject of the next chapter.

CHAPTER V

PYROLYSIS OF POLY(STYRENE/DIVINYLBENZENE) DERIVATIVES

A. Introduction

Due to the unsatisfactory pyrolysis results obtained with the poly(styrene/divinylbenzene) resins, several functionalized derivatives of these resins were synthesized and pyrolyzed. In addition to the incorporation of a reducible functional group into the polymer structure, four levels of crosslinking were investigated for each derivative. The selection of the various functional groups was made based on the ability of the group to be reduced via the evolution of a small molecule (SO_2 , CO_2 , Cl_2 , Br_2 , N_2 , NO_2 , H_2S)^{60,61,63}. The formation of new carbon-carbon bonds during the reduction increases the crosslinking and the thermal stability of the polymers, thereby providing higher carbon yields (Figure 5-1). Another attractive property of the functionalized polymers is their retention of the macroporous structure with uniform shrinkage after heating which is attributed to the additional crosslinking through sites originally supporting the functional groups^{50,56,66}.

The conditions for pyrolysis were established during the experiments with the non-functionalized polymers. These conditions entail a slow heating rate ($0.5\text{ }^\circ\text{C}/\text{min}$) and a temperature range of room temperature to about $800\text{ }^\circ\text{C}$ in an inert atmosphere (nitrogen or argon).

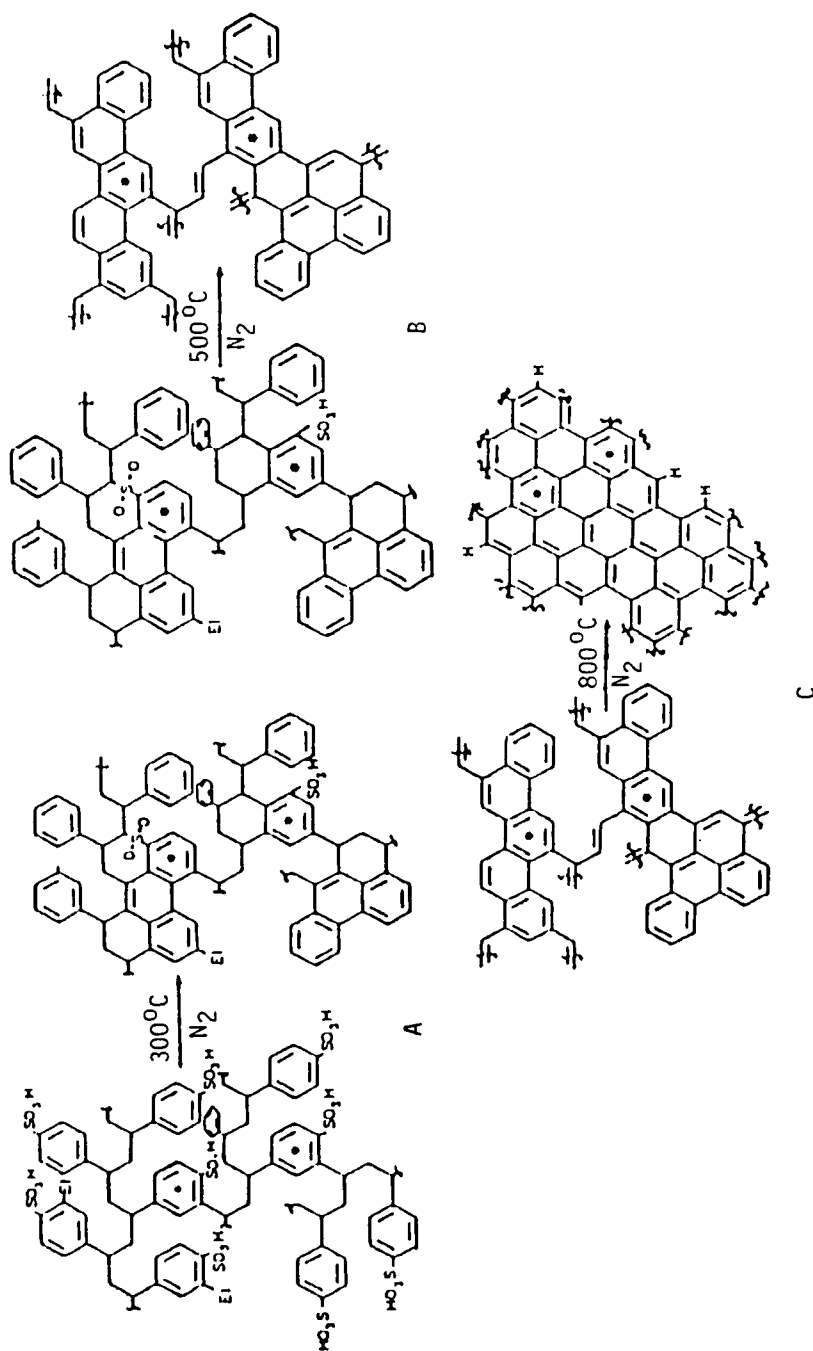


Figure 5-1. Proposed Chemical Structures for the Pyrolysis of Sulfonated Styrene/Divinylbenzene Copolymer A) Room Temperature to 300°C B) 300°C to 500°C C) 500°C to 800°C .

The thermal behavior of the polymers during pyrolysis was of interest; therefore, in order to observe the thermal decompositions, thermal gravimetric studies were performed on those derivatives which provided ideal pyrolysis results, (e.g., high carbon yields with retention of shape). In thermal gravimetric analysis (TGA) a sensitive microbalance is used to follow the weight change of a sample as a function of temperature^{56,80}. Two sample crucibles are heated in a controlled environment at a precisely programmed rate. One sample is a standard of known thermal behavior while the other sample is the unknown polymer of interest. Reaction product gases are drawn into a quadropole mass analyzer and identified by their mass-charge ratios⁸⁰.

B. Experimental

1. General

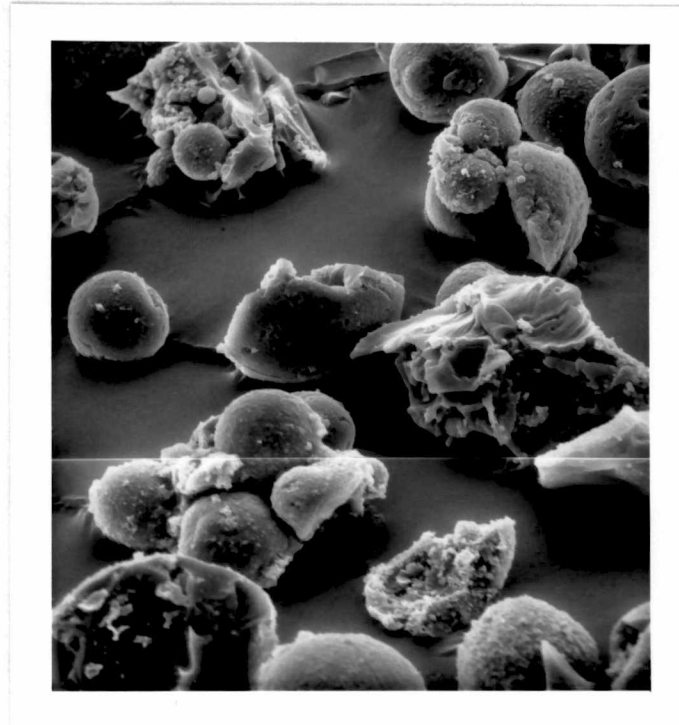
All pyrolysis experiments were conducted in a Trans-Temp 6" quartz furnace with the temperature programmed using a Therm-X LFE #2010 temperature controller. The temperature was monitored with a Kipp and Zonen Model #BD41 strip chart recorder. A chromel-alumel thermocouple was used to convey heat readings from the furnace to the temperature controller. Argon flow rates were measured with a Gasmet gas chromatography flow meter and found to be <30 cc/min. Thermal Gravimetric Analyses were recorded on a Mettler TA 4500 System using nitrogen as the carrier gas.

2. Sulfonated Resin

The sulfonated resin (2.80 g, 4% divinylbenzene) was placed between two ceramic boats, wrapped with copper wire, and placed in the quartz tube. The furnace was purged with argon to maintain a slight positive pressure, and the argon was released into a mineral oil bubbler (where the flow was measured) and then into a hypochlorous acid trap. The temperature controller was programmed to increase the furnace temperature from room temperature to about 800 °C at a rate of 0.5 °C/min. After reaching approximately 800 °C, the controller automatically turned off and the furnace was allowed to cool to room temperature under an argon flow. This afforded 1.10 g (92.0% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 88.46; H, 1.09. The SEM photograph is presented in Figure 5-2.

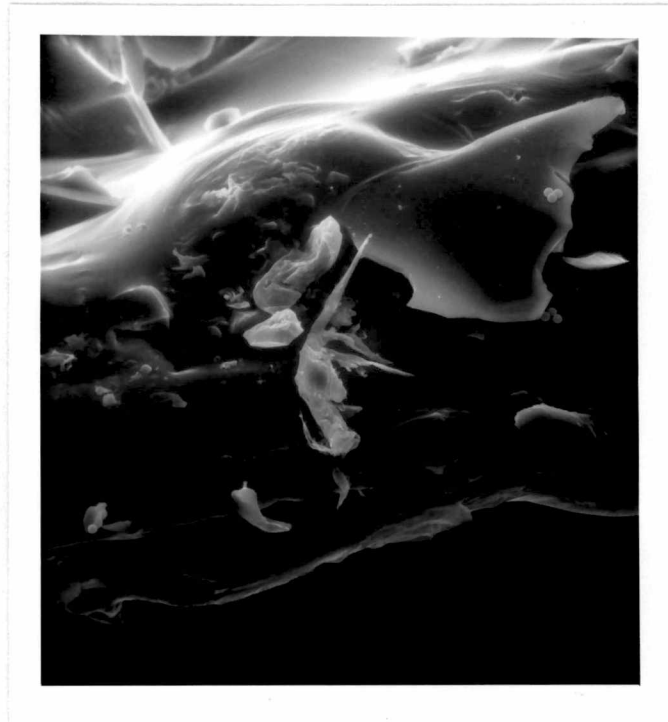
3. Methylcarboxylated Resin

The methylcarboxylated resin (2.00 g; 15% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.27 g (16% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 93.06; H, 0.72. The SEM photograph is shown in Figure 5-3.




4 mm = 12 μm

Figure 5-2. SEM of Pyrolyzed Sulfonated Resin.



5 mm = 12.5 μ m

Figure 5-3. SEM of Pyrolyzed Methylcarboxylated Resin.

4. Chlorinated Resin

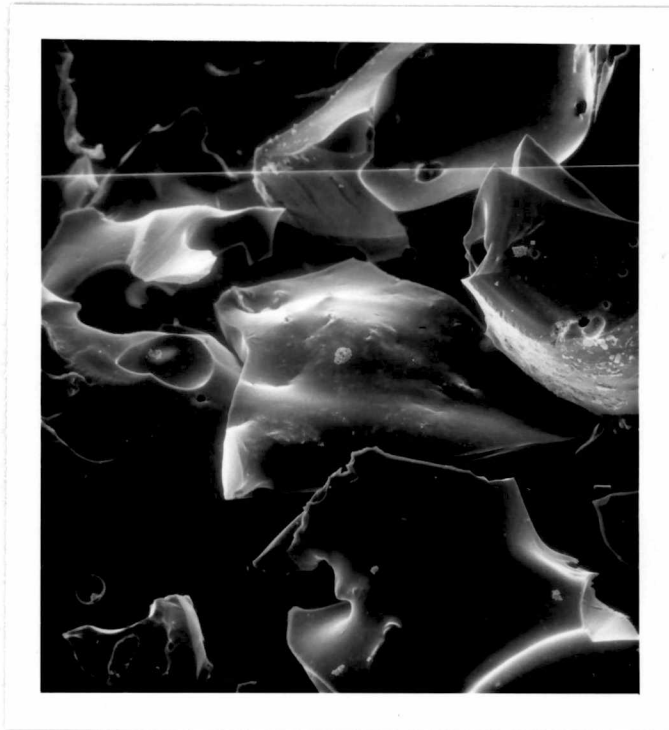
The chlorinated resin (2.58 g; 15% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.30 g (14% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 90.77; H, 0.77. The SEM photograph is presented in Figure 5-4.

5. Brominated Resin

The brominated resin (2.83 g; 15% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.36 g (21% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 97.89; H, 0.57. The SEM photograph is presented in Figure 5-5.

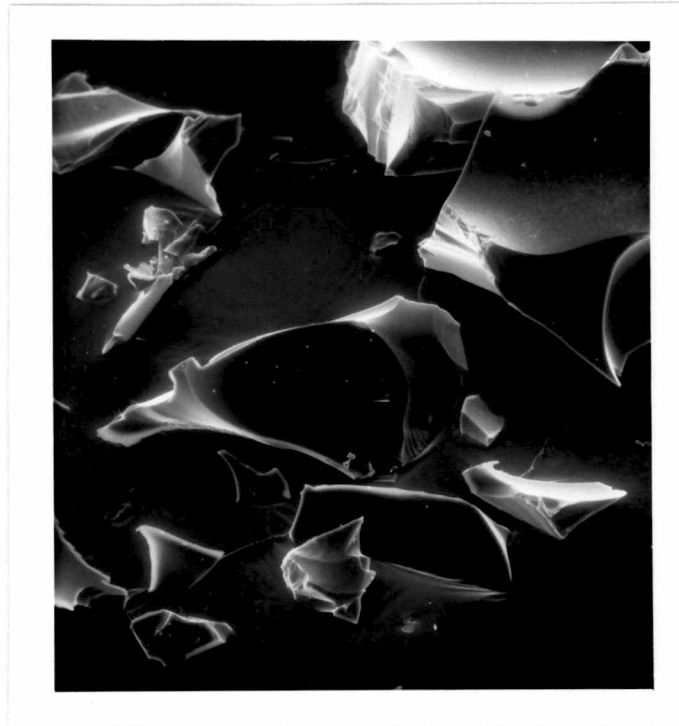
6. Chloromethylated Resin

The chloromethylated resin (2.01 g; 11% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.59 g (35% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 93.56; H, 0.93. The SEM photograph is presented in Figure 5-6.



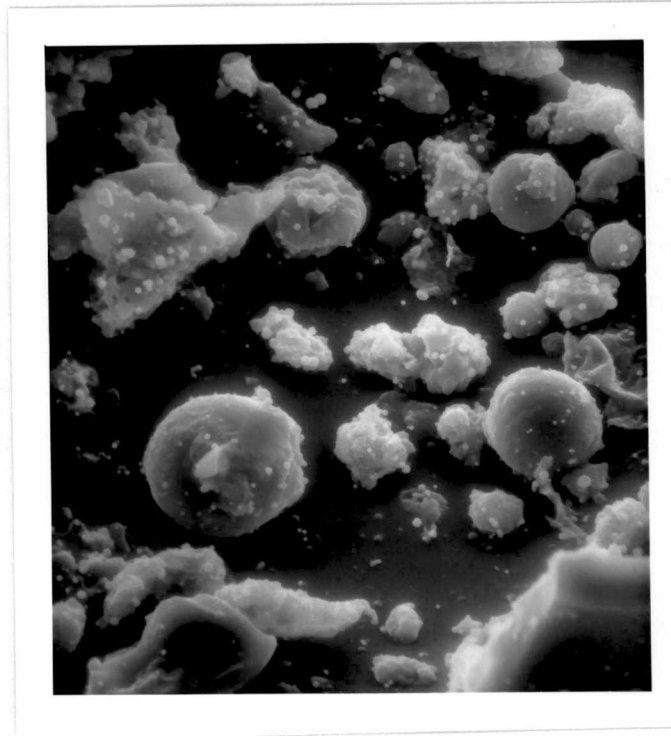

5 mm = 50 μ m

Figure 5-4. SEM of Pyrolyzed Chlorinated Resin.




5 mm = 50 μ m

Figure 5-5. SEM of Pyrolyzed Brominated Resin.



5 mm = 5 μ m

Figure 5-6. SEM of Pyrolyzed Chloromethylated Resin.

7. Methylsulfonated Resin

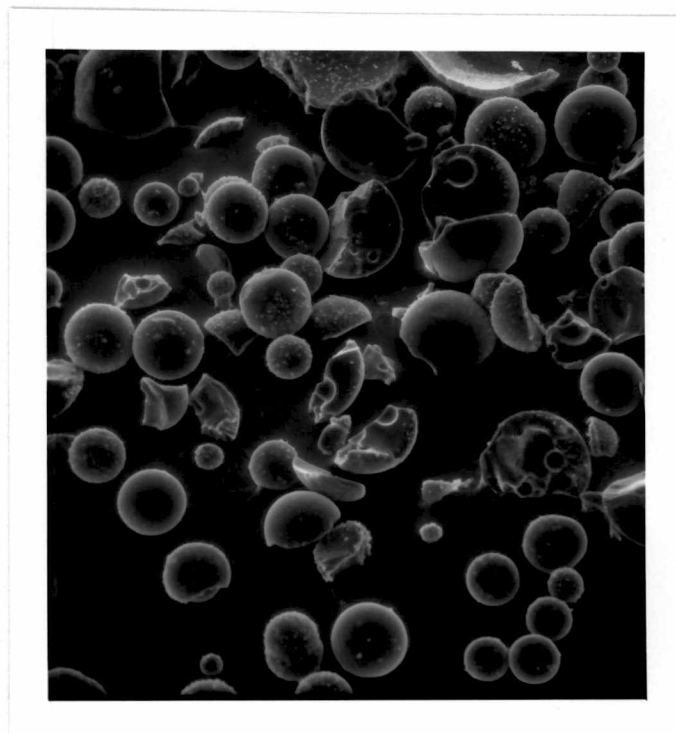
The methylsulfonated resin (1.00 g; 11% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.31 g (42% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 93.45; H, 0.80. The SEM photograph and the TGA graph are presented in Figures 5-7 and 5-8.

8. Nitrated Resin

The nitrated resin (1.04 g; 11% divinylbenzene) was pyrolyzed according to the general procedure (p. 107). This afforded 0.040 g (43% yield based on the carbon in the polymer sample) of carbon. Anal. Calcd for C, 100; H, 00. Found: C, 80.10; H, 1.94. The SEM photograph is presented in Figure 5-9.

C. Results and Discussion

Prior to the syntheses and pyrolyses of the poly(styrene/divinylbenzene) derivatives, several pyrolysis experiments were conducted with commercially available sulfonated and chloromethylated resins. Retention of the bead-like shapes along with higher carbon yields encouraged the work on several other derivatives. The resins that were




5 mm = 50 μ m

Figure 5-7. SEM of Pyrolyzed Methylsulfonated Resin.

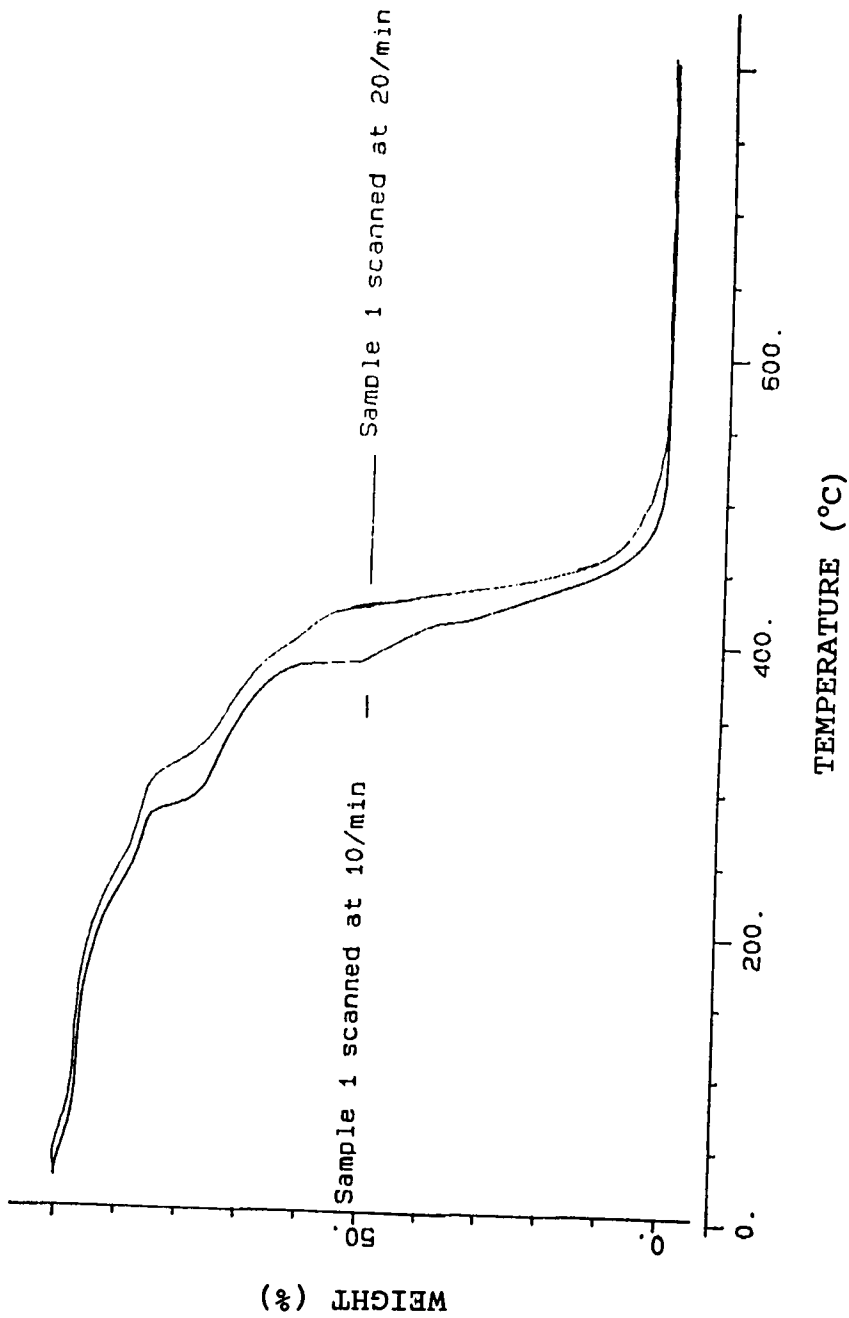
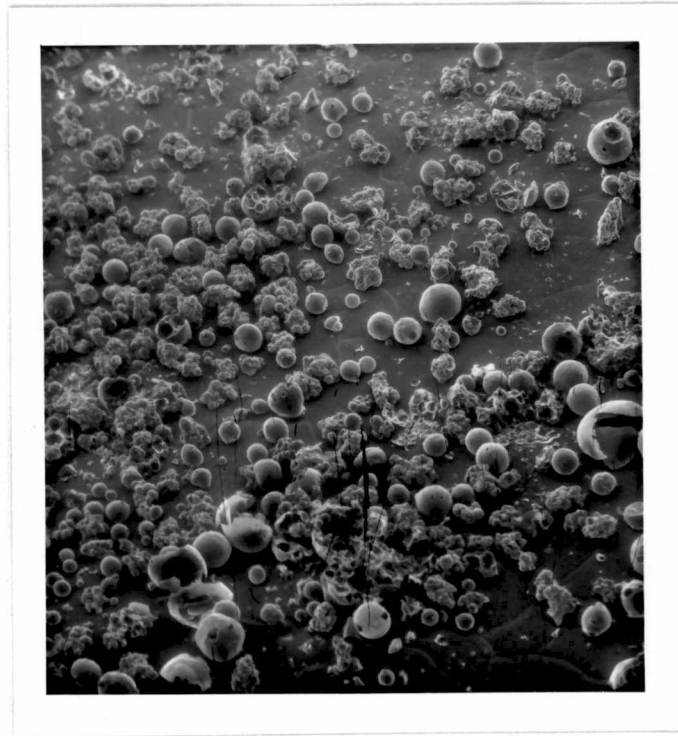


Figure 5-8. TGA of Methylsulfonated Resin.



┌┐┐┐┐
4 mm = 218 μ m

Figure 5-9. SEM of Pyrolyzed Nitrated Resin.

studied were the sulfonated, methyl carboxylated, chlorinated, brominated, chloromethylated, methylsulfonated, and the nitrated derivatives of poly(styrene/divinylbenzene).

Each resin was pyrolyzed and then analyzed via scanning electron microscopy (size/shape determinations), and elemental analysis [degree of functionalization (DF), and carbon yields]. The sulfonated, chloromethylated, methylsulfonated, and nitrated resins afforded beads after pyrolysis with high yields of carbon (25-92%), while the methyl carboxylated, chlorinated, and brominated resins produced shiny slivers of carbon (as in the case with the non-functionalized polymer) in low yields (8-21%).

D. Conclusion

Four of the functionalized poly(styrene/divinylbenzene) derivatives produced beads which appeared suitable for the eventual use in cyclotron targets for the production of nitrogen-13. These resins were studied at UCLA using a CS-22 cyclotron. The experiments are discussed in the next chapter.

CHAPTER VI

CYCLOTRON EVALUATION OF SYNTHESIZED MATERIALS

A. Introduction

The development of a new carbon-13 labelled material for the cyclotron production of nitrogen-13 labelled ammonia is the eventual goal of this research. The research outlined in this dissertation details the syntheses and evaluation of carbon-12 based systems as models for the eventual preparation of carbon-13 labelled materials. Microscopic, spherical carbon-12 poly(styrene/divinylbenzene) derivatives were synthesized and then pyrolyzed to yield carbon-12 beads.

The physical stability of the materials was tested with the cyclotron conditions appropriate for preparing nitrogen-13 using the CTI Cyclotron Systems, Inc. 11 MeV proton only, negative ion cyclotron. In addition, the nuclear reactions of the carbon-12 based polymer derivatives that provided favorable pyrolysis results, (e.g., high carbon yields and retention of spherical shape) were studied at UCLA using a 22 MeV proton, multi-particle, positive ion cyclotron.

The choice of the UCLA cyclotron with a degraded beam energy of 6 MeV deuterons was decided upon based on the following criteria: 1) polymers contain carbon-12 which requires irradiation with deuterons in order to produce nitrogen-13 via the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ nuclear reaction; 2) the

recoil range of nitrogen-13 from the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ reaction at 6 MeV is comparable to the recoil range of nitrogen-13 from the $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$ reaction at 10.7 MeV (on target) and 3) deuteron irradiation at 6 MeV produces nitrogen-13 from only the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ nuclear reaction whereas proton irradiation at 10.7 MeV produces nitrogen-13 via two nuclear reactions: $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$ and $^{16}\text{O}(\text{p},\alpha)^{13}\text{N}$. Since the $^{16}\text{O}(\text{d},\alpha\text{n})^{13}\text{N}$ reaction requires energies greater than 6 MeV to occur, the yield of nitrogen-13 from the carbonized beads can be determined without interference from the $^{16}\text{O}(\text{d},\alpha\text{n})^{13}\text{N}$ reaction.

Initial proton studies were conducted on the non-functionalized carbon-12 styrene/10% divinylbenzene copolymers (20-100 μm pieces) at 3-5 μA for 13 min. After several irradiations, no blockage of the stainless steel frits occurred and insignificant amounts of nitrates and nitrites were produced from this target.

Final deuteron experiments were conducted on four of the functionalized derivatives (SO_3H , NO_2 , CH_2Cl , $\text{CH}_2\text{SO}_3\text{H}$). The derivatives provided pyrolysis yields of 35-92% carbon with retention of shape.

B. Experimental

A detailed description of the experimental set-up is provided in Figure 6-1. Three different foil combinations were used with a 10 mm diameter by 2 mm deep gold-plated copper target body in these experiments: 1) a 0.001" titanium foil; 2) two 0.0005" Arnavar foils and 3) a 0.001"

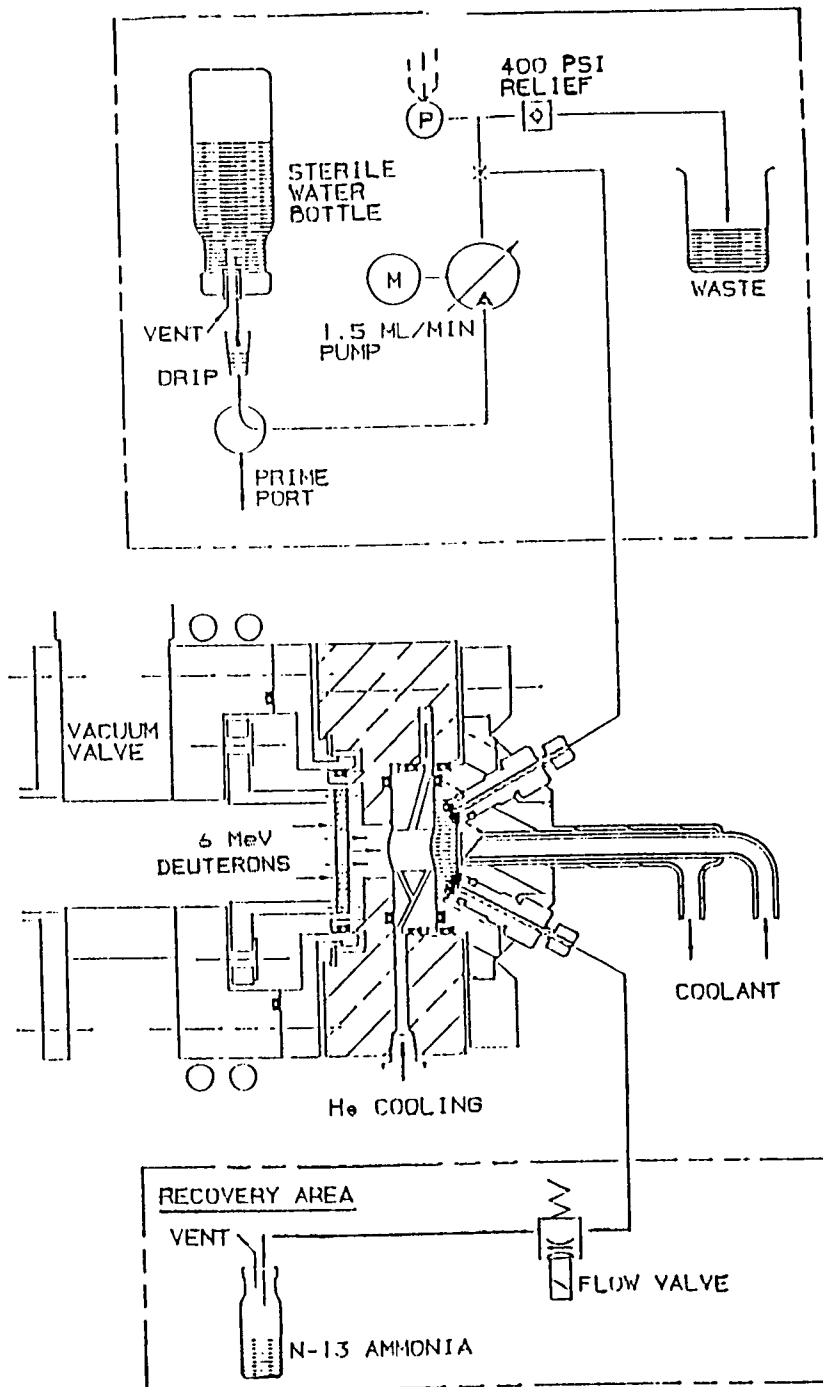


Figure 6-1. N-13 Target System.

Havar foil. All target combinations provided water cooling of the target body and helium cooling of the target foils. The target was loaded with carbon-12 polymer beads (0.095-0.174 g). Prior to irradiation, a flow of water through the carbon-12 bed and beam strike, maintained by an HPLC pump, was established for the desired flow rate. The flow control valve was closed and the target pressure was maintained at 400 psi. For nitrogen-13 production, the slurry was irradiated with an approximately 6 MeV deuteron beam (on target) at 5 μ A for 10 min., the flow control valve opened, and the aqueous activity delivered through 46 meters of 0.0625" OD, 0.020" ID Teflon tubing to a collection vessel. The collection was continued until the activity no longer increased, as determined by a radiation survey meter. The activity was assayed in a dose calibrator, recorded every minute for 30 min., and, plotted in order to determine the half-life for comparison with the half-life of nitrogen-13.

The radiolabelled products from these experiments were analyzed by radio-HPLC ion chromatography. Conditions for HPLC anion analyses were: Wescan Anion/R column, 250 mm X 4.1 mm ID, 4 mM p-hydroxybenzoic acid, pH 8.4, 1.5 mL/min., Wescan Model 215100 conductivity detector coupled to a NaI radiation detector. Retention times of the radiolabelled products were compared with the calibrated retention times of known standards. The only products observed were $^{13}\text{NH}_4^+$ and $^{17}\text{F}^-$.

C. Results and Discussion

The results of the deuteron irradiation on carbon-12 polymer beads experiments are summarized in Table 6-1. The end of bombardment (EOB) yields of nitrogen-13 were determined from the activity vs. time plots extrapolating to $x = 0$. The saturation factors (SF) and saturation yields (SY) were calculated using the following equations:

$$SF = 1 - e^{-\lambda t} = 1 - e^{-(\ln 2 / t_{1/2}) * t} \quad (6-1)$$

$$SY = EOB \text{ } ^{13}\text{N} / (I * SF) \quad (6-2)$$

where I = Current (μA)

As anticipated for beads of these sizes, the recovered nitrogen-13 (EOB) yields are quite low. Monte Carlo TRIM Code calculations predict the recoil range for 2.29 MeV nitrogen-13 recoil ions to be about $1.72 \mu\text{m}$. This suggests that a high fraction of the nitrogen-13 produced remains in the carbon particles, thus contributing to the low yields of nitrogen-13 at EOB. This problem should be alleviated via the production of smaller particles using high speed stirrers⁵⁷. Decreasing the particle size will increase the amount of nitrogen-13 that can recoil out of the carbon particles, and therefore, will increase the yields of nitrogen-13 at EOB.

Table 6-1: Deuteron Irradiation Experiments on Carbon-12 Polymer Beads

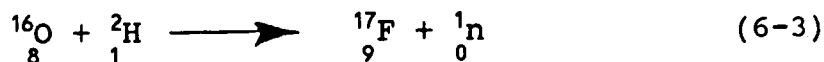
Run #	Sample	Size (μ m)	Packing Density (g/cc)	Target Foil	E_p (MeV) (on target)	Irrad'n. Cond'n's. (μ A X time)	EOB N-13 (mCi)	Sat. Yld. (mCi/ μ A)
1	CH ₂ Cl	1.3-19.4	0.52	1 Ti	6.5	5 X 10		
2	CH ₂ Cl	1.3-19.4	0.52	1 Ti	6.5	5 X 10		
3*	CH ₂ Cl	1.3-19.4	0.52	1 Ti	6.5	10 X 10		
4*	CH ₂ SO ₃ H	25.8-116	0.71	1 Ti	6.5	5 X 10		
5*	SO ₃ H	25-64	0.42	2 X 1/2 A	6.3	5 X 10		
6 ^b	SO ₃ H	25-64	0.42	2 X 1/2 A	6.3	5 X 10	1.5-2.0	0.6-0.8
7*	SO ₃ H	25-64	0.42	2 X 1/2 A	6.3	5 X 10		
8 ^b	NO ₂	43-291	0.27	2 X 1/2 A	6.3	5 X 10		
9 ^b	NO ₂	43-291	0.27	2 X 1/2 A	6.3	5 X 10	2.0	0.8
10*	NO ₂	43-291	0.27	2 X 1/2 A	6.3	5 X 10		
11 ^b	CH ₂ SO ₃ H	25.8-116	0.50	1 H	6.3	5 X 10	2.0	0.8
12*	CH ₂ SO ₃ H	25.8-116	0.50	1 H	6.3	5 X 10		

* Lost target foil

* For sample injection study

^b For decay analysis

The results from the radio-HPLC ion chromatography are shown in Figure 6-2. The products of the current carbon-13/oxygen-16 slurry target and their retention times are identified in Figure 6-2a. The results of the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ reactions on the carbon-12 polymer beads (Figure 6-2b) reveal that nitrogen-13 labelled ammonia is present along with an unidentified product. To determine if this were real or an artifact, the column was allowed to clear of solution and another aliquot of sample was injected. The product spectrum for the second injection (Figure 6-2c) shows only one peak which corresponds to that of $^{13}\text{NH}_4^+$. However, the presence of the unidentified peak was detected in each initial injection for each of the four derivatives but disappeared by the time the second injection was made. Thus, the unidentified peak can be attributed to the presence of a short-lived (< 10 min.) radioisotope. Examination of the literature revealed that deuteron irradiation of naturally occurring oxygen-16 (present in water) produces fluorine-17 as described by the following nuclear reaction:



The half-life of fluorine-17 is 65 seconds, which makes it a likely candidate for the unidentified product. In support of this theory, a sample of fluorine-18 was injected into the column. The fluorine-18 peak emerged with the same

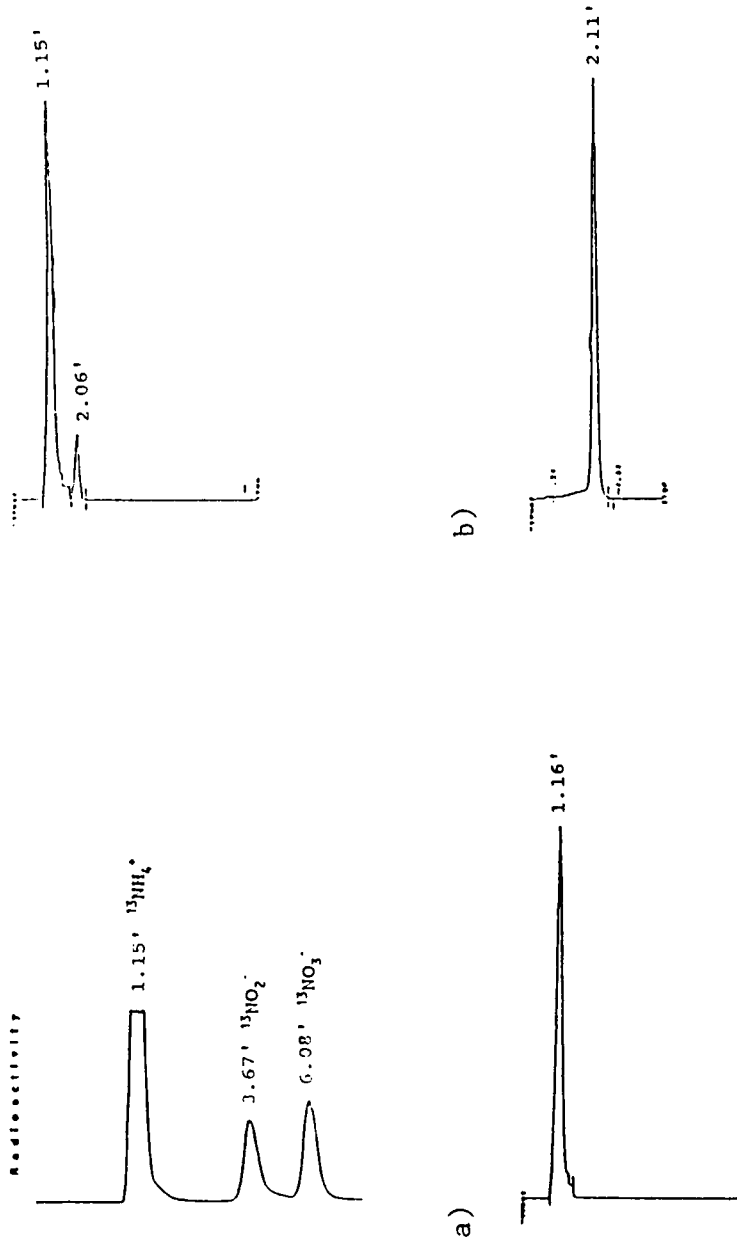


Figure 6-2. Radio-HPLC Ion Chromatography a) Current Slurry Target b) C-12 Polymer Beads (1st Injection) c) C-12 Polymer Beads (2nd Injection) d) F-18 Injection.

retention time as the unidentified peak (Figure 6-2d). Since radioisotopes of the same element possess the same retention time, it is reasonable to conclude that fluorine-17 is present. Further evidence for the assignment of the unidentified peak to fluorine-17 fluoride ion was obtained from decay curve analysis (Figure 6-3). The data indicate a half-life on the order of 80 seconds for the short-lived isotope (^{17}F ; $t_{1/2} = 65$ s. However, approximately five minutes had passed before any data was collected. This corresponds to about five half-lives of fluorine-17. The plot shows that the unidentified material is short-lived). The data provide a half-life of 9.9 min. for the latter stages of decay (^{13}N ; $t_{1/2} = 9.97$ min.). Finally, the irradiated particles were examined by scanning electron microscopy (Figure 6-4). No deterioration of the spheres developed after three irradiations at $5\ \mu\text{A}$ for 10 min.

D. Conclusion

Formation of fluorine-17 by the reaction of oxygen-16 with the accelerated deuteron is an unexpected bonus. Eventually these polymers will be synthesized with carbon-13 labelled reagents and irradiated with protons. The proton reaction with oxygen-16 produces nitrogen-13! Carbon-13 polymer beads should, therefore, successfully produce pure nitrogen-13 labelled ammonia via two reactions. Thus, the

new materials appear to be excellent targets for cyclotrons used in the production of short-lived isotopes.

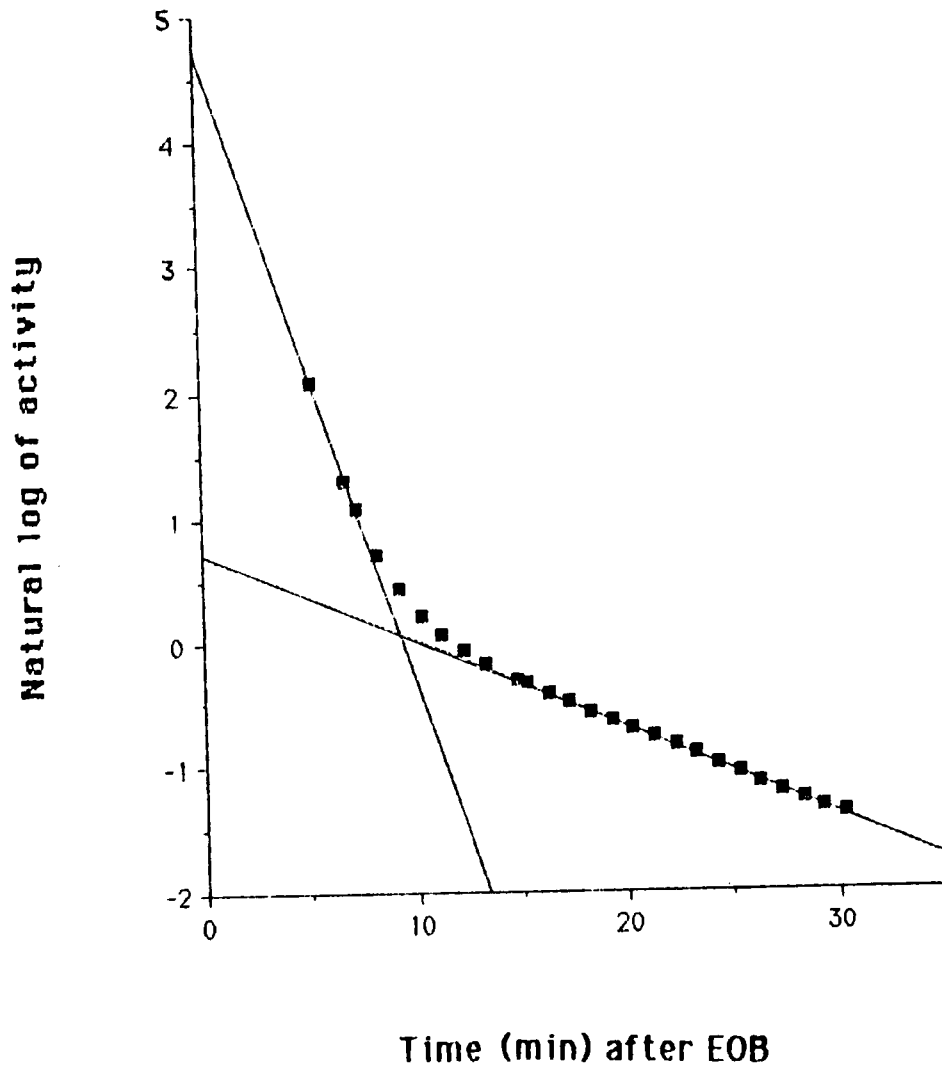
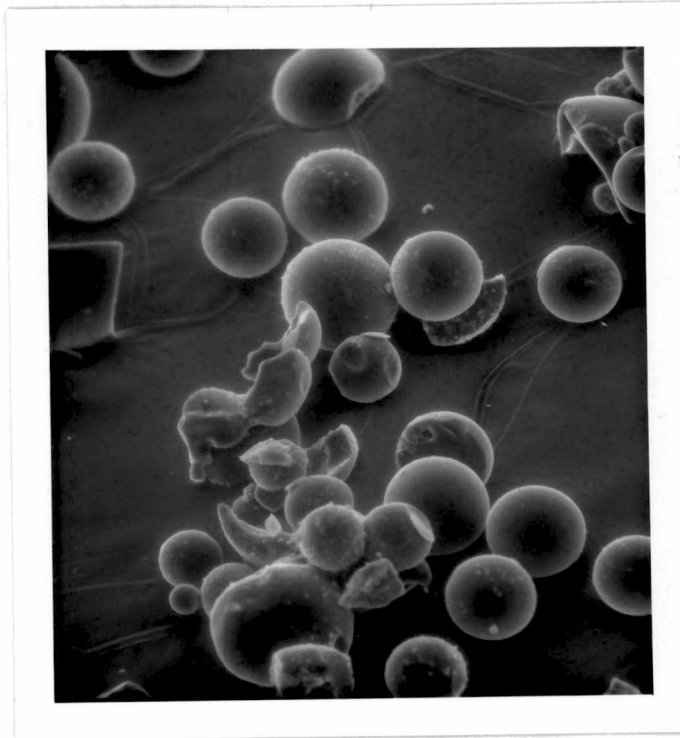


Figure 6-3. Decay Curve Analysis.




6 mm = 50 μ m

Figure 6-4. SEM of C-12 Polymer Beads after Irradiation with Deuterons.

LIST OF REFERENCES

LIST OF REFERENCES

1. Positron Emission Tomography; Phelps, M. E.; Mazziotta, J. C.; Schelbert, H. R., Eds.; Raven: New York, 1986; p 237.
2. Bair, J. K.; Miller, P. D.; Wieland, B. W. Int. J. Appl. Radiat. Isot. **1981**, 32, 389.
3. "CTI Leaders in Advanced Diagnostic Imaging"; 1985.
4. Bida, G. T., CTI Cyclotron Systems, Inc., Berkeley, CA, personal communication, 1991.
5. Harper, P. V.; Lathrop, K. A.; Krizek, H.; Lembares, N.; Stark, V.; Hoffer, P. B. J. Nucl. Med. **1990**, 31, 278.
6. Hoop, B., Jr.; Smith, T. W.; Burnham, C. A.; Correll, J. E.; Brownell, G. L.; Sanders, C. A. J. Nucl. Med. **1990**, 31, 181.
7. Rosenspire, K. C.; Schwaiger, M.; Mangner, T. J.; Hutchins, G. D.; Sutorik, A.; Kuhl, D. E. J. Nucl. Med. **1990**, 31, 163.
8. Himi, T.; Endo, M.; Nakagawa, K.; Niwayama, H.; Kagaya, A.; Yamasaki, T.; Tatenno, Y. J. Nucl. Med. **1990**, 31, 802.
9. Smith, G. T.; Huang, S. C.; Wu, Y.; Hubner, K. F.; Schelbert, H. R. J. Nucl. Med. **1990**, 31, 862.
10. Bellina, C. R.; Parodi, O.; Camici, P.; Salvadori, P.; Taddei, L.; Fusani, L.; Guzzardi, R.; Klassen, G.; L'Abbate, A.; Donato, L. J. Nucl. Med. **1990**, 31, 1335.
11. Bianco, J. A. J. Nucl. Med. **1990**, 31, 1431.
12. Barrio, J. R.; Baumgartner, F. J.; Henze, E.; Stauber, M. S.; Egbert, J. E.; MacDonald, N. S.; Schelbert, H. R.; Phelps, M. E.; Liu, F-T. J. Nucl. Med. **1983**, 24, 937.
13. Hales, C. A.; Kazemi, H. N. Engl. J. Med. **1974**, 290, 761.
14. MacDonald, N. S. In The UCLA Biomedical Cyclotron Facility; Serafini, A. N.; Beaver, J. E., Eds.; Prog. Nucl. Med.; S. Karger: New York, 1978; Vol. 4, p 23.

15. Tilbury, R. S.; Dahl, J. R.; Monahan, W. G.; Laughlin, J. S. Radiochem. Radioanal. Letters **1971**, 8, 317.
16. Straatmann, M. G. Int. J. Appl. Radiat. Isot. **1977**, 28, 13.
17. Rosenzweig, D. Y.; Hughes, J. M.; Jones, T. Respiration Physiology **1969**, 8, 86.
18. Hunter, W. W.; Monahan, W. G. J. Nucl. Med. **1990**, 31, 368.
19. Kothari, P. J.; Finn, R. D.; Kabalka, G. W.; Vora, M. M.; Boothe, T. E.; Emran, A. M. Int. J. Appl. Radiat. Isot. **1986**, 37, 469.
20. Kabalka, G. W.; Green J. F.; Wang, Z.; Goodman, M. M J. Label. Compds. Radiopharm. **1989**, 26, 90.
21. Kabalka, G. W.; Varma, R. S. Tetrahedron **1989**, 45, 6601.
22. Kabalka, G. W.; Wang, Z.; Goodman, M. M Int. J. Appl. Radiat. Isot., submitted.
23. Radionuclide Production; Helus, F., Ed.; CRC: Boca Raton, Florida, 1983; Vol. 2, p 57.
24. Hendry, G. O.; Straatmann, M. G.; Carroll, L. R.; Ramsey, F. A.; Wieland, B. W.; Padgett, H. C.; Bida, G. T.; Schmidt, D. G.; Ruth, T. J. Siemens Design and Performance of a Compact Radioisotope Delivery System.
25. Harvey, B. G. Pure and Applied Physics; Academic: 1974; Vol. 40A, Chapter 1B, p 35.
26. Wolf, A. P.; Jones, W. B. Radiochimica Acta **1983**, 34, 1.
27. Buonocore, E.; Hubner, K. F.; Kabalka, G. W. Diagnostic Imaging **1987**, 110.
28. Comar, D.; Crouzel, C. Nucl. Med. Biol. **1986**, 13, 101.
29. "CTI RDS 112 Radioisotope Delivery System."
30. "Siemens Production and Delivery of Positron Emitting Radioisotopes: Radioisotope Delivery System."
31. Friedlander, G.; Kennedy, J. W.; Miller, J. M. Nuclear and Radiochemistry, 2nd ed.; John Wiley and Sons: New York, 1964; p 365.

32. Ferrieri, R. A.; Schlyer, D. J.; Wieland, B. W.; Wolf, A. P. Int. J. Appl. Radiat. Isot. **1983**, 34, 897.
33. Bida, G.; Schmidt, D.; Hendry, G. O.; Wieland, B. W. U.S. Pat. 4,752,432, 1988.
34. Bida, G.; Wieland, B. W.; Ruth, T. J.; Schmidt, D. G.; Hendry, G. O.; Keen, R. E. J. Label. Compds. Radiopharm. **1986**, 23, 1217.
35. Austin, S. M.; Galonsky, A.; Bortins, J.; Wolk, C. P. Nucl. Instr. Methods **1975**, 126, 373.
36. Root, J. W.; Krohn, K. A. Short-Lived Radionuclides in Chemistry and Biology; Adv. Chem. Ser. No. 197; American Chemical Society; Washington, D.C., 1981, Chapters 11, 13 and 19.
37. Wieland, B. W.; Bida, G. T.; Padgett, H. C.; Hendry, G. O. Abstract of Papers, Proceedings of the Third Workshop on Targetry and Targetry Chemistry, Vancouver, B.C.; 1989.
38. Tilbury, R. S.; Dahl, J. R. Radiation Research **1979**, 79, 22.
39. Wieland, B.; Bida, G.; Padgett, H.; Hendry, G.; Zippi, E.; Kabalka, G.; Morelle, J-L.; Verbruggen, R.; Ghyoot, M. Int. J. Radiat. Appl. Instr. Part A, submitted.
40. Wieland, B.; Bida, G.; Padgett, H.; Hendry, G.; Zippi, E.; Kabalka, G.; Morelle, J-L.; Verbruggen, R.; Ghyoot, M. Abstract of Papers, 8th Int. Symp. Radiopharm. Chem., Princeton, NJ; 1990, p 162.
41. Welch, M. J.; Straatmann, M. G. Radiochimica Acta **1973**, 20, 124.
42. Mulholland, G. K.; Kilbourn, M. R.; Moskwa, J. J. Abstract of Papers, 8th Int. Symp. Radiopharm. Chem., Princeton, NJ; 1990, p 86.
43. Vaalburg, W.; Kamphius, J. A.; Beerling-van der Molen, H. D.; Reiffers, S.; Rijskamp, A.; Woldring, M. G. Int. J. Appl. Radiat. Isot. **1975**, 26, 316.
44. Parks, N, J.; Krohn, K. A. Int. J. Appl. Radiat. Isot. **1978**, 29, 754.
45. Patt, J. T.; Nebeling, B.; Stocklin, G. Abstract of Papers, 8th Int. Symp. Radiopharm. Chem., Princeton, NJ; 1990, p 118.

46. Welch, M. J. Chem. Comm. **1968**, 1354.
47. Welch, M. J.; Lifton, J. F. J. Am. Chem. Soc. **1971**, 93, 3385.
48. Firouzbakht, M.; Schlyer, D. J.; Wolf, A. P. Abstract of Papers, 8th Int. Symp. Radiopharm. Chem., Princeton, NJ; 1990, p 108.
49. Stewart, G. W.; Dymerski, P. P.; Hower, C. O. J. Chem. Physics **1974**, 61, 483.
50. Winslow, F. H.; Baker, W. O.; Pape, N. R.; Matreyek, W. J. Polym. Sci. **1955**, 16, 101.
51. Schmitt, L. A. Thesis, University of Tennessee at Knoxville, 1989, 8.
52. Tari, A. M. Thesis, University of Tennessee at Knoxville, 1989, 4.
53. Suslick, K. S. Scientific American **1989**, 80.
54. "Operation Instructions: Artek Systems Corporation Ultrasonic Dismembrators".
55. Odian, G. Principles of Polymerization, 2nd ed.; John Wiley and Sons: New York, 1981; Chapters 3-4, pp 287, 320.
56. Billmeyer, F. W. Textbook of Polymer Science, 3rd ed.; John Wiley and Sons: New York, 1984; Chapter 6, p 132.
57. Alexandratos, S. D.; Strand, M. A.; Quillen, D. R.; Walder, A. J. Macromolecules **1985**, 18, 829.
58. Braun, D.; Cherdron, H.; Kern, W. Synthesis of Macromolecular Substances; p 137.
59. Mohamed, A. Bio-Rad Laboratories, Richmond, CA, personal communication, 1990.
60. Shafizadeh, F.; Sarkanen, K. V.; Tillman, D. A. Thermal Uses and Properties of Carbohydrates and Lignins; Academic: New York, 1976; Chapter 6, p 101.
61. Brown, R. F. Pyrolytic Methods in Organic Chemistry; Academic: New York, 1980; Chapter 1, p 5.
62. Wen, C. Y.; Lee E. S. Coal Conversion Technology; Addison-Wesley: Reading, MA, 1979; Chapter 2, p 59.

63. Gavalas, G. R. Coal Pyrolysis; Elsevier Scientific: New York, 1982; Chapters 2,4-5, pp 3, 49, 77.
64. Albright, L F.; Crynes, B. L. Industrial and Laboratory Pyrolyses; Library of Congress: Washington, D.C., 1975; Chapter 5, p 72.
65. Oblad, A. G.; Davis, H. G.; Eddinger, R. T. Thermal Hydrocarbon Chemistry; Library of Congress: Washington, D.C., 1979; Chapter 11, p 194.
66. Neely, J. W. Carbon 1981, 19, 27.
67. Marsh, H.; Wynne-Jones, W. F. Carbon 1964, 1, 269.
68. Kipling, J. J.; Sherwood, J. N.; Shooter, P. V.; Thompson, N. R. Carbon 1964, 1, 315.
69. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectrometric Identification of Organic Compounds; John Wiley and Sons: New York, 1981; Chapters 4-5, pp 237, 288.
70. Tuleen, D. L.; Hess, B. A. J. Chem. Ed. 1971, 48, 476.
71. Broos, R.; Tavernier, D.; Anteunis, M. J. Chem. Ed. 1978, 55, 813.
72. Marvel, C. S.; Overberger, C. G. J. Am. Chem. Soc. 1945, 67, 2250.
73. Leebrick, J. R.; Ramsden, H. E. J. Org. Chem. 1958, 23, 935.
74. Black, T. H. Aldrichimica Acta 1983, 16, 3.
75. Vowinkel, E. Chem. Ber. 1967, 100, 16.
76. Pepper, K. W. J. Appl. Chem. 1951, 1, 124.
77. Ergozhin, E. E.; Rafikov, F. T. Izv. Akad. Nauk 1965, 15, 82.
78. Ranganathan, D.; Rathi, R.; Sharma, S. J. Org. Chem. 1990, 55, 4009.
79. Doscher, F.; Klein, J.; Pohl, F.; Widdecke, H. Makromol. Chem. 1980, 1, 297.
80. "Thermal Gravimetric Analysis Manual", Oak Ridge National Laboratory, TN.

VITA

Elizabeth M. Zippi was born in Jeannette, Pennsylvania on July 9, 1965. She attended Sacred Heart Elementary School and Jeannette Senior High School, graduating with High Honors in June 1983. She attended The Pennsylvania State University, University Park for one semester and then transferred to Indiana University of Pennsylvania. She graduated Summa Cum Laude from IUP in May 1987 with a B. S. in Chemistry and a minor in Mathematics. After completing summer research fellowship appointments at the University of Tennessee, Knoxville in 1986 and 1987, she began graduate studies under the direction of Professor George W. Kabalka. During part of her time in graduate school, she was employed as a consultant for CTI Cyclotron Systems, Inc. in Berkeley, California and as a Visiting Scholar at the University of California, Berkeley. She has coauthored a publication which will appear in the International Journal of Radiation Applications and Instrumentation, Part A. She has presented a paper at a national meeting of The American Chemical Society, a poster at an international radiopharmaceutical symposium, and a paper at an intercollegiate student chemists convention. She has accepted a position as a Postdoctoral Research Associate at the National Tritium Labeling Facility in the Lawrence Berkeley Laboratory, Berkeley, California.