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Bret E. Vanzo
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SYNTHESIS, CHARACTERIZATION, AND HYDROLYSIS
BEHAVIOR OF POLY(ALKYL STYRENESULFONATES)

A Dissertation Presented

By

BRET E. VANZO

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1984

Polymer Science and Engineering

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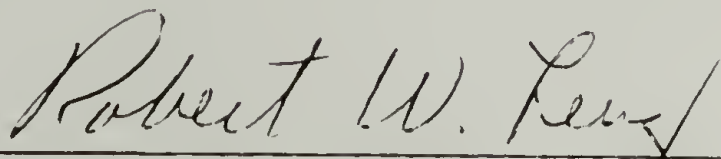
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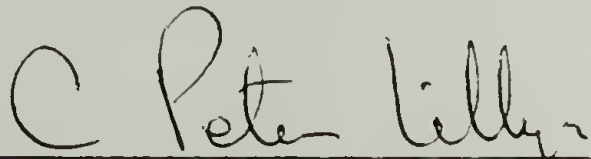
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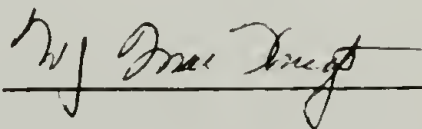
Robert W. Lenz, Chairman of Committee



William J. MacKnight, Member



C. Peter Lillya, Member



W. J. MacKnight, Department Head
Polymer Science and Engineering

Dedicated to my parents
who made all of this possible

and

To Lisa
whose love kept me going

"He who, for the sake of learning,
lowers himself by exposing his ignorance,
will ultimately be elevated."

- Ben Azzai

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ABSTRACT

Synthesis, Characterization and Hydrolysis Behavior of Poly(alkyl styrenesulfonates)

(May 1984)

Bret E. Vanzo

B.S., Pennsylvania State University

M.S., University of Massachusetts

Directed by: Professor Robert W. Lenz

Alkyl esters of styrenesulfonic acid were synthesized, homopolymerized, and copolymerized with a variety of comonomers. The polymers were investigated for hydrolysis behavior under a variety of reaction conditions.

Several methods for the synthesis of alkyl styrenesulfonates were investigated. Methyl, ethyl, n-propyl, and isopropyl styrenesulfonates were successfully synthesized in yields of 65, 55, 50, and 40 percent, respectively, starting with sodium styrenesulfonate. Monomer synthesis procedures involving the sulfochlorination of (2-bromoethyl)benzene were found to be inferior because of sulfone formation which led to insoluble, crosslinked resins.

Alkyl styrenesulfonates were homopolymerized and copolymerized by free-radical initiation. Bulk, solution, and emulsion polymerization systems were successfully employed. Comonomers investigated included styrene, acrylamide, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, maleic anhydride, sodium styrenesulfonate, and sodium 2-sulfoethyl methacrylate. Copolymerization reactivity ratios (r_1 , r_2) for the copolymerization of methyl styrenesulfonate with styrene, acrylic acid, and maleic anhydride were determined.

Hydrolysis studies in aqueous dimethyl sulfoxide solutions were performed. The effect of a variety of variables, including copolymerization, solvent, temperature, alkalinity, acidity, and molecular weight, on the kinetics of hydrolysis was investigated. The various homopolymers and copolymers were found to behave similarly to low molecular weight analogs and exhibited the following reactivity towards hydrolysis: methyl > isopropyl > ethyl > n-propyl. However, in solvent systems containing high concentrations of dimethyl sulfoxide (≥ 90 vol %) the reaction is characterized by two different steps, a first rapid step analogous to the reaction of low molecular weight alkyl toluenesulfonates, and a second, slower step. This retardation has been attributed to neighboring group effects in which the sulfonic acid groups formed during the

hydrolysis reaction "tie" up surrounding water molecules via hydrogen bonding thus inhibiting reaction with and/or solvation of neighboring unreacted ester groups.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	vi
ABSTRACT	vii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
Chapter	
I. INTRODUCTION	1
A. Methods of Preparation of Functional Polymers	3
B. Preparation of Styrenesulfonic Acid Esters	4
C. Polymerization of Styrenesulfonic Acid Esters	9
D. Hydrolysis of Sulfonic Acid Esters	12
1. Carboxylic vs. Sulfonic Acid Ester Hydrolysis	12
2. Kinetics	14
3. Mechanism	17
4. Results for Hydrolysis of Low Molecular Weight Substituted Alkyl Benzenesulfonates	20
5. Hydrolysis of Polymers	23
E. Summary	28
II. EXPERIMENTAL SECTION	30
A. Materials	30
B. Purification of Reagents and Solvents	32
C. Monomer Synthesis via (2-Bromoethyl)-benzene	34
1. p-(2-Bromoethyl)benzenesulfonyl Chloride	34
2. Methyl p-(2-Bromoethyl)benzenesulfonate	34
3. Methyl p-Styrenesulfonate	35
4. Purity of Methyl p-Styrenesulfonate: Homopolymerization	36
5. Bis-[p-(2-Bromoethyl)benzene]sulfone	36
6. Purity of Methyl p-(2-Bromoethyl)benzenesulfonate by Analytical HPLC	37
7. Recrystallization of Methyl p-(2-Bromoethyl)benzenesulfonate	39
8. Preparative HPLC Purification of Methyl p-(2-Bromoethyl)benzenesulfonate	39

D.	Monomer Synthesis via Sodium Styrene-	
	sulfonate	39
1.	Purity of Sodium Styrenesulfonate by	
	Analytical HPLC	39
2.	p-Styrenesulfonyl Chloride	43
3.	Methyl p-Styrenesulfonate	43
4.	Purity of Methyl p-Styrenesulfonate:	
	Homopolymerization	45
5.	Ethyl, n-Propyl, and Isopropyl	
	p-Styrenesulfonates	47
6.	Distillation of Alkyl Styrene-	
	sulfonates	49
E.	Miscellaneous Preparations	49
1.	Synthesis of Sodium Acrylate	49
2.	Synthesis of Sodium Styrenesulfonate. .	50
3.	Synthesis of Sodium 2-Sulfoethyl	
	Methacrylate	51
F.	Homopolymerization of Alkyl	
	Styrenesulfonates	52
1.	Bulk Homopolymerization of Alkyl	
	Styrenesulfonates	52
2.	Solution Homopolymerization of Methyl	
	p-Styrenesulfonate	54
3.	Emulsion Homopolymerization of Methyl	
	p-Styrenesulfonate	54
4.	Homopolymerization of Methyl	
	p-Styrenesulfonate in the Presence of	
	Lauryl Mercaptan	55
G.	Copolymerization of Alkyl Styrene-	
	sulfonates	56
1.	Copolymerization of Alkyl Styrene-	
	sulfonates with Styrene	56
2.	Copolymerization of Alkyl Styrene-	
	sulfonates with Acrylic Acid	57
3.	Copolymerization of Alkyl Styrene-	
	sulfonates with Sodium Acrylate	60
4.	Copolymerization of Alkyl Styrene-	
	sulfonates with Maleic Anhydride	60
5.	Copolymerization of Methyl p-Styrene-	
	sulfonate with Sodium 2-Sulfoethyl	
	Methacrylate	61
6.	Copolymerization of Methyl p-Styrene-	
	sulfonate with 2-Acrylamido-2-methyl-	
	propanesulfonic Acid	62
7.	Attempted Copolymerization of Alkyl	
	Styrenesulfonates with Acrylamide . . .	63
8.	Preparation of Alkyl Styrenesulfonate-	
	Sodium Styrenesulfonate Copolymers . .	64
9.	Copolymerization Reactivity Ratios . .	65
10.	% Comonomer Versus Water Solubility . .	65
	a. Copolymers of Alkyl Styrene-	
	sulfonates and Acrylic Acid	65

	b. Copolymers of Alkyl Styrene-sulfonates and Sodium Styrene-sulfonate	69
H.	Synthesis of Alkyl Toluenesulfonates	69
I.	Polymer Characterization	73
	1. Homopolymer Molecular Weight Determination	73
	2. Thermal Analysis	76
	a. Differential Scanning Calorimetry	76
	b. Thermogravimetric Analysis	76
	3. Spectroscopic Analysis	78
	a. Infrared Spectroscopy	78
	b. ^1H NMR	78
	c. ^{13}C NMR	78
	4. Elemental Analysis	81
J.	Hydrolysis Studies	81
	1. General Procedure	81
	2. Neutral Hydrolysis of Alkyl Toluene-sulfonates in 90/10 (v/v) DMSO/H ₂ O	83
	3. Neutral Hydrolysis of Poly(alkyl styrenesulfonates) in 90/10 (v/v) DMSO/H ₂ O	83
	4. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate-co-styrene) in 90/10 (v/v) DMSO/H ₂ O	83
	5. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O	83
	6. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v), 50/50 (v/v), and 0/100 (v/v) DMSO/H ₂ O	89
	7. Basic Hydrolysis of Poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O	89
	8. Acidic Hydrolysis of Poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O	89
	9. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O: Effect of Molecular Weight	89
	10. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate) Emulsion in 100% H ₂ O	91
	11. Neutral Hydrolysis of Poly(methyl p-styrenesulfonate) in 80/20 (v/v) DMSO/H ₂ O: Solution Viscosity Versus % Hydrolysis	91

12.	Attempted Hydrolysis of Poly(methyl p-styrenesulfonate-co-acrylic acid) in 100% H ₂ O	94
K.	Miscellaneous	94
1.	Titration Curves for Poly(styrene-sulfonic acid-co-acrylic acid), Poly(styrenesulfonic acid) and Poly(acrylic acid)	94
2.	Conductiometric Titration of Poly(styrenesulfonic acid-co-acrylic acid)	98
3.	Viscosity of Poly(methyl p-styrene-sulfonate-co-sodium styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O and 100% H ₂ O	98
III.	RESULTS AND DISCUSSION	101
A.	Objectives	101
B.	Preparation of Alkyl Styrenesulfonates	102
1.	Synthesis of Alkyl Styrenesulfonates via (2-Bromoethyl)benzene	102
2.	Synthesis of Alkyl Styrenesulfonates via Sodium Styrenesulfonate	104
C.	Homopolymerization of Alkyl Styrene-sulfonates	106
D.	Copolymerization of Alkyl Styrene-sulfonates	110
1.	Copolymerization with Styrene	110
2.	Copolymerization with Acrylic Acid	110
3.	Copolymerization with Maleic Anhydride	111
4.	Copolymerization with 2-Acrylamido-2-methyl-propanesulfonic acid	112
5.	Copolymerization with Sodium 2-Sulfoethyl Methacrylate	112
6.	Attempted Copolymerization with Acrylamide	112
7.	Attempted Copolymerization with Sodium Acrylate	113
8.	Attempted Copolymerization with Sodium Styrenesulfonate	115
9.	Preparation of Alkyl Styrenesulfonate-Sodium Styrenesulfonate Copolymers	115
10.	Copolymerization Reactivity Ratios	117
11.	Q-e Scheme	125
12.	Copolymer Water Solubility Studies	129
E.	Hydrolysis Studies	130
1.	Neutral Hydrolysis of Alkyl Toluenesulfonates	134
2.	Neutral Hydrolysis of Poly(alkyl styrenesulfonates)	141

3.	Neutral Hydrolysis of Poly(alkyl styrenesulfonate) Copolymers	153
a.	Poly(methyl styrenesulfonate-co-styrene)	153
b.	Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	159
c.	Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O	161
d.	Attempted Hydrolysis of Poly(methyl styrenesulfonate-co-acrylic acid)	163
4.	Molecular Weight Effects	163
5.	Solvent Effects	166
6.	Effect of Acid and Base on the Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate)	170
7.	Poly(methyl styrenesulfonate) Emulsion	173
F.	Thermal Analysis of Homopolymers	175
G.	Conclusions and Further Work	178

.

REFERENCES	181
----------------------	-----

APPENDIX	188
--------------------	-----

A.	Proton Nuclear Magnetic Resonance Spectra	188
B.	Carbon-13 Nuclear Magnetic Resonance Spectra	197
C.	Infrared Spectra	205
D.	Hydrolysis Data	215

LIST OF TABLES

Table

1.	Alkyl p-Vinylbenzenesulfonates	8
2.	Comparison of Activation Energies, E, and Frequency Factors, A, in the Alkaline Hydrolysis of Ethyl Benzoate and Ethyl Benzenesulfonate in Water . . .	15
3.	Rates of Hydrolysis of the Ethyl Esters of Ring Substituted Benzenesulfonates in 70% Aqueous Dioxane.	18
4.	Hydrolysis of Benzenesulfonic Acid Esters in 56% Acetone at 50°C.	20
5.	Neutral Hydrolysis of Benzenesulfonic Acid Esters in 56 Wt% Acetone-Water.	21
6.	Alkaline Hydrolysis of Benzenesulfonic Acid Esters in 56 Wt% Acetone-Water.	22
7.	Purification of Methyl p-(2-Bromoethyl)benzenesulfonate by Preparative HPLC.	42
8.	Monomer Synthesis.	48
9.	Homopolymer Synthesis.	53
10.	Copolymerization of Alkyl Styrenesulfonates with Styrene.	58
11.	Copolymerization of Alkyl Styrenesulfonates with Acrylic Acid	59
12.	Copolymerization of Alkyl Styrenesulfonates with Maleic Anhydride	62
13.	Copolymerization of Styrene and Methyl Styrenesulfonate	66
14.	Copolymerization of Acrylic Acid and Methyl Styrenesulfonate	67
15.	Copolymerization of Maleic Anhydride and Methyl Styrenesulfonate	68
16.	% Comonomer vs. Water Solubility: Methyl Styrenesulfonate-Acrylic Acid Copolymers.	70
17.	% Comonomer vs. Water Solubility: Methyl Styrenesulfonate-Sodium Styrenesulfonate Copolymers . . .	71
18.	Synthesis of Alkyl Toluenesulfonates	72
19.	Homopolymer Molecular Weight Analysis By Viscosity	75
20.	Differential Scanning Calorimetry (DSC).	77
21.	Thermogravimetric Analysis (TGA)	80
22.	Viscosity of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) Solutions in Water and Aqueous DMSO	100
23.	Homopolymer Synthesis Results.	107
24.	Copolymerization Reactivity Ratios	123
25.	Reactivity Ratios of Styrenesulfonic Acid Derivatives.	124

26.	Alfrey-Price Q-e Values for Methyl Styrenesulfonate	128
27.	Alfrey-Price Q-e Values for Styrenesulfonic Acid Derivatives	128
28.	Values of k_1 , E, and Log A for the Neutral Hydrolysis of Alkyl Toluenesulfonates in 90/10 DMSO/H ₂ O	140
29.	Values of k_1 , E, and Log A for the Neutral Hydrolysis of Poly(alkyl styrenesulfonates) in 90/10 DMSO/H ₂ O	150
30.	Values of k_1 , E, and Log A for the Neutral Hydrolysis of Methyl Styrenesulfonate Copolymers	156
31.	Values of k_1 for the Neutral Hydrolysis of Various Molecular Weight Poly(methyl styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H ₂ O.	165
32.	Values of k_1 for the Neutral Hydrolysis of Poly(methyl styrene-co-sodium styrenesulfonate) at 70°C in Various Solvents.	168
33.	Values of k_1 for the Neutral, Acidic, and Basic Hydrolysis of Poly(methyl styrene-co-sodium styrenesulfonate) at 70°C in 100% H ₂ O	172
34.	Glass Transition Temperatures of Poly(alkyl styrenesulfonates)	176
35.	Glass Transition Temperatures of Poly(alkyl acrylates and Poly(alkyl methacrylates).	176
36.	Glass Transition Temperatures of Poly(alkyl styrenes).	176

LIST OF FIGURES

Figure

1.	Hydrolysis of Sulfonic Acid Ester Containing Polymers	2
2.	Preparation of Styrenesulfonic Acid Esters	5
3.	Purity of Methyl p-(2-Bromoethyl)benzenesulfonate by Analytical HPLC	38
4.	Preparative HPLC Purification of Methyl p-(2-Bromoethyl)benzenesulfonate	40
5.	Analytical HPLC of Methyl p-(2-Bromoethyl)-benzenesulfonate	41
6.	Analytical HPLC of Sodium Styrenesulfonate	44
7.	Analytical HPLC of Methyl Styrenesulfonate	46
8.	Poly(Sodium Styrenesulfonate) Calibration Curve for Homopolymer Molecular Weight Analysis.	74
9.	Thermogravimetric Analysis (TGA) of Poly(Methyl Styrenesulfonate).	79
10.	Hydrolysis Apparatus	82
11.	Neutral Hydrolysis of Methyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	84
12.	Neutral Hydrolysis of Ethyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	84
13.	Neutral Hydrolysis of n-Propyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	85
14.	Neutral Hydrolysis of Isopropyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	85
15.	Neutral Hydrolysis of Poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O.	86
16.	Neutral Hydrolysis of Poly(ethyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O.	86
17.	Neutral Hydrolysis of Poly(n-propyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	87
18.	Neutral Hydrolysis of Poly(isopropyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	87
19.	Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-styrene) in 90/10 (v/v) DMSO/H ₂ O.	88
20.	Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O	88
21.	Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in Various Solvent Systems at 70°C	90
22.	Acidic and Basic Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H ₂ O at 70°C.	90
23.	Neutral Hydrolysis of Poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O.	92

24.	Neutral Hydrolysis of Poly(methyl styrenesulfonate) Emulsion in 100% H ₂ O	92
25.	Neutral Hydrolysis of Poly(methyl styrenesulfonate): Solution Viscosity versus % Hydrolysis	93
26.	Titration Curves for Poly(styrenesulfonic acid-co-acrylic acid)	95
27.	Titration Curve for Poly(styrenesulfonic acid)	96
28.	Titration Curve for Poly(acrylic acid)	97
29.	Conductimetric Titration Curve for Poly(styrenesulfonic acid-co-acrylic acid) in 100 % H ₂ O	99
30.	Mechanism of Sulfone Formation	103
31.	Ionic Crosslinks in Alkyl Styrenesulfonate-Acrylamide Copolymers.	114
32.	Preparation of Alkyl Styrenesulfonate-Sodium Styrenesulfonate Copolymers.	116
33.	Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Styrene	121
34.	Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Acrylic Acid.	121
35.	Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Maleic Anhydride.	122
36.	Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Alkyl Toluenesulfonates at 70°C in 90/10 (v/v) DMSO/H ₂ O.	135
37.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	136
38.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Ethyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	136
39.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of n-Propyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	137
40.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Isopropyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	137
41.	Arrhenius Plot for the Neutral Hydrolysis of Methyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	138
42.	Arrhenius Plot for the Neutral Hydrolysis of Ethyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	138
43.	Arrhenius Plot for the Neutral Hydrolysis of n-Propyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	139
44.	Arrhenius Plot for the Neutral Hydrolysis of Isopropyl Toluenesulfonate in 90/10 (v/v) DMSO/H ₂ O	139

45.	Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Poly(alkyl styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H ₂ O.	142
46.	Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate and Poly(methyl styrenesulfonate) at 70°C in 90/10 (v/v) DMSO/H ₂ O	144
47.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate and Poly(methyl styrenesulfonate) at 70°C in 90/10 (v/v) DMSO/H ₂ O	144
48.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	145
49.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Poly(ethyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	145
50.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Poly(n-propyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	146
51.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Poly(isopropyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	146
52.	Neighboring Group Effects in the Hydrolysis of Poly(alkyl styrenesulfonates).	148
53.	Arrhenius Plot for the Neutral Hydrolysis of Poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	151
54.	Arrhenius Plot for the Neutral Hydrolysis of Poly(ethyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	151
55.	Arrhenius Plot for the Neutral Hydrolysis of Poly(n-propyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	152
56.	Arrhenius Plot for the Neutral Hydrolysis of Poly(isopropyl styrenesulfonate) in 90/10 (v/v) DMSO/H ₂ O	152
57.	Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate, Poly(methyl styrenesulfonate), and Poly(methyl styrenesulfonate-co-styrene) at 70°C in 90/10 (v/v) DMSO/H ₂ O.	154
58.	Plot of Ln(100/100-p) vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-styrene) in 90/10 (v/v) DMSO/H ₂ O	155
59.	Arrhenius Plot for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-styrene) in 90/10 (v/v) DMSO/H ₂ O	155
60.	Alkyl Styrenesulfonate-Styrene Copolymers.	158

61.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in 90/10 (v/v) DMSO/ H_2O	160
62.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H_2O	162
63.	Arrhenius Plot for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H_2O	162
64.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Various Molecular Weight Poly(methyl styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/ H_2O	164
65.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in 50/50 (v/v) DMSO/ H_2O	167
66.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in 100% H_2O	167
67.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral, Acidic, and Basic Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in 100% H_2O	171
68.	Plot of $\text{Ln}(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(methyl styrenesulfonate) at 75°C in 90/10 (v/v) DMSO/ H_2O and Poly(methyl styrenesulfonate) Emulsion at 80°C in 100% H_2O	174

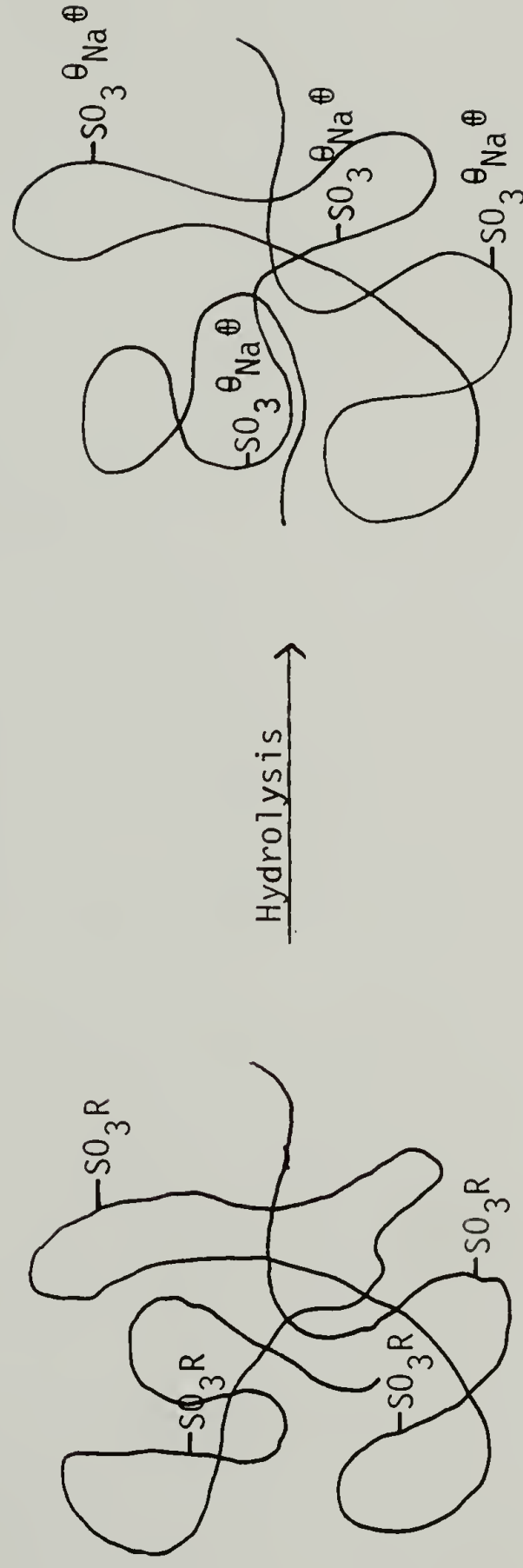
C H A P T E R I

INTRODUCTION

Polyelectrolytes find applications in a variety of fields including polymer processing (1), oil recovery (2), ion exchange resins (3), catalysts for organic reactions (4), and as soil conditioners in agriculture (5). In many applications a controlled release of the polyelectrolyte over a certain interval of time would be desirable. One possible approach to this end is to mask the polyelectrolyte acid functionality in the form of an ester which can be hydrolyzed at a controlled rate to release the acid functionality over a certain interval of time (see Figure 1).

The objective of this dissertation has been the preparation and characterization of sulfonic acid ester containing polymers for just such applications. Specifically, polymers chosen for consideration are substituted styrene homopolymers and copolymers, i.e. polymers derived from styrenesulfonic acid esters. In addition to preparation and characterization, the present work has also been concerned with investigation of the hydrolysis behavior of styrenesulfonic acid ester containing polymers under a variety of conditions. The effects of ester type, copolymerization, molecular weight, reaction

Figure 1. Hydrolysis of Sulfonic Acid Ester Containing Polymers.



solvent, pH, and temperature on hydrolysis kinetics has been investigated. Comonomers chosen for consideration include styrene and various water-soluble comonomers such as acrylic acid, acrylamide, maleic anhydride, sodium styrenesulfonate, sodium 2-sulfoethyl methacrylate (NaSEM), and 2-acrylamido-2-methylpropanesulfonic acid (AMPS).

In the following pages of this chapter pertinent literature concerning functional polymer preparation, synthesis and polymerization of styrenesulfonic acid esters, hydrolysis behavior of low molecular weight sulfonic acid esters, and general hydrolysis behavior of polymers is reviewed.

A. Methods of Preparation of Functional Polymers

Three synthetic approaches to the problem of preparing polymers containing functional groups can be employed. These include oligomer endcapping, functionalization of an existing polymer, and direct homo- or copolymerization of functional monomers.

Endcapping of oligomers provides low or moderate molecular weight polymers which are terminated by a functional group. While this is an increasingly important area of polymer chemistry, it is clearly limited in the

amount of functional groups which can be incorporated.

Performing reactions on polymers provides versatility regarding the type and functionality able to be included, but difficulties with limiting conversion and removal of side products (which may be polymer-bound) from the product polymer complicate this method.

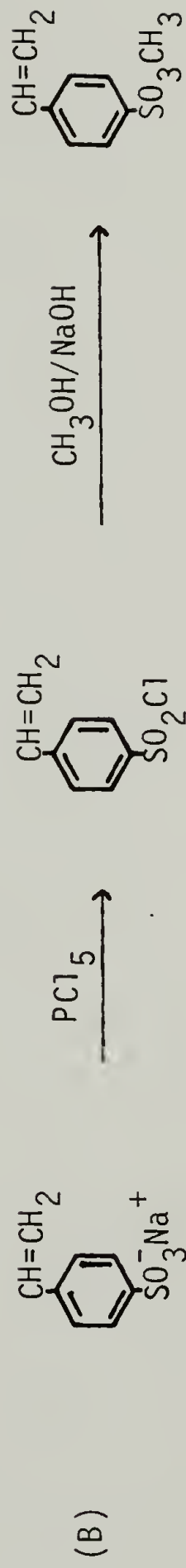
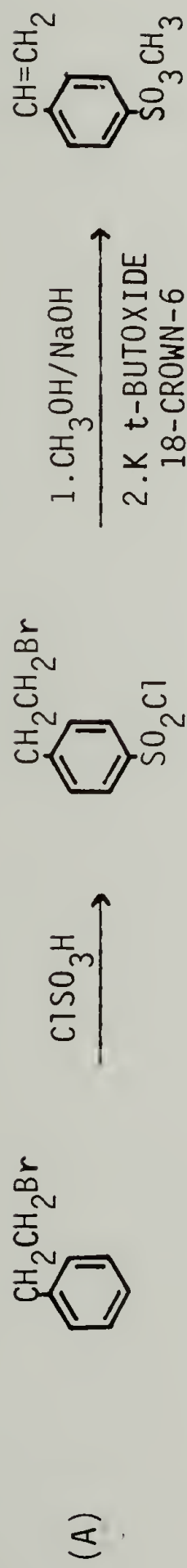
Direct homo- or copolymerization of functional monomers offers perhaps the greatest flexibility with respect to the amount of functional moiety which can be incorporated into the final product. Also, properties of the resultant polymer can be specifically tailored for a desired application by proper comonomer selection.

B. Preparation of Styrenesulfonic Acid Esters

Two approaches to the synthesis of styrenesulfonic acid esters have been reported in the literature. These include: (1) synthesis via (2-bromoethyl)benzene; and (2) synthesis via sodium styrenesulfonate. Both of these approaches are illustrated in Figure 2.

The preparation of styrenesulfonic acid esters was first reported by Spinner, Ciric, and Graydon in 1954 (6). Sulfochlorination of (2-bromoethyl)benzene with chlorosulfonic acid, in accordance with the procedure of

Figure 2. Preparation of Styrenesulfonic Acid Esters; (A) Synthesis via (2-Bromoethyl)benzene (B) Synthesis via Sodium Styrenesulfonate.



Inskeep and Deanin (7), led to (2-bromoethyl)benzenesulfonyl chloride (56% yield) which was subsequently esterified under basic conditions with the appropriate alcohol and dehydrohalogenated in the presence of potassium hydroxide. Using this method the methyl (75% yield), ethyl (55% yield), n-propyl, and n-butyl esters of styrenesulfonic acid were prepared.

In 1958 Chen and Hammet reported the preparation of ethyl, n-butyl, n-hexyl, n-octyl, and benzyl esters of styrenesulfonic acid from (2-bromoethyl)benzene (8). They found that the method of Spinner, Ciric, and Graydon (6) worked well for the ethyl ester but gave low yields for higher esters due to the fact that the high temperatures required for removal of excess alcohol, even in vacuo, tended to cause decomposition and polymerization of the product. Improved yields (60-80%) were obtained by use of a zinc oxide/pyridine catalyst system which permitted for much lower excesses of alcohol to be used.

Several additional authors have reported the synthesis of various styrenesulfonic acid esters from (2-bromoethyl)benzene according to the procedure of Spinner, Ciric, and Graydon (6). Aylward reported the synthesis of n-propyl styrenesulfonate for the preparation of stereoregular poly(styrenesulfonic acid) (9). Siadat (10) synthesized methyl

and 2-butyl styrenesulfonates for the preparation of isoprene copolymers; Whicher and Brash (11) reported the preparation of methyl, n-propyl, isopropyl, and s-butyl styrenesulfonates for anionic polymerization studies. Brydges et al. (12) reported the synthesis of n-propyl styrenesulfonate for the preparation of ion-exchange resins. Rosenblum et al. (13) synthesized ethyl, n-propyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, phenyl, and β -naphthyl styrenesulfonates for the preparation of ion-exchange resins.

The second approach for the synthesis of styrene-sulfonic acid esters, employing sodium styrenesulfonate, was first reported in 1967 by Gritsai and Prib (14). Sodium styrenesulfonate was conveniently converted to the acid chloride by reaction with phosphorous pentachloride (73% yield). The acid chloride was subsequently treated with excess alcohol under basic conditions to yield the styrene-sulfonic acid ester. Using this procedure a number of alkyl (14) and unsaturated (15) esters of styrenesulfonic acid were prepared. Yields and properties of these esters are summarized in Table 1. The only other preparation of styrenesulfonic acid esters using this method was reported in 1979 by Siadat (10). He reported the synthesis of styrenesulfonyl chloride as well as the methyl and 2-butyl esters of styrenesulfonic acid. No yields were given.

Table 1. Alkyl p-Vinylbenzenesulfonates
 $\text{CH}_2=\text{CHC}_6\text{H}_4\text{SO}_2\text{OR}$ (14,15).

R	Yield (%)	d_4^{20}	n_D^{20}
Methyl	71	1.1769	1.1521
Ethyl	78	1.1599	1.5128
n-Propyl	78	1.1751	1.5120
n-Butyl	70	1.1498	1.5100
Isobutyl	69	1.1319	1.5060
n-Pentyl	81	1.1319	1.5438
n-Hexyl	82	1.1688	1.5210
Allyl	71	1.1564	1.5260
Crotyl	72	1.1938	1.5458
Cinnamyl	68	1.2390	1.5918
Propargyl	84	1.1944	1.5288

C. Polymerization of Styrenesulfonic Acid Esters

Several authors have reported the homo- and co-polymerization of styrenesulfonic acid esters prepared as described previously. While most reports involve free radical copolymerization with divinylbenzene for the preparation of crosslinked ion-exchange resins, several reports of homopolymerization and copolymerization to linear, soluble polymers have been published.

Spinner, Ciric, and Graydon (6) reported the suspension copolymerization of divinylbenzene with methyl, ethyl, n-propyl and n-butyl styrenesulfonates using benzoyl peroxide. Hydrolysis of the resulting crosslinked copolymers led to ion-exchange resins whose properties were compared to those of sulfonated polystyrenes prepared by conventional techniques.

Chen and Hammet (8) reported the copolymerization of ethyl, n-butyl, n-hexyl, n-octyl, and benzyl esters of styrenesulfonic acid with divinylbenzene using benzoyl peroxide. Partial hydrolysis of the resulting crosslinked copolymers led to sulfonic acid containing polymers whose catalytic efficiencies for the hydrolysis of ethyl acetate, ethyl butyrate, ethyl hexanoate, and methyl phenyl acetate

were determined.

Rosenblum et al. (13) prepared copolymers of a variety of alkyl and aromatic styrenesulfonates with styrene and divinylbenzene in order to study the effect of ester bulkiness on ion-exchange properties of the resultant hydrolyzed copolymers. Copolymers of ethyl, n-propyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, phenyl, and β -naphthyl styrenesulfonates with styrene and divinylbenzene were prepared in the bulk with benzoyl peroxide. The resultant membranes were hydrolyzed and analyzed for moisture content, ion-exchange capacities, and flexibility. It was found that larger esters led to greater porosities and correspondingly greater capacities, moisture content, and flexibility.

Brydges et al. (12) reported the copolymerization of n-propyl styrenesulfonate with styrene and divinylbenzene using benzoyl peroxide. The resultant membranes were hydrolyzed to form ion-exchange resins. Properties of the resins such as capacity, water content, swelling, and elastic modulus were determined.

Gritsai and Prib (14,15) mentioned that saturated as well as unsaturated esters of styrenesulfonic acid (Table 1) homopolymerize spontaneously to a transparent mass when stored at room temperature for extended periods of time.

However, no physical properties or polymer yields were reported.

Aylward (9) reported the anionic homopolymerization of n-propyl styrenesulfonate with n-butyllithium in tetrahydrofuran at -75°C . The homopolymer obtained was of low molecular weight (M.W. 4,000-5,000) and was proposed to be highly syndiotactic. Aylward also reported the homopolymerization of n-propyl styrenesulfonate using a Ziegler-Natta catalyst system (16). n-Propyl styrenesulfonate was polymerized at 50°C using a $\text{Et}_3\text{Al} - \text{TiCl}_4$ catalyst to give crystalline poly(n-propyl styrenesulfonate). The glass transition temperature (T_g) and melting point of the polymer were determined by differential thermal analysis (DTA) to be 217°C and 349°C respectively. The homopolymer was assumed to be isotactic.

Siadat (10) reported the preparation of copolymers of isoprene with methyl and 2-butyl styrenesulfonates by emulsion copolymerization. Hydrolysis of the copolymers led to elastomeric ionomers with increased sulfonate content over that possible by the direct emulsion copolymerization of isoprene and sodium styrenesulfonate.

Whicher and Brash (11) reported the anionic homopolymerization of methyl, n-propyl, and isopropyl styrenesulfonates using radical anions of naphthalene. Only a limited degree

of polymerization (DP) could be achieved over a wide variety of polymerization conditions (M.W. 4,000-11,000). It was suggested that the living polymeric anions become dormant owing to a complexation between the anion and nearby sulfonate groups on the polymer chain.

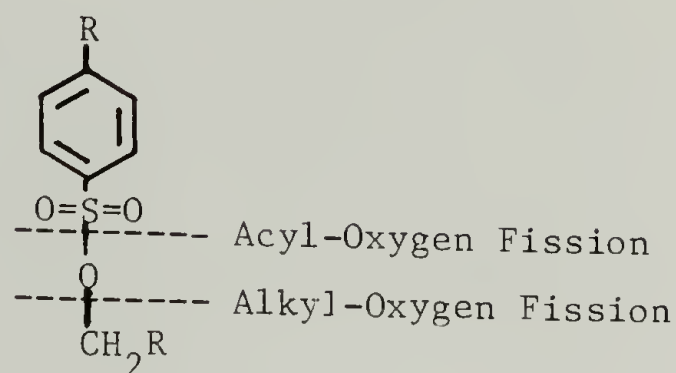
D. Hydrolysis of Sulfonic Acid Esters

In this section the general hydrolysis behavior of sulfonic acid esters is reviewed. Subjects covered include a comparison of carboxylic and sulfonic acid ester hydrolysis, as well as a brief discussion of hydrolysis kinetics and mechanism. Finally, a review of the pertinent literature concerning the hydrolysis of low molecular weight sulfonic acid esters is presented.

1. Carboxylic vs. Sulfonic Acid Ester Hydrolysis. The hydrolysis of esters involving the carbonyl group has been widely discussed in the literature (17-23), but considerably less work has been reported on the corresponding reaction involving the sulfonyl group. Although the sulfonyl group ($--SO_2--$) owes its name to the formal resemblance to the carbonyl group, the reactions of these two groups, and specifically hydrolysis, are, in fact, quite different.

The hydrolysis of esters may take place by either an

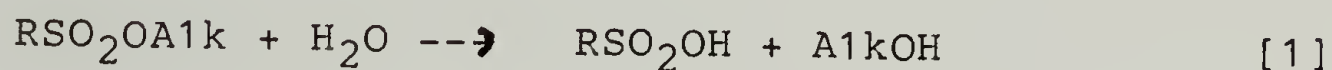
acyl-oxygen mechanism (24-27), by an alkyl-oxygen mechanism



(28-34), or more rarely by both mechanisms at the same time (35-38). While hydrolysis in carboxylic acid esters can involve fission of the acyl-oxygen bond, only alkyl-oxygen bond breaking occurs with sulfonate esters as shown with certainty by use of water containing heavy oxygen in the study of alkyl sulfonate hydrolysis (39). Thus, while most nucleophilic substitution reactions in carbonyl compounds involves the nucleophilic reagent attacking the carbonyl carbon (40,41), nucleophilic substitution occurs quite differently in sulfonyl compounds. Even though the sulfur atom is positively charged, nucleophilic attack on the sulfur atom in the $-\text{SO}_2-$ group is difficult, mainly for steric reasons (i.e. the transition state involves a crowded penta-coordinate structure as opposed to a tetravalent structure in carbonyl compounds). The $-\text{SO}_2-$ group draws the electrons in the alkyl chain towards itself: $\text{S} \leftarrow \text{O} \leftarrow \text{C}$; and as a result, the alkyl carbon acquires a weak

positive charge, so the hydroxyl ion attacks this atom. However, the attraction between the negative ion and the carbon atom is weak, and consequently the activation energies and frequency factors for the hydrolysis of alkyl sulfonates are far higher than those for corresponding carboxylic acid esters as illustrated in Table 2.

2. Kinetics. In the absence of bases, the hydrolysis of alkyl benzenesulfonates occurs according to the equation:



and obeys the following first order rate law:

$$\frac{dx}{dt} = k_1(a-x) \quad [2]$$

where k_1 is the first order rate constant and $a-x$ is the concentration of the ester (43). In the presence of bases, the hydrolysis of alkyl benzenesulfonates occurs according to the equation:



and obeys the following kinetic equation:

Table 2. Comparison of Activation Energies, E, and Frequency Factors, A, in the Alkaline Hydrolysis of Ethyl Benzoate and Ethyl Benzenesulfonate in Water (42).

Compound	E (cal./mol.)	Log A
Ethyl Benzoate	12,700	7.76
Ethyl Benzenesulfonate	21,100	12.70

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)(b-x) \quad [4]$$

where $a-x$ is the ester concentration, $b-x$ the hydroxide-ion concentration, k_1 the first order rate constant from Equation [2], and k_2 is the rate constant for the bimolecular reaction (44). If relatively high alkali concentrations are used, the neutral hydrolysis can be neglected, and the rate equation is given by Equation [5].

$$\frac{dx}{dt} = k_2(a-x)(b-x) \quad [5]$$

Finally, it should be mentioned that it has been well-documented that the hydrolysis of sulfonic acid esters is not catalyzed by acids (45-49). This is a result of the fact that the basicity of sulfonic esters is relatively low, and as a result, the concentration of the protonated form in acidic solution is quite small.

Studies of the hydrolysis of methyl, ethyl, n-propyl, and isopropyl benzenesulfonates in aqueous solution have shown that the reaction velocities follow the order n-propyl < ethyl < methyl < isopropyl, i.e. the order of decreasing electron-repulsive character of the alkyl group in the alcohol (45). In other words, as the ester group $-OCH_2R$ is varied in the direction of increasing negative charge on C (i.e. $H < CH_3 < CH_2CH_3$), repulsion between

this C atom and the attacking nucleophilic reagent will increase and the reaction velocity decreases. Isopropyl benzenesulfonate does not follow this behavior and reacts much faster than expected due to a change in reaction mechanism ($S_N2 \rightarrow S_N1$) as described in the next section. This conclusion is supported by the fact that the rate of hydrolysis of the isopropyl ester has been found to be independent of the concentration of hydroxide ions and remains constant in alkaline, neutral, and acidic media, indicative of an S_N1 mechanism (43).

The influence of aryl substituents, transmitted through the benzene ring to the sulfonate group, according to results obtained for the alkaline hydrolysis of alkyl sulfonates (46), follows the same general rules. Electron withdrawing substituents increase, whereas electron-donor substituents decrease, the rate of hydrolysis. This trend is illustrated in Table 3 where the results for the alkaline hydrolysis of various substituted ethyl benzenesulfonates are summarized (51).

3. Mechanism. As discussed above, it is believed that in a series of aliphatic esters of benzenesulfonic acid, a change in the nature of the alcohol component affects not only the rate but also the mechanism of hydrolysis. If R in the ester $XC_6H_4SO_2OR$ is derived from a primary alcohol,

Table 3. Rates of Hydrolysis of the Ethyl Esters of Ring Substituted Benzenesulfonates in 70% Aqueous Dioxane (51).

Ring Substituent	$10^3 k_1$ @ 50°C (sec ⁻¹)	Ethyl Sulfonates $\text{XC}_6\text{H}_4\text{SO}_2\text{OC}_2\text{H}_5$ E (cal.mol.)	Log A
4-CH ₃ O	0.248	20,880	10.49
4-CH ₃	0.291	20,150	10.10
H	0.596	19,070	9.65
4-Cl	1.445	18,800	9.88
4-Br	1.440	18,270	9.52
4-NO ₂	6.52	17,710	9.80

the reaction takes place by an S_N2 mechanism (43,51); if R is derived from a cycloalkyl, secondary, or tertiary aliphatic alcohol, hydrolysis takes place by a pre-ionization S_N1 mechanism (50,52). The change in mechanism in going from primary to either secondary or tertiary alcohols can be rationalized in terms of repulsion between the attacking reagent (OH^- or H_2O) and the alkyl carbon atom. In the hydrolysis of sulfonic acid esters $XC_6H_4SO_2OCH_2R$, when $R = H$, repulsion is insignificant and the reaction occurs by an S_N2 mechanism. When, however, the energy of repulsion between the attacking reagent and the alkyl carbon is significant, as in the case of secondary or tertiary alcohols, reaction takes place by an S_N1 mechanism. In conformity with this, the S_N1 mechanism usually requires a greater activation energy than does the S_N2 mechanism for similar molecules. However, the frequency factor is typically greater for the former than the latter type of process, as exemplified by the results presented in Table 4 (50).

Table 4. Hydrolysis of Benzenesulfonic Acid Esters in 56% Acetone at 50°C (50).

ESTER	$10^7 k_1$ (sec ⁻¹)	E (cal./mol.)	Log A
C ₆ H ₅ SO ₂ OPr(n)	48.2	21,800	9.42
C ₆ H ₅ SO ₂ OPr(iso)	839	22,780	11.34

4. Results for hydrolysis of low molecular weight substituted alkyl benzenesulfonates. A number of studies involving the hydrolysis of low molecular weight alkyl benzenesulfonates and substituted alkyl benzenesulfonates have been reported in the literature. Of particular interest in this investigation are the results reported by Tommila et al. (34,50,53) for the neutral and alkaline hydrolysis of benzenesulfonic acid esters as summarized in Tables 5 and 6. A brief summary of other relevant literature concerning the hydrolysis of substituted benzenesulfonic acid esters is given below. Several excellent reviews concerning sulfonate ester hydrolysis have been published (54,55).

Numerous authors have investigated the alkaline hydrolysis of alkyl benzenesulfonates and alkyl toluene-

Table 5. Neutral Hydrolysis of Benzenesulfonic Acid Esters in 56 Wt% Acetone-Water (50).

Ester	$10^7 k_1 \text{ sec}^{-1}$				E (cal./mol.)	Log A
	25.00°C	40.00°C	50.00°C	60.00°C	75.00°C	
Methyl	-	71.0	201	529	-	9.25
Ethyl	-	29.1	86.8	242	974	9.64
n-Propyl	-	16.3	48.2	21.7	-	9.42
Isopropyl	43.1	284	839	-	-	11.34
Sec-Butyl	66.7	390	1,230	-	-	11.15

Table 6. Alkaline Hydrolysis of Benzenesulfonic Acid Esters in 56 Wt% Acetone-Water (34).

Ester	$10^4 k_2 \text{ l} \cdot \text{mol}^{-1} \text{ sec}^{-1}$			E (cal./mol.)	Log A
	25.00°C	40.00°C	50.00°C 60.20°C		
Methyl	7.96	35.8	90.5 217	18,750	10.63
Ethyl	0.490	2.67	7.50 19.9	20,800	10.94
n-Propyl	0.227	1.25	3.60 9.43	20,950	10.72

sulfonates (41,44,51,56-66). A number of solvent systems have been studied, including aqueous ethanol (44,57), acetone (57, 61, 66), dioxane (41, 51, 62) and water (56-59). Systematic studies concerning the effects of solvent composition (57, 61, 62), ester composition (57, 59, 66), and aryl substituents (51,66) have been reported.

Studies concerning the neutral hydrolysis of alkyl benzenesulfonates and alkyl toluenesulfonates are much less abundant than those for alkaline hydrolysis, although some have been reported (53,66-73). Solvent systems studied include aqueous acetone (66,72), aliphatic alcohols (69, 70,73), dioxane (72,73) and water (53,67,68,70,71).

5. Hydrolysis of polymers. Functional groups attached to a polymer chain undergo the same reactions as their low molecular weight analogs, but their reaction rates may vary considerably. While in many cases reaction rates for functional groups attached to a polymer chain are similar to those of low molecular weight analogs, there are also many cases in which reactions proceed either at faster or slower rates than the analogous nonpolymeric reactions. The differences in rates observed are mainly due to the fact that reaction along a polymer chain involves introduction of a new functional group (e.g., conversion of ester groups to acid groups in hydrolysis) which may either retard or

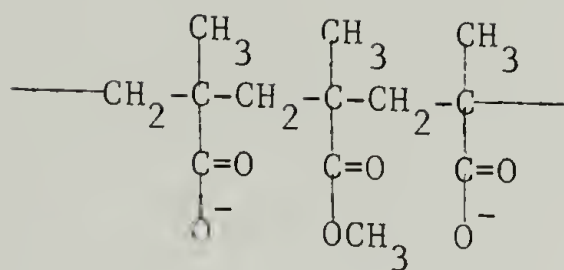
accelerate the reaction of neighboring groups. Also, conversion of functional groups along the polymer chain may result in changes in the microenvironment (e.g., changes in reactant concentration) within the polymer coil thus complicating reaction kinetics.

While there have been numerous studies concerning the hydrolysis of low molecular weight sulfonic acid esters (see previous section), there have been no reports on the hydrolysis behavior of polymers containing sulfonic acid esters. However, numerous studies concerning the hydrolysis behavior of polymers containing carboxylic acid esters have been reported (74-82), and several examples serve to illustrate the diverse behavior observed in polymer systems.

The hydrolysis of poly(vinyl acetate) has been investigated extensively. Lee and Sakurada (74) investigated the hydrolysis of poly(vinyl acetate) by sodium hydroxide in aqueous methanol. The data indicated a bimolecular reaction occurred whose rate constant agreed with those for the hydrolysis of monomeric vinyl acetate and ethyl acetate under the same conditions. Minsk et al. (75) studied the alcoholysis of poly(vinyl acetate) in methanol. They reported no change in the hydrolysis kinetics of either the base or acid catalyzed reactions with molecular weights over the molecular weight range 23,000 to 75,000. Fujii et

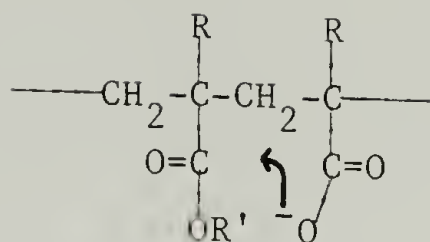
al. (76) also reported little effect of molecular weight on the alkaline hydrolysis of poly(vinyl acetate) for the molecular weight range 26,000 to 86,000. However, these investigators did report an effect of tacticity on hydrolysis kinetics. In the alkali-catalyzed hydrolysis of poly(vinyl acetate), in 70% aqueous dioxane, it was found that syndiotactic and atactic poly(vinyl acetates) exhibited approximately the same hydrolysis behavior while isotactic poly(vinyl acetate) hydrolyzed at a slower rate. No explanation was given.

Plate (77) studied the alkaline hydrolysis of poly-(methyl methacrylate). The rate was found to decrease by an order of magnitude as the reaction proceeded. This result was proposed to arise from the fact that hydrolysis of a few ester groups yielded a polymer in which the remaining uncharged groups were flanked by charged carboxylate groups, as shown below:



The presence of these negatively charged groups would be expected to retard the approach of the reagent (OH^-) to the adjacent ester groups, with a corresponding decrease in the reaction rate. This result is indeed what was observed. Similar results have been reported for the alkaline hydrolysis of poly(acrylamide) (78) and poly(methacrylamide) (79). At low degrees of conversion, however, the kinetic parameters for the hydrolysis of methacrylamide units are essentially identical to those for trimethylacetamide, its homologous analog (80).

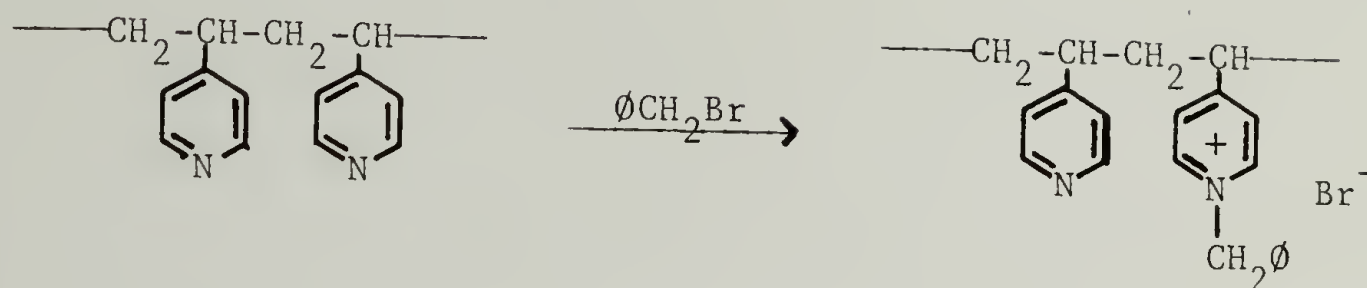
Several cases are known where the presence of a charged carboxylate ion actually accelerates the rate of hydrolysis for a neighboring ester functionality. For example, copolymers of acrylic acid and p-nitrophenyl methacrylate are hydrolyzed much more rapidly than are the p-nitrophenyl esters of small molecule carboxylic acids (81). This result occurs because the carboxylate ion itself can attack the adjacent ester function, as shown below:



Such intermolecular effects are dependent on geometric factors and are especially predominant when five- or six-membered cyclic intermediates are formed. Similar neighboring group effects are observed in the hydrolysis of isotactic poly(methyl methacrylate). A rate enhancement of 1-2 orders of magnitude is observed for the hydrolysis of isotactic poly(methyl methacrylate) in pyridine-water at 145 C, whereas no effect is observed for the syndiotactic polymer (77,82). The isotactic structure has neighboring functional groups in the optimum orientation for interaction with each other to form the cyclic intermediate.

Finally, polymer reactions involving the conversion of uncharged functional groups to charged groups can exhibit a decrease in reactivity with conversion even when a neutral reagent is involved (such as in neutral hydrolysis). The quaternization of poly(4-vinylpyridine) serves to illustrate this point. It has been observed that the reaction between poly(4-vinylpyridine) and benzyl bromide, as shown below,

becomes progressively slower:



with increasing conversion. This result is presumably due to the difficulty of forming a cationic group in close proximity to previously formed positive ions (83-85).

E. Summary

This chapter has addressed those matters which have a direct bearing on the work described in the remainder of this dissertation.

The methods available for the preparation of functional polymers were discussed. Preparation and polymerization of functional monomers is the method of choice in that it offers the greatest flexibility and control in polymer preparation.

Synthetic routes to styrenesulfonic acid esters were treated. Preparation of styrenesulfonic acid ester containing homopolymers and copolymers, as reported in the literature, was also reviewed.

Finally, the general hydrolysis behavior of sulfonic acid esters and macromolecular compounds were discussed. Examples illustrating effects peculiar to macromolecular compounds, including retardation and acceleration, were presented.

C H A P T E R I I

EXPERIMENTAL SECTION

A. Materials

The following chemicals were obtained from the indicated sources.

Acetone (MCB)	N,N-Dimethylformamide (F)
Acrylamide (A)	Dimethyl sulfoxide (A)
2-Acrylamido-2-methyl- propanesulfonic acid (S)	2,2-Diphenyl picrylhydrazol (E)
Acrylic acid (A)	Ethanol (MCB)
Ammonium hydroxide (A)	Ethyl ether (MCB)
Azobisisobutyronitrile (A)	Ethyl toluenesulfonate (A)
Benzene (MCB)	Isopropanol (A)
2-Bromoethyl benzene (A)	Lauryl mercaptan (A)
p-Benzoquinone (E)	Magnesium sulfate (MCB)
Bromothymol blue (E)	Maleic anhydride (A)
Calcium hydride (A)	Methanol (A)
Chlorosulfonic acid (A)	Methyl ethyl ketone (MCB)
18-Crown-6 (A)	Methyl toluenesulfonate (A)
Cupric chloride (F)	N-Methyl pyrrolidinone (A)
Dichloromethane (BJ)	Phosphorous pentachloride (A)
Poly(sodium styrenesulfonate) (S)	Sodium methoxide (A)
Potassium hydroxide (F)	Sodium styrenesulfonate (D)

Potassium persulfate (F)	Styrene (A)
Potassium t-butoxide (A)	2-Sulfoethyl methacrylate (DC)
n-Propanol (A)	Tetrachlorobenzoquinone (MCB)
Sodium bisulfite (F)	Tetrahydrofuran (BJ)
Sodium chloride (MCB)	Toluene (MCB)
Sodium hydroxide (F)	Toluenesulfonyl chloride (A)
Sodium lauryl sulfate (F)	

Sources:

A = Aldrich Chemical Company;
BJ = Burdick & Jackson Labs, Inc.;
DC = Dow Chemical Company;
D = E.I. DuPont Company;
E = Eastman Organic Chemicals;
F = Fisher Scientific Company;
MCB = MCB Manufacturing Chemists, Inc.;
S = Scientific Polymer Products, Inc.

B. Purification of Reagents and Solvents

Acrylamide was recrystallized twice from acetone and dried under vacuum at room temperature for 12 hours.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was recrystallized from methanol and dried under vacuum at 50°C for 12 hours.

Acrylic acid was distilled under reduced pressure (b.p. 30°C/3 mm) immediately prior to use.

Azobisisobutyronitrile (AIBN) was recrystallized from ethyl ether and dried under vacuum at room temperature for 12 hours.

p-Benzoquinone was recrystallized from ethyl ether and dried under vacuum at 50°C for 12 hours.

Cupric chloride was dehydrated by heating at 120°C under vacuum.

Dimethyl sulfoxide was dried over calcium hydride and distilled (b.p. 42°C/1 mm) prior to use.

Ethanol was refluxed over calcium hydride and distilled. The fraction boiling between 78°C and 79°C was collected and stored over 4A molecular sieves until use.

Ethyl toluenesulfonate was recrystallized from chloro-

form and dried under vacuum at 30°C for 12 hours.

Maleic anhydride was recrystallized from chloroform and dried under vacuum at 30°C for 12 hours.

Methyl toluenesulfonate was recrystallized from ethyl ether and dried under vacuum at 30°C for 12 hours.

N-Methyl pyrrolidinone was dried over calcium hydride and distilled (b.p. 65°C/2 mm) prior to use.

Styrene was distilled at 41-42°C (18 mm) and stored under argon in the cold until use.

Tetrachlorobenzoinone (chloranil) was recrystallized from acetone and dried under vacuum at 50°C for 12 hours.

Toluenesulfonyl chloride was recrystallized from petroleum ether (b.p. 30-60°C) and dried under vacuum at 30°C for 12 hours.

Water used for hydrolysis studies was twice distilled and freed of CO₂ by bubbling CO₂-free nitrogen through the water for several hours.

All other solvents and reagents were used as received.

C. Monomer Synthesis via (2-Bromoethyl)benzene

1. p-(2-Bromoethyl)benzenesulfonyl chloride (6,7,86). A 2 liter, three-neck, round-bottomed flask (equipped with a mechanical stirrer, addition funnel, and nitrogen inlet and outlet) was charged with 1 Kg (8.5 moles) of chlorosulfonic acid. The flask was cooled to 0°C in an ice-water bath and 232 ml (315g; 1.7 moles) of (2-bromoethyl)benzene added over a period of 6 hours, the temperature being held below 10°C. After an additional 2 hours, the reaction mixture was poured over a large quantity of ice, the aqueous layer decanted, and the product extracted with ethyl ether. The ether solution was dried over anhydrous magnesium sulfate, the ether volume reduced, and the product crystallized at dry ice temperature. The product was filtered and dried at 30°C under vacuum to yield 289g (60%) of a white crystalline solid (m.p. 53-54°C). Spectra: IR No. 1, ¹³C NMR No. 1, ¹H NMR No. 1.

2. Methyl p-(2-bromoethyl)benzenesulfonate (6,11). A 1 liter, three-neck, round-bottomed flask (equipped with a magnetic stirrer, addition funnel, and nitrogen inlet and outlet) was charged with 100g (0.353 moles) of p-(2-bromoethyl)benzenesulfonyl chloride and 600g of dry methanol. After stirring to dissolve, the solution was cooled in an ice-water bath and 80.0g of a 25 wt.% solution of sodium

methoxide (20.0g; 0.370 moles NaOCH_3) in methanol added over a period of 1 hour, maintaining the temperature below 10°C . After an additional 3 hours, the solution was diluted to 2 liters with ice-water and the ester extracted with ethyl ether. The ether phase was dried over anhydrous magnesium sulfate, filtered, the ether volume reduced, and the product crystallized at dry ice temperature. The product was filtered and dried at 30°C under vacuum to yield 55.2g (56%) of a white crystalline solid (m.p. $65-66^\circ\text{C}$). Spectra: IR No. 2, ^{13}C NMR No. 2, ^1H NMR No. 2.

ANAL. Calcd. for $\text{C}_9\text{H}_{11}\text{O}_3\text{SBr}$: C, 38.72%; H, 3.97%; S, 11.48%; Br, 28.62%. Found: C, 39.21%; H, 3.94%; S, 11.21%; Br, 28.51%.

3. Methyl p-styrenesulfonate. A 250 ml, three-neck, round-bottomed flask (equipped with a magnetic stirrer, thermometer, and nitrogen inlet and outlet) was charged with 100 ml of anhydrous ethyl ether, 0.42g (75 mmol) of potassium t-butoxide, 0.99g (3.75 mmol) of 18-crown-6, and 13.96g (50 mmol) of methyl p-(2-bromoethyl)benzenesulfonate. The mixture was stirred at room temperature for 24 hours and covered to prevent light from entering the reaction vessel. The resulting solution was washed with five 50 ml portions of water and the organic layer dried over anhydrous magnesium sulfate. The solution was filtered and the ether removed by rotary evaporation at room temperature to yield

5.95g (60%) of a clear, light yellow oil. Spectra: ^1H NMR No. 3.

4. Purity of methyl p-styrenesulfonate: homopolymerization. Homopolymerization affords a simple but sensitive test for determination of the presence or absence of sulfone. Insoluble, crosslinked homopolymerization products indicate the presence of sulfone while soluble, linear products indicate negligible sulfone content.

A glass polymerization tube was flushed with argon and charged with 3.2g (16 mmol) of methyl p-styrenesulfonate and 0.0132g (0.08 mmol) of azobisisobutyronitrile (AIBN). The contents were degassed and sealed under vacuum. The tube was placed on a shaker/oil bath at 60°C for 6 hours and allowed to cool. The clear, light yellow solid obtained was insoluble in toluene, tetrahydrofuran, ethanol, N-methyl pyrrolidinone (NMP), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO).

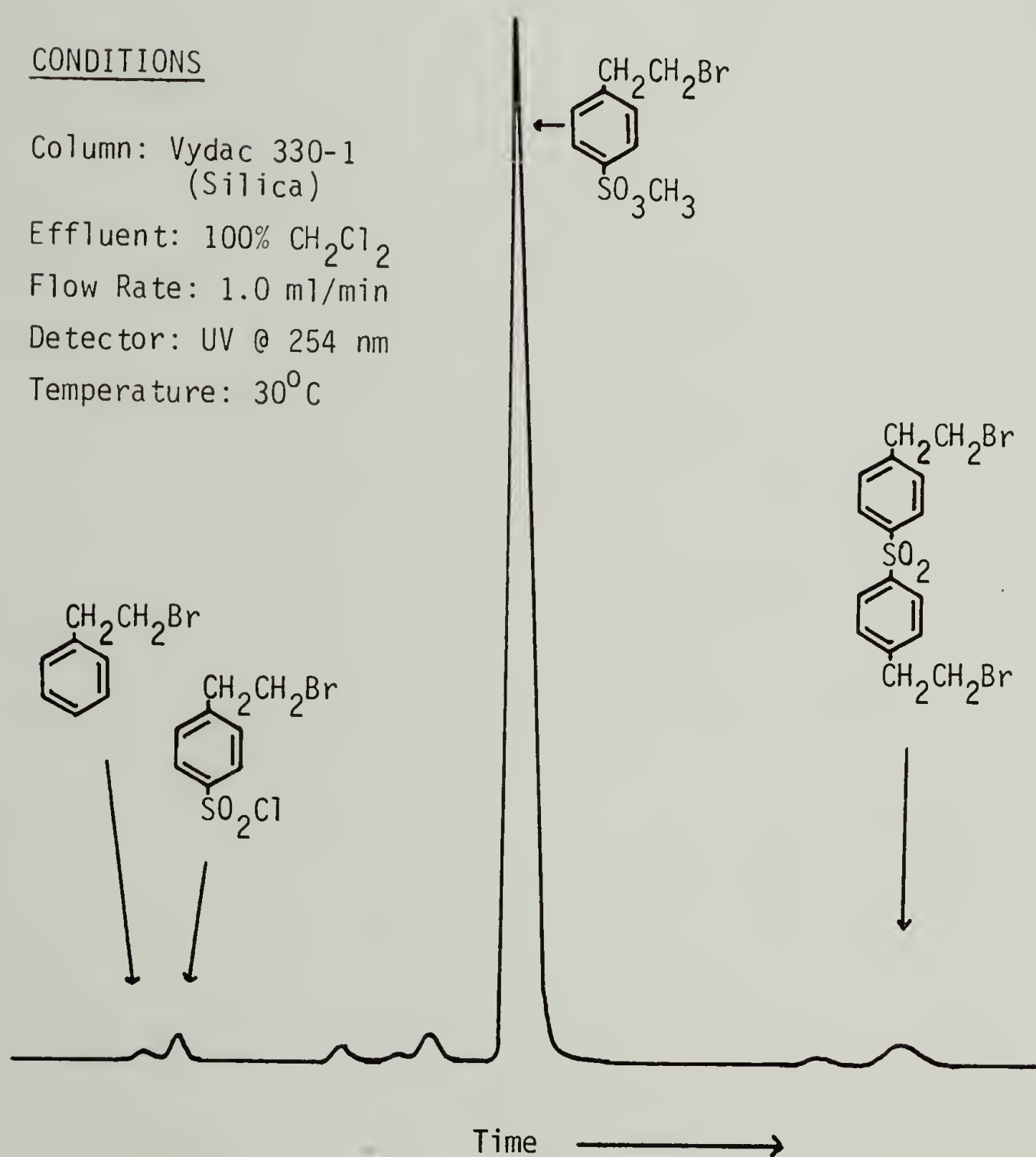
5. Bis-[p-(2-bromoethyl)benzene]sulfone (87,88). 300g (1.74 moles) of (2-bromoethyl)benzene was chlorosulfonated with 1000g (8.58 moles) of chlorosulfonic acid at 25°C. The addition required 20 minutes. After an additional 4 hours at room temperature, the mixture was poured over 3 liters of ice, the aqueous layer decanted, and the product washed with

2 liters of ice-water. The sulfonyl chloride (300g; 1.05 moles) was slowly introduced into an excess of ammonium hydroxide (52.6g; 1.5 moles), heated under reflux for 15 minutes, and allowed to stand overnight. The solid was filtered and washed with water. The crude p-(2-bromoethyl)-benzene sulfonamide was dissolved in 6 liters of 5% sodium hydroxide and filtered. The residue was washed with 300 ml water and dried. The crude sulfone was recrystallized twice from hot methanol to yield 5.0g (1.3%) of pure sulfone (m.p. 158-159°C). Spectra: IR No. 3, ^1H NMR No. 4.

ANAL: Calcd. for $\text{C}_{16}\text{H}_{16}\text{SO}_3\text{Br}_2$: C, 44.70%; H, 3.73%; S, 7.42%; Br, 36.98%. Found: C, 44.71%; H, 3.54%; S, 7.30%; Br, 35.51%.

6. Purity of methyl p-(2-bromoethyl)benzenesulfonate by analytical HPLC. Analytical high performance liquid chromatography (HPLC) allows separation and detection of methyl p-(2-bromoethyl)benzenesulfonate and impurities. A typical chromatogram is shown in Figure 3. Identification of impurities, as shown in Figure 3, was accomplished by comparison with chromatograms of pure, suspected impurities. It was for this purpose that bis-[p-(2-bromoethyl)benzene]-sulfone was prepared as reported previously. Major impurities appeared to be starting materials and sulfone.

Figure 3. Purity of Methyl p-(2-Bromoethyl)benzenesulfonate by Analytical HPLC



7. Recrystallization of methyl p-(2-bromoethyl)benzenesulfonate. 27.5g (0.099 moles) of methyl p-(2-bromoethyl)benzenesulfonate was dissolved in 400 ml warm anhydrous ethyl ether. The ether solution was cooled at dry ice temperature and filtered to yield 25.3g (92%) of a white crystalline solid (m.p. 65-66°C). Dehydrohalogenation followed by homopolymerization, as described previously, led to insoluble, crosslinked products. Repeated recrystallization, dehydrohalogenation, and homopolymerization led to analogous results.

8. Preparative HPLC purification of methyl p-(2-bromoethyl) benzenesulfonate. Attempted purification of methyl p-(2-bromoethyl)benzenesulfonate was performed using a Waters Associates Prep LC/System 500A and a PrepPAK-500/silica column with dichloromethane solvent at 200 ml/min (Figure 4). Sulfone content was monitored by analytical HPLC (Figure 5). The results are summarized in Table 7. Dehydrohalogenation and homopolymerization of monomer purified 2x led to insoluble, crosslinked products.

D. Monomer Synthesis Via Sodium Styrenesulfonate

1. Purity of sodium styrenesulfonate by analytical HPLC.

Analytical high performance liquid chromatography (HPLC)

Figure 4. Preparative HPLC Purification of Methyl p-(2-Bromoethyl)benzenesulfonate: (A) Sulfonate (B) Sulfonate with Sulfone added

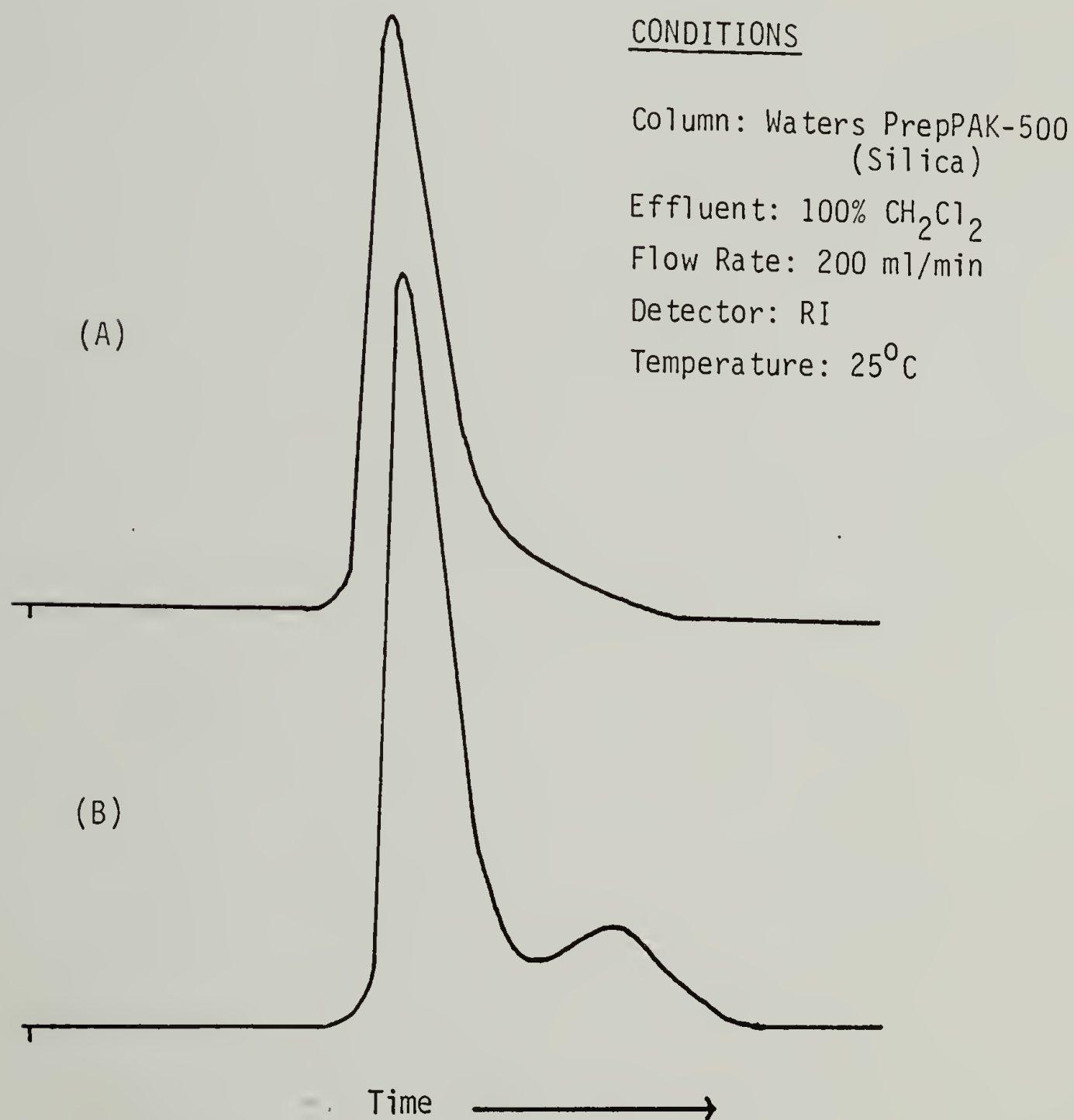
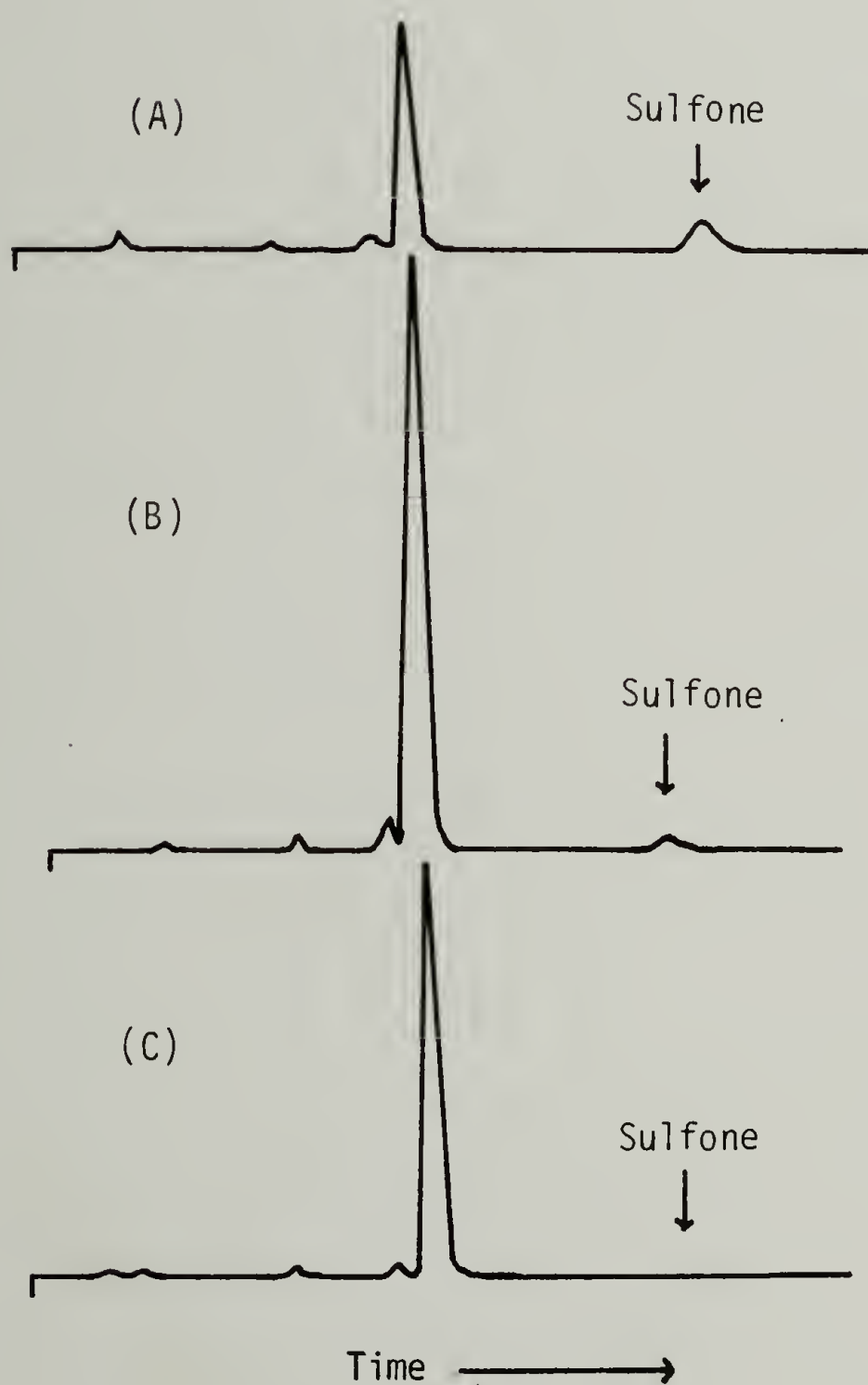


Figure 5. Analytical HPLC of Methyl p-(2-Bromoethyl)benzene-sulfonate: (A) Original (B) Purified 1X by Preparative HPLC (C) Purified 2X by Preparative HPLC



CONDITIONS

Column: Vydac 330-1
(Silica)

Effluent: 100% CH₂Cl₂

Flow Rate: 1.0 ml/min

Detector: UV @ 254 nm

Temperature: 30°C

Table 7. Purification of Methyl p-(2-Bromoethyl)-benzenesulfonate by Preparative HPLC.

Number of Times Purified by Prep. HPLC*	Sulfone Content (mole %)
0	8.8
1	1.4
2	< 0.5

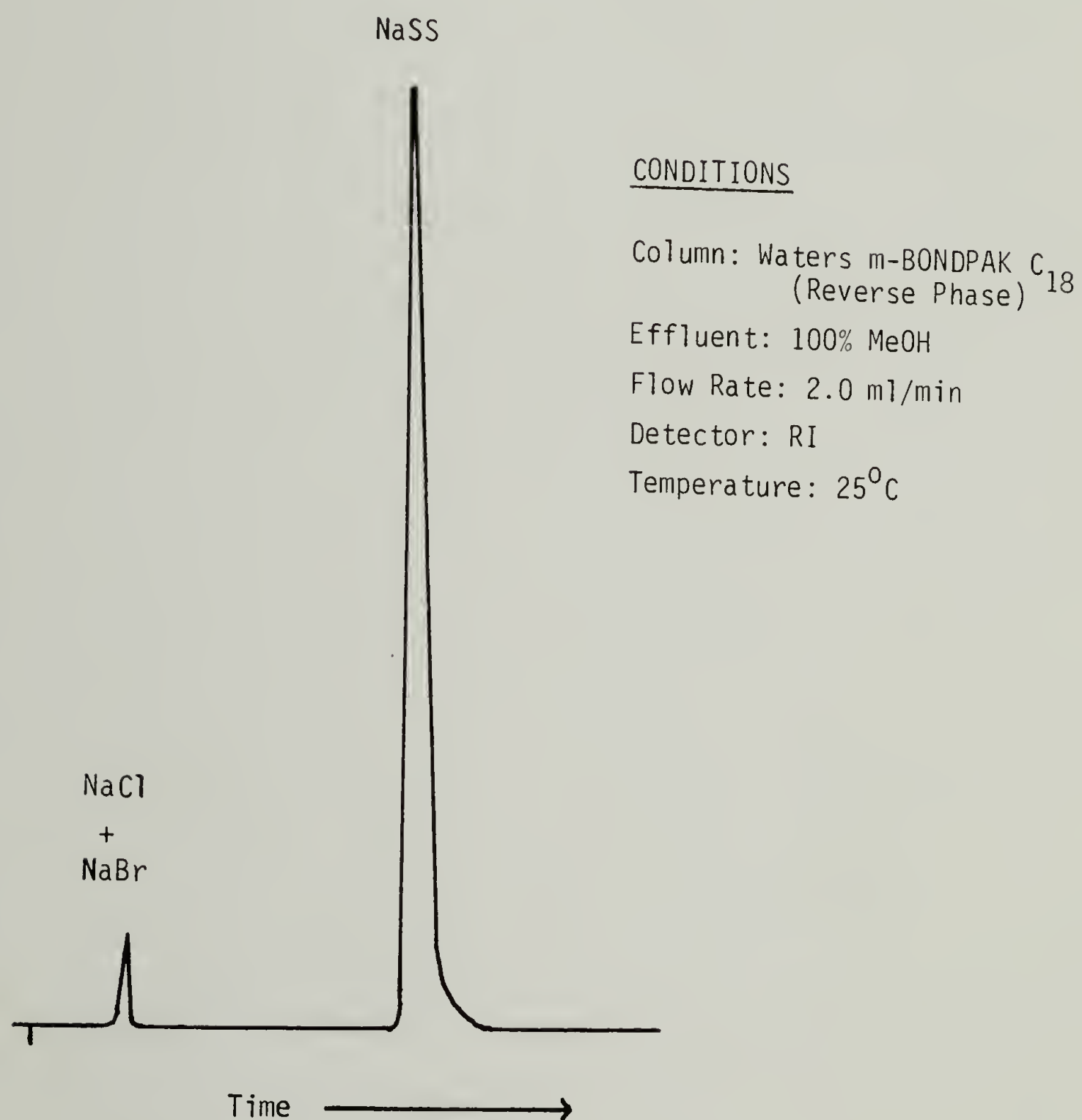
* Conditions: Column: Silica; Effluent: CH_2Cl_2 ;
Flow Rate 200 ml/min; Detector: RI.

allows separation and detection of sodium styrenesulfonate and impurities. A typical chromatogram is shown in Figure 6. Identification of impurities was accomplished by comparison with chromatograms of pure, suspected impurities. For subsequent monomer syntheses, sodium styrenesulfonate was used as is.

2. p-Styrenesulfonyl chloride (89). A 500 ml, three-neck, round-bottomed flask (equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet and outlet) was charged with 20.8g (0.10 moles) of phosphorous pentachloride. 17.4g (0.084 moles) of sodium styrene-sulfonate was added slowly with ice-bath cooling. After 30 minutes the mixture was heated under reflux at 60-65°C for 2 hours. The product was cooled, poured over 100g of crushed ice and extracted with 100 ml of ethyl ether. The organic layer was separated, washed several times with distilled water, and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation at room temperature to yield 14.8g (87%) of a clear yellow oil. Spectra: IR No. 4, ^{13}C NMR No. 3, ^1H NMR No. 5.

3. Methyl p-styrenesulfonate (14). A 2 liter, three-neck, round-bottomed flask (equipped with a magnetic stirrer, thermometer, and nitrogen inlet and outlet) was charged with 147.3g (0.73 moles) of p-styrenesulfonyl chloride and 1000

Figure 6. Analytical HPLC of Sodium Styrenesulfonate



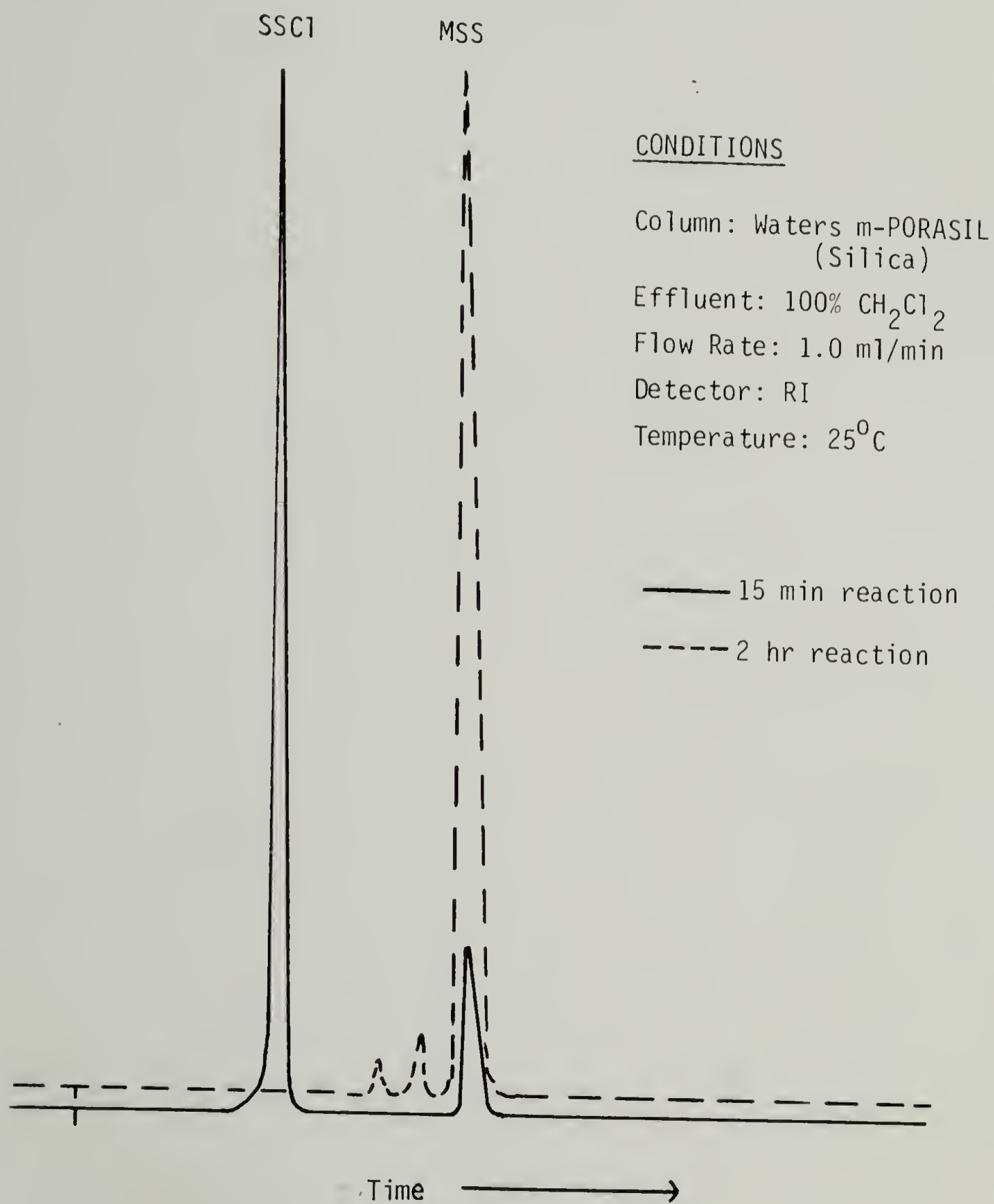
ml of anhydrous ethyl ether. 35.3 ml (27.9g; 0.87 moles) of dry methanol was added and the solution cooled to -10 to -15 °C in a benzyl alcohol/dry ice bath. 114.2g (2.04 moles) of finely powdered potassium hydroxide was added slowly in small portions and the reaction mixture kept at -2°C until all of the sulfonyl chloride had reacted. The reaction was conveniently monitored by analytical HPLC (Figure 7). The product was poured into 1 liter of ice-water, the ether layer separated, washed with ice-water until neutral, and dried over anhydrous magnesium sulfate. The ether was removed under vacuum to yield 96.0g (67%) of a clear, light yellow oil. Spectra: IR No. 5, ^{13}C NMR No. 4, ^1H NMR No. 6.

ANAL. calcd. for $\text{C}_9\text{H}_{10}\text{SO}_3$: C, 54.53%; H, 5.08%; S, 16.17%. Found: C, 53.14%; H, 4.95%; S, 17.15%.

4. Purity of methyl p-Styrenesulfonate: homopolymerization. Homopolymerization affords a simple but sensitive test for determination of the presence or absence of sulfone. Insoluble, crosslinked homopolymerization products indicate the presence of sulfone while soluble, linear products indicate negligible sulfone content.

A glass polymerization tube was flushed with argon and charged with 3.2g (16.0 mmol) of methyl p-styrenesulfonate

Figure 7. Analytical HPLC of Methyl Styrenesulfonate



and 0.0132g (0.08 mmol) of azobisisobutyronitrile (AIBN). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 6 hours and allowed to cool. The clear, light yellow solid obtained was insoluble in ether, toluene, methyl ethyl ketone, THF, methanol, ethanol, and acetone, but was soluble in DMSO, DMF, and N-methyl pyrrolidinone.

5. Ethyl, n-propyl, and isopropyl p-styrenesulfonates.

The alkyl styrenesulfonates were prepared by addition of the appropriate alcohol to p-styrenesulfonyl chloride using the procedure described previously for methyl p-styrenesulfonate. Reaction conditions and yields are summarized in Table 8. All products were obtained as clear yellow oils. Spectra: ethyl p-styrenesulfonate, IR No. 6, ^{13}C NMR No. 5, ^1H NMR No. 7; n-propyl p-styrenesulfonate, IR No. 7, ^{13}C NMR No. 6, ^1H NMR No. 8; isopropyl p-styrenesulfonate, IR No. 8, ^{13}C NMR No. 7, ^1H NMR No. 9.

ANAL. Ethyl p-styrenesulfonate, calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$: C, 56.59%; H, 5.70%; S, 15.10%. Found: C, 55.13%; H, 5.62%; S, 14.67%. n-Propyl p-styrenesulfonate, calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}$: C, 58.39%; H, 6.24%; S, 14.17%. Found: C, 57.57%; H, 6.01%; S, 13.77%. Isopropyl p-styrenesulfonate, calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}$: C, 58.39%; H, 6.24%; S, 14.17%. Found: C, 56.92%; H, 5.80%; S, 13.69%.

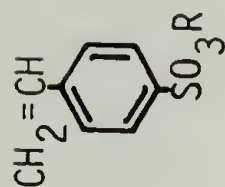


Table 8. Monomer Synthesis*

R	Moles SSCl	Moles ROH	Moles KOH	Temp. (°C)	Time (hrs)	Yield (%)
Methyl	1.00	1.20	2.80	0	3.0	67
Ethyl	1.00	1.40	2.80	0	3.5	55
n-Propyl	1.00	1.20	3.40	0	2.0	50
Isopropyl	1.00	2.00	2.80	0	5.0	40

* 0.05 mole SSCl / 100 ml ethyl ether

6. Distillation of alkyl styrenesulfonates. Distillation of alkyl styrenesulfonates was found to be difficult because of their high boiling points (approx. $100^{\circ}\text{C}/5 \times 10^{-3}\text{mm}$) and polymerization and degradation which occur at these temperatures. Several polymerization inhibitors were evaluated for effectiveness in the distillation of alkyl styrenesulfonates. While p-benzoquinone and tetrachloro-benzoquinone were found to codistill, 2,2-diphenylpicrylhydrazol (DPPH) was effective although some polymerization did occur. The best inhibitor was found to be anhydrous cupric chloride which did not codistill and afforded high monomer distillation yields. Vacuum distillation at $5 \times 10^{-5}\text{mm Hg}$ on a short path column (1-2 cm) in the presence of cupric chloride yielded clear water-white oils in the cases of methyl p-styrenesulfonate (b.p. $78^{\circ}\text{C}/5 \times 10^{-5}\text{mm}$) and ethyl p-styrenesulfonate (b.p. $96^{\circ}\text{C}/5 \times 10^{-5}\text{mm}$). Attempted distillations of n-propyl p-styrenesulfonate and isopropyl p-styrenesulfonate in the presence of cupric chloride were unsuccessful and only polymers were obtained. For polymerizations these monomers were used as is.

E. Miscellaneous Preparations

1. Synthesis of sodium acrylate. A 500 ml, three-neck, round-bottomed flask (equipped with a magnetic stirrer,

addition funnel, and nitrogen inlet and outlet) was charged with 300 ml of ethyl ether and 10.0 ml (10.51g; 0.146 moles) of acrylic acid. The solution was cooled to 0-5°C in an ice-water bath and 14.6 ml 10 M sodium hydroxide solution (0.146 moles) added dropwise. After 15 minutes the product was filtered, washed with ether, and dried under vacuum at 50°C for 12 hours to yield 3.83g (28%) of a white powder.

2. Synthesis of sodium styrenesulfonate (6,7,90,91). A 2 liter, three-neck, round-bottomed flask (equipped with a mechanical stirrer, addition funnel, and nitrogen inlet and outlet) was charged with 1000 g (8.5 moles) of chlorosulfonic acid. The flask was cooled in an ice-water bath and, with stirring, 232 ml (315g; 1.7 moles) of (2-bromoethyl)benzene added dropwise over a period of 6 hours. After an additional two hours at 5-10°C, the reaction mixture was poured over a large quantity of ice, the aqueous layer decanted, and the product extracted with ethyl ether. The ether solution was dried over anhydrous magnesium sulfate, the ether volume reduced, and the product crystallized at dry ice temperature.

170.1g (0.60 moles) of (2-bromoethyl)benzenesulfonyl chloride was dissolved in 350 ml 90% ethanol and 160.0 g (4.00 moles) of sodium hydroxide in 1000 ml 95% ethanol added slowly. The solid thus collected was filtered, washed with

an additional 500 ml hot ethanol, and the combined filtrates cooled to -20°C to precipitate the crude product. The product was taken up in the minimum amount of hot water and filtered. The filtrate was extracted with benzene and cooled to precipitate the product. A final recrystallization from 95% ethanol yielded 66.5g (30%) of sulfone-free sodium styrenesulfonate.

3. Synthesis of sodium 2-sulfoethyl methacrylate (92).

A 1000 ml, three-neck, round-bottomed flask (equipped with a mechanical stirrer and nitrogen inlet and outlet) was charged with 148 ml of acetone and 5 ml of distilled water. 20.0g (0.103 moles) of 2-sulfoethyl methacrylate followed by 11.4 ml 8 N sodium hydroxide solution (0.091 moles) was added to the flask. The mixture was kept well-stirred and the time of addition adjusted so that there was not an excess of sodium hydroxide at any time. The solution was warmed to complete dissolution, filtered hot, and cooled to -20°C to crystallize the product. The product was filtered, washed with cold 90% aqueous acetone, and dried under vacuum at 50°C for 12 hours to yield 9.3g (42%) of a white crystalline solid. Crystalline sodium 2-sulfoethyl methacrylate is subject to air oxidation and must be protected from exposure to air.

F. Homopolymerization of
Alkyl Styrenesulfonates

1. Bulk homopolymerization of alkyl styrenesulfonates. A glass polymerization tube was flushed with argon and charged with 20.0g (0.10 moles) of methyl p-styrenesulfonate and 0.0827g (0.5 mmoles) of azobisisobutyronitrile (AIBN). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 18 hours and allowed to cool. The polymer was dissolved in the minimum volume of N,N-dimethylformamide (DMF) and precipitated in diethyl ether. The product was filtered, washed with additional ether, and dried under vacuum at 50°C for 12 hours to yield 13.8g (70%) of a white stringy polymer. Spectra: IR No. 9, ¹³C NMR No. 8, ¹H NMR No. 10.

ANAL. calcd. for C₉H₁₀O₃S: C, 54.53%; H, 5.08%; S, 16.7%. Found: C, 53.92%; H, 4.98%; S, 15.30%.

Poly(ethyl p-styrenesulfonate), poly(n-propyl p-styrenesulfonate) and poly(isopropyl p-styrenesulfonate) were prepared analogously. Reaction conditions and yields are summarized in Table 9. Spectra: poly(ethyl p-styrenesulfonate), IR No. 10, ¹³C NMR No. 9, ¹H NMR No. 11; poly(n-propyl p-styrenesulfonate), IR No. 11, ¹³C NMR No. 10, ¹H NMR No. 12; poly(isopropyl p-styrenesulfonate), IR No. 12, ¹³C NMR No. 11, ¹H NMR No. 13.

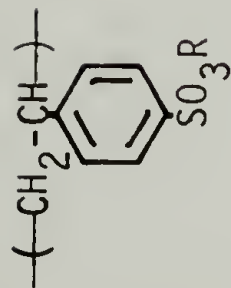


Table 9. Homopolymer Synthesis*

R	Mole % AIBN	Temp. ($^{\circ}\text{C}$)	Time (hrs)	Yield (%)
Methyl	0.1	60	18	63
Ethyl	0.1	60	18	70
n-Propyl	0.1	60	16	50
Isopropyl	1.0	60	24	30

* Bulk Polymerization

ANAL. Poly(ethyl p-styrenesulfonate), calcd. for $C_{10}H_{12}O_3S$: C, 56.59%; H, 5.70%; S, 15.10%. Found: C, 56.06%; H, 5.74%; S, 14.52%. Poly(n-propyl p-styrenesulfonate), calcd. for $C_{11}H_{14}O_3S$: C, 58.39%; H, 6.24%; S, 14.17%. Found: C, 57.96%; H, 6.11%; S, 13.51%.

Poly(isopropyl p-styrenesulfonate), calcd. for $C_{11}H_{14}O_3S$: C, 58.39%; H, 6.11%; S, 13.51%. Found: C, 58.58%; H, 5.80%; S, 13.71%.

2. Solution homopolymerization of methyl p-styrenesulfonate. A glass polymerization tube was flushed with argon and charged with 0.50g (2.52 mmol) of methyl p-styrenesulfonate, 0.0414g (0.25 mmol) of azobisisobutyronitrile (AIBN), and 2.1 ml of dry N,N-dimethylformamide (20% solids). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 18 hours and allowed to cool. The product was precipitated in 100% ethanol, filtered, and dried under vacuum at 50°C for 12 hours to yield 0.35g (70%) of a white powder.

3. Emulsion homopolymerization of methyl p-styrenesulfonate (93). A 50 ml, three-neck, round-bottomed flask (fitted with a mechanical stirrer and nitrogen inlet and outlet) was charged with 30 ml of distilled water and 0.30g sodium lauryl sulfate. The solution was heated to 60°C and

purged with nitrogen for 2 hours. 4.6g (23.2 mmol) of methyl p-styrenesulfonate was added and the milky solution stirred vigorously for 10 minutes. A solution of 0.02g (0.074 mmol) of potassium persulfate in 0.5 ml of distilled water was added, followed after one minute by 0.02g (0.192 mmol) of sodium bisulfite in 0.5 ml of distilled water. After 2 hours the aqueous dispersion was coagulated to a curdy white precipitate by addition of a saturated sodium chloride solution. The product was filtered, washed with distilled water to remove salt and absorbed soap, and dried under vacuum at 60°C for 12 hours to yield 3.3g (72%) of a white powder. Titration of the product with 0.200 N sodium hydroxide indicated less than 1% sulfonic acid content.

4. Homopolymerization of methyl p-styrenesulfonate in the presence of lauryl mercaptan. A glass polymerization tube was flushed with argon and charged with 1.22g (6.15 mmol) of methyl p-styrenesulfonate, 0.0101g (0.062 mmol) of azobis-isobutyronitrile (AIBN) and 0.0012g (0.0062 mmol) of lauryl mercaptan (0.1 mole %). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 24 hours and allowed to cool. The polymer was dissolved in the minimum volume of N,N-dimethylformamide (DMF) and precipitated in diethyl ether. The product was filtered, washed with additional ethyl ether, and dried

under vacuum at 60°C for 12 hours to yield 0.71g (58%) of a white stringy polymer. This procedure was repeated using 1 mole % and 2 mole % lauryl mercaptan.

G. Copolymerization of Alkyl Styrenesulfonates

1. Copolymerization of alkyl styrenesulfonates with styrene. A glass polymerization tube was flushed with argon and charged with 13.8g (70.0 mmol) of methyl p-styrenesulfonate, 8.0 ml (7.25g; 70.0 mmol) of styrene and 0.2204g (1.40 mmol) of azobisisobutyronitrile (AIBN). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 7 hours and allowed to cool. The copolymer was dissolved in methyl ethyl ketone and precipitated in toluene. The product was filtered, washed with additional toluene, and dried under vacuum at 50°C for 12 hours to yield 12.8g (65%) of a white stringy polymer. Spectra: IR No. 13, ¹³C NMR No. 12, ¹H NMR No. 14.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.50}(\text{C}_8\text{H}_8)_{0.50}\text{---}$: C, 67.52%; H, 6.00%; S, 10.60%. Found: C, 65.82%; H, 5.98%; S, 10.53%.

Copolymers of styrene with ethyl p-styrenesulfonate, n-propyl p-styrenesulfonate, and isopropyl p-styrenesulfonate (50/50 mole % feeds) were prepared analogously.

Reaction conditions and yields are summarized in Table 10.

2. Copolymerization of alkyl styrenesulfonates with acrylic acid. A glass polymerization tube was flushed with argon and charged with 1.22g (6.15 mmol) of methyl p-styrenesulfonate, 0.42 ml (0.44g; 6.15 mmol) of freshly distilled acrylic acid, 0.0202g (0.12 mmol) of azobisisobutyronitrile (AIBN) and 6.9 ml of N-methyl pyrrolidinone (20% solids). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 24 hours and allowed to cool. The copolymer was precipitated in 50/50 (v/v) ethyl ether/100% ethanol, filtered, washed with additional ethyl ether, and dried under vacuum at 50°C for 12 hours to yield 1.45g (87%) of a white powder. Spectra: IR No. 14, ¹³C NMR No. 13, ¹H NMR No. 15.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.41}(\text{C}_3\text{H}_4\text{O}_2)_{0.41}\text{---}$: C, 52.93%; H, 5.26%; S, 10.47%. Found: C, 51.48%; H, 5.58%; S, 10.48%.

Copolymers of acrylic acid with ethyl p-styrenesulfonate, n-propyl p-styrenesulfonate, and isopropyl p-styrenesulfonate (50/50 mole % feeds) were prepared analogously. Reaction conditions and yields are summarized in Table 11.

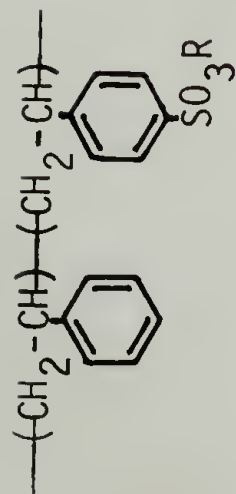


Table 10. Copolymerization of Alkyl Styrene-sulfonates With Styrene*

R	Mole % Styrene	Mole % AIBN	Temp. (°C)	Time (hrs)	Yield (%)
Methyl	50	1.0	60	7	65
Ethyl	50	1.0	60	7	68
n-Propyl	50	1.0	60	24	63
Isopropyl	50	1.0	60	24	71

* Bulk Copolymerization

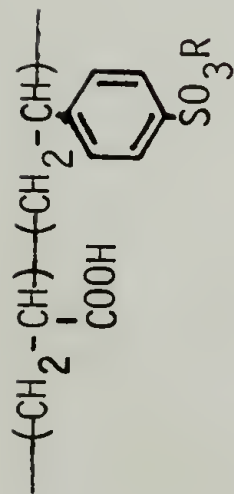


Table 11. Copolymerization of Alkyl Styrene-sulfonates With Acrylic Acid*

R	Mole % Acrylic Acid	Mole % AIBN	Temp. (°C)	Time (hrs)	Yield (%)
Methyl	50	1.0	60	24	87
Ethyl	50	1.0	60	24	75
n-Propyl	50	1.0	60	24	54
Isopropyl	50	1.0	60	24	62

* Solution Copolymerization in N-Methyl Pyrrolidinone (20% Solids)

3. Attempted copolymerization of alkyl styrenesulfonates with sodium acrylate. As sodium acrylate and alkyl styrenesulfonates are insoluble in one another, numerous copolymerization solvents were investigated including methanol, ethanol, N,N-dimethylformamide, dimethyl sulfoxide, acetonitrile, and N-methyl pyrrolidinone. However, none of these solvent systems were found to dissolve sodium acrylate to any appreciable extent so that copolymerization of these monomer pairs was not possible.
4. Copolymerization of alkyl styrenesulfonates with maleic anhydride. A glass polymerization tube was flushed with argon and charged with 6.1g (30.8 mmol) of methyl p-styrenesulfonate, 30.0g (30.8 mmol) of maleic anhydride, and 0.1010g (0.62 mmol) of azobisisobutyronitrile (AIBN). The contents were degassed and sealed under vacuum. The tube was placed on a shaker/oil bath at 60°C for 10 hours and allowed to cool. The copolymer was dissolved in the minimum volume of N,N-dimethylformamide and precipitated in ethyl ether. The product was filtered, washed with additional ether, and dried under vacuum at 60°C for 12 hours to yield 5.3g (58%) of a white stringy polymer. Spectra: IR No. 15; ¹³C NMR No. 14; ¹H NMR No. 16.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.60}(\text{C}_4\text{H}_2\text{O}_3)_{0.40}$: C, 53.16%; H, 4.33%; S, 12.16%. Found: C, 54.63%; H, 4.64%;

S, 12.21%.

Copolymers of maleic anhydride and ethyl p-styrenesulfonate, n-propyl p-styrenesulfonate, and isopropyl p-styrenesulfonate (50/50 mole % feeds) were prepared analogously. Reaction conditions and yields are summarized in Table 12.

5. Copolymerization of methyl p-styrenesulfonate with sodium 2-sulfoethyl methacrylate (NaSEM). A glass polymerization tube was flushed with argon and charged with 0.3442g (1.59 mmol) of sodium 2-sulfoethyl methacrylate, 0.3157g (1.59 mmol) of methyl p-styrenesulfonate, 0.0052g (0.032 mmol) of azobisisobutyronitrile (AIBN) and 6.0 ml of N-methyl pyrrolidinone. The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 24 hours and allowed to cool. The copolymer was precipitated in 50/50 (v/v) ethyl ether/95% ethanol, filtered, washed with additional ether, and dried under vacuum at 50°C for 12 hours to yield 0.5685g (86%) of a white, water-soluble powder. Spectra: IR No. 16.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.50}(\text{C}_6\text{H}_9\text{O}_5\text{SNa})_{0.50}$: C, 43.48%; H, 4.62%; S, 15.47%. Found: C, 43.13%; H, 5.33%; S, 11.70%.

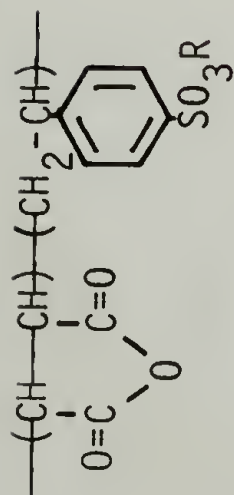


Table 12. Copolymerization of Alkyl Styrene-sulfonates With Maleic Anhydride*

R	Mole % Maleic Anhydride	Mole % AIBN	Temp. (°C)	Time (hrs)	Yield (%)
Methyl	50	1.0	60	10	58
Ethyl	50	1.0	60	10	51
n-Propyl	50	1.0	60	24	61
Isopropyl	50	1.0	60	24	68

* Bulk Copolymerization

6. Copolymerization of methyl p-styrenesulfonate with 2-acrylamido-2-methylpropanesulfonic acid (AMPS). A glass polymerization tube was flushed with argon and charged with 0.3432g (1.66 mmol) of 2-acrylamido-2-methylpropanesulfonic acid (AMPS), 0.3286g (1.66 mmol) of methyl p-styrenesulfonate, 0.0054g (0.033 mmol) of azobisisobutyronitrile (AIBN), and 3.1 ml of N,N-dimethylformamide (20% solids). The contents were degassed and sealed under vacuum. The tube was placed in a shaker/oil bath at 60°C for 24 hours and allowed to cool. The copolymer was precipitated in 50/50 (v/v) ethyl ether/100% ethanol, filtered, washed with additional ethyl ether, and dried under vacuum at 50°C for 12 hours to yield 0.4382g (67%) of a white, water-soluble powder. Spectra: IR No. 17.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.50}(\text{C}_7\text{H}_{13}\text{O}_4\text{NS})_{0.50}\text{---}$: C, 47.42%; H, 5.72%; S, 15.82%. Found: C, 47.63%; H, 6.22%; S, 13.42%.

7. Attempted copolymerization of alkyl styrenesulfonates with acrylamide. A glass polymerization tube was flushed with argon and charged with 0.61g (3.08 mmol) of methyl p-styrenesulfonate, 0.2187g (3.08 mmol) of acrylamide, 0.0101g (0.062 mmol) of azobisisobutyronitrile (AIBN), and 2.3 ml N-methyl pyrrolidinone (30% solids). The contents were degassed and sealed under vacuum. The tube was placed in a

shaker/oil bath at 60°C for 24 hours and allowed to cool. The clear, light yellow gel obtained was insoluble in water, strong base, DMF, DMSO, and N-methyl pyrrolidinone and was assumed to be crosslinked. Similar results were obtained for copolymerizations performed in N,N-dimethylformamide and dimethyl sulfoxide.

8. Preparation of alkyl styrenesulfonate-sodium styrenesulfonate copolymers. As in the case of sodium acrylate, no copolymerization solvent could be found which allows for the direct copolymerization of alkyl styrenesulfonates and sodium styrenesulfonate. These copolymers, however, can be conveniently prepared by hydrolysis of the corresponding homopolymer as described below.

3.0g (15.1 mmol) of poly(methyl p-styrenesulfonate) was dissolved in 20.0 ml of dimethyl sulfoxide and several drops of bromothymol blue added. 8.19 ml of a 1.00 N sodium hydroxide solution (8.2 mmol) was added slowly and the reaction mixture stirred until neutral. The product was precipitated in 50/50 (v/v) ethyl ether/100% ethanol, filtered, washed with additional ethyl ether, and dried under vacuum at 60°C for 12 hours to yield 2.47g (81%) of a white, water-soluble polymer.

ANAL. calcd. for $\text{---}(\text{C}_9\text{H}_{10}\text{O}_3\text{S})_{0.57}(\text{C}_8\text{H}_7\text{O}_3\text{SNa})_{0.43}$: C, 51.26%; H, 4.35%, S, 15.90%; Na, 4.90%. Found: C, 48.06%;

H, 4.43%; S; 14.41%; Na, 4.90%.

9. Copolymerization reactivity ratios. All copolymerization experiments for the determination of reactivity ratios were carried out at 50°C in sealed glass tubes with 1 mole% azobisisobutyronitrile (AIBN). Copolymerizations were carried out in the bulk in order to circumvent the difficulty of solvent (DMSO or DMF) removal. Because of the high reactivity of methyl styrenesulfonate, various polymerization times were required to ensure low yields. Copolymers were precipitated in a non-solvent (100% ethanol, ethyl ether, or toluene), filtered, dried under vacuum at 60°C, and analyzed for composition by elemental analysis (%S). Experimental conditions and results for the copolymerization of methyl p-styrenesulfonate with styrene, acrylic acid, and maleic anhydride are summarized in Tables 13, 14, and 15, respectively.

10. % Comonomer versus water solubility.

a. Copolymers of alkyl styrenesulfonates and acrylic acid. Copolymers of methyl p-styrenesulfonate and acrylic acid of various feed compositions were prepared according to the previously described procedure in order to determine % acrylic acid content necessary to impart

Table 13. Copolymerization of Styrene and Methyl Styrenesulfonate*

ST (M ₁) in Monomer Feed (mole %)	Polymerization Time (Minutes)	PPT Solvent	Yield (%)	%S	ST in Copolymer (mole %)
30.0	15	100% EtOH	2.8	14.14	21.0
50.0	20	Toluene	3.0	12.58	35.0
70.0	25	100% EtOH	3.5	10.48	51.0
90.0	30	100% EtOH	1.9	5.85	77.0

* Copolymerization Conditions: Bulk, 1 mole % AIBN, 50°C. St = Styrene;
PPT = Precipitation; %S determined by Elemental Analysis.

Table 14. Copolymerization of Acrylic Acid and Methyl Styrenesulfonate*

AA (M_1) in Monomer Feed (mole %)	Polymerization Time (Minutes)	PPT Solvent	Yield (%)	%S	AA in Copolymer (mole %)
50.0	25	Ether	5.2	13.95	30.0
70.0	30	"	5.6	12.51	45.0
80.0	30	"	3.8	11.60	52.0
90.0	40	"	5.3	9.37	67.0

* Copolymerization Conditions: Bulk, 1 mole % AIBN, 50°C. AA = Acrylic Acid; %S determined by Elemental Analysis; PPT = Precipitation.

Table 15. Copolymerization of Maleic Anhydride and Methyl Styrenesulfonate*

MA (M ₁) in Monomer Feed (mole %)	Polymerization Time (Minutes)	PPT Solvent	Yield (%)	%S	AA in Copolymer (mole %)
30.0	15	Ether	0.2	11.98	41.0
40.0	15	"	1.5	12.56	37.0
50.0	20	"	6.9	12.08	41.0
60.0	20	"	4.8	12.55	37.0

* Copolymerization Conditions: Bulk, 1 mole % AIBN, 50°C. MA = Maleic Anhydride; PPT = Precipitation; %S determined by Elemental Analysis.

water solubility to the copolymer. The experimental results are summarized in Table 16.

b. Copolymers of alkyl styrenesulfonates and sodium styrenesulfonate. Poly(isopropyl p-styrenesulfonate) (1.00g) was dissolved in 10.0 ml of 90/10 (v/v) dimethyl sulfoxide/water at 50°C. Samples were taken at specific intervals during the hydrolysis reaction, precipitated in 70/30 (v/v) ethyl ether/100% ethanol, filtered, and dried under vacuum at 60°C for 12 hours. For each sample the extent of hydrolysis (i.e. sulfonic acid content) was determined by titration and water solubility tested. The results are summarized in Table 17.

H. Synthesis of alkyl toluenesulfonates

Methyl toluenesulfonate and ethyl toluenesulfonate were obtained commercially (Aldrich) and recrystallized from ethyl ether. N-Propyl and isopropyl toluenesulfonates were prepared from toluenesulfonyl chloride in an analogous fashion to that previously reported for alkyl styrenesulfonates. Experimental conditions and results are summarized in Table 18.

Table 16. % Comonomer vs. Water Solubility: Methyl Styrenesulfonate-Acrylic Acid Copolymers*

AA (M_1) in Monomer Feed (mole %)	Yield (%)	AA in Copolymer (mole %)	H ₂ O Soluble? ($>0.1\text{g}/100\text{ml}$)
50	87	59	No
70	84	74	Yes
90	83	92	Yes

* Copolymerization Conditions: Solution Copolymerization in N-Methyl Pyrrolidinone (20% Solids), 1 mole % AIBN, 60°C, 24 hrs. Copolymers ppt'd in 50/50 (v/v) ether/100%EtOH. AA Content determined by Elemental Analysis (%S).

Table 17. % Comonomer vs. Water Solubility: Methyl Styrenesulfonate-Sodium Styrenesulfonate Copolymers*

Hydrolysis Time (minutes)	% Hydrolysis	H ₂ O Soluble? (>0.1g/100ml)
3.0	26	No
7.0	34	No
10.0	41	Yes
15.0	54	Yes
26.0	61	Yes
32.0	66	Yes
40.0	83	Yes

* Hydrolysis Conditions: Solvent 90/10 (v/v) DMSO/H₂O, Temperature 50°C. Samples ppt'd in 80/20 (v/v) ether /100% EtOH. % Hydrolysis determined by titration with 1.00 N NaOH.

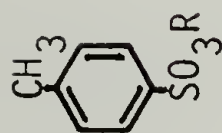


Table 18. Synthesis of Alkyl Toluene sulfonates*

R	Moles TSCl	Moles ROH	Moles KOH	Temp. (°C)	Time (hrs)	Yield (%)
n-Propyl	1.00	1.07	2.50	0	3.0	72
Isopropyl	1.00	1.20	2.80	0	5.0	42

* 0.05 mole Toluene sulfonyl Chloride (TSCl) / 100 ml ethyl ether

I. Polymer Characterization

1. Homopolymer molecular weight determination.

Determination of molecular weights and molecular weight distributions by gel permeation chromatography (GPC) was not possible due to the insolubility of the homopolymers in common GPC solvents (toluene or tetrahydrofuran). However, a procedure was developed, as described below, which enabled determination of molecular weights by solution viscosity techniques.

A glass tube was charged with 1.942×10^{-4} moles of homopolymer and 10.0 ml of 0.5 M aqueous sodium chloride. The tube was sealed and hydrolyzed at 80°C for 24 hours. The resultant clear, water-white liquid was neutralized with 1.00 N sodium hydroxide, filtered, and the reduced viscosity determined at 30.0°C in a Ubbelohde-type viscometer according to equation (1)

$$\eta_{\text{red}} = \frac{t - t_0}{t_0 c} \quad (1)$$

where η_{red} is the reduced viscosity, t is the efflux time for the polymer solution, t_0 is the efflux time for the pure solvent, and c is the polymer concentration in grams per deciliter. Comparison of these reduced viscosities with those of commercially available narrow distribution

Figure 8. Poly(Sodium Styrenesulfonate) Calibration Curve for Homopolymer Molecular Weight Analysis

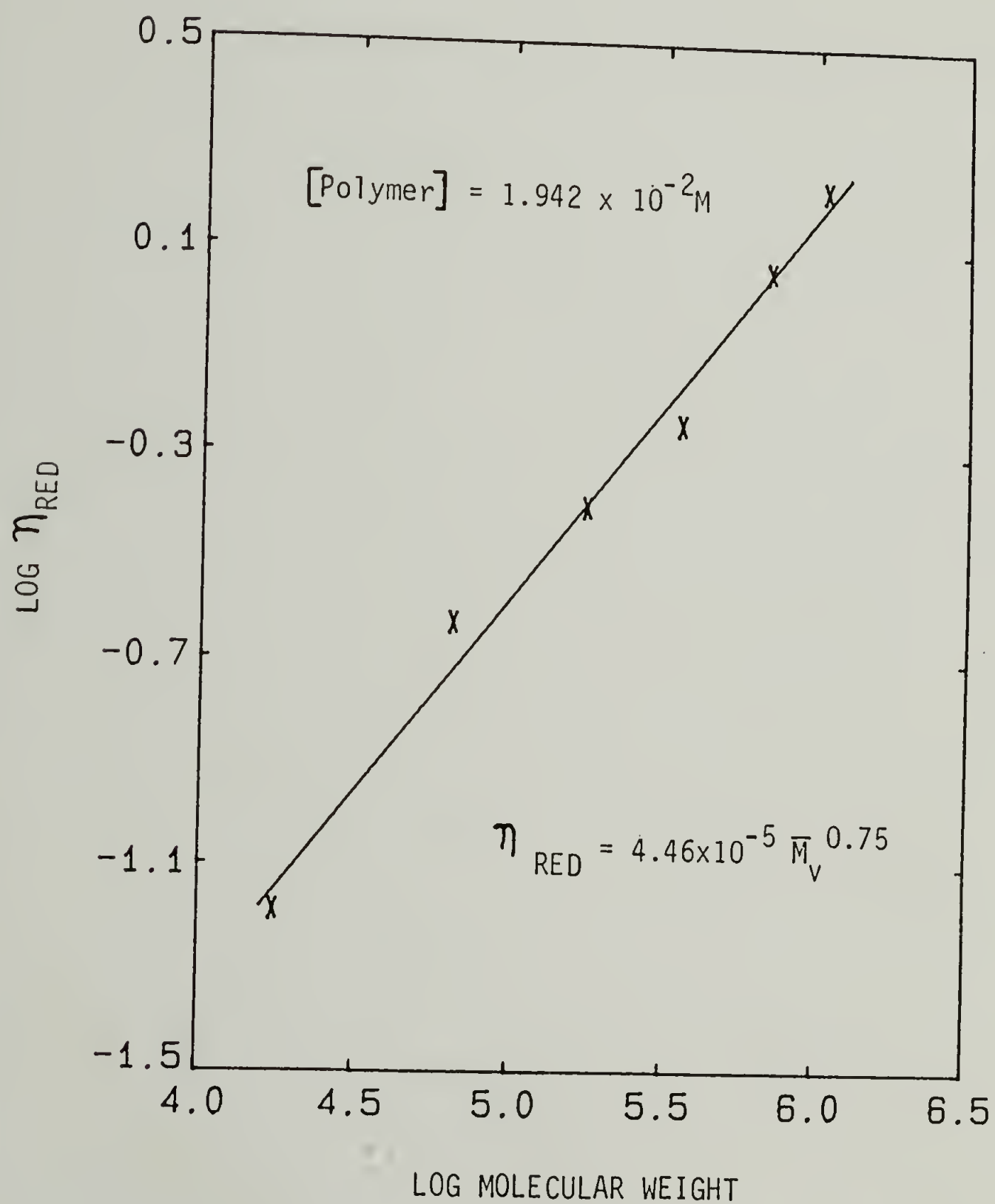


Table 19. Homopolymer Molecular Weight Analysis
By Viscosity*

Polymer	Mole % Lauryl Mercaptan	η_{red}	\bar{M}_v
PMSS	-	0.735	391,700
"	0.1	0.449	203,300
"	1.0	0.161	52,000
"	2.0	0.134	41,000
PESS	-	1.108	676,000
PNPSS	-	0.400	175,000
PIPSS	-	0.254	96,000

* Reduced Viscosities determined at 30°C in 0.5 M aqueous NaCl. Polymer concentration 1.942×10^{-2} M. PESS prepared from distilled monomer.

poly(sodium styrenesulfonates) enabled determination of viscosity average molecular weights (\bar{M}_v). The calibration curve constructed from the standards is presented in Figure 8 and results from the homopolymers summarized in Table 19.

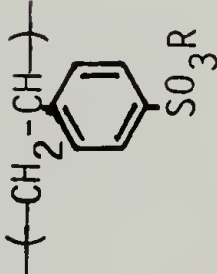
2. Thermal analysis.

a. Differential scanning calorimetry (DSC)

Glass transition temperature (t_g) determinations were performed on a Perkin-Elmer Model DSC-II differential scanning calorimeter (DSC). The weight of each sample, typically 5-20 mg, was measured on a Perkin-Elmer AD-2 Autobalance to a precision of 0.01 mg. A heating rate of 20 deg/min was used in all cases. Results for the various homopolymers are summarized in Table 20. Glass transition temperatures reported were determined as the mid-point of the transition.

b. Thermogravimetric analysis (TGA) Homopolymer degradation behavior was determined by thermogravimetric analysis on a Perkin-Elmer TGS-2 Thermogravimetric Analyzer. Samples were run under a nitrogen atmosphere with a flow rate of 40 ml/min. Heating rates were 20 deg/min and generally 2.5 to 3.0 mg of sample was used. A typical degradation curve is shown in Figure 9

Table 20. Differential Scanning Calorimetry (DSC)

	R	Heating Rate (°C/min)	T _g (°C)
	Methyl	20	177
	Ethyl	20	147
	n-Propyl	20	123
	Isopropyl	20	167

and the homopolymer results summarized in Table 21.

3. Spectroscopic analysis.

- a. Infrared spectroscopy. Infrared spectra were recorded on a Perkin-Elmer Model 283 Spectrometer with a 12 minute scan rate. Solid samples were measured as KBr pellets and liquid samples as smears between NaCl plates. Typical spectra are presented in the appendix.
- b. ^1H NMR. ^1H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer. Solutions were made in either CDCl_3 , d_6 -DMSO, d_6 -acetone, or D_2O and were generally 10 to 20% concentration. Chemical shift values were measured as δ (ppm) relative to TMS as an internal standard. Typical spectra are presented in the appendix.
- c. ^{13}C NMR. ^{13}C NMR Spectra were recorded on a Varian CFT-20, 100 MHz spectrometer. Spectra were obtained fully proton decoupled and chemical shift values were measured as δ (ppm) relative to TMS as an internal standard. Solutions were made in either CDCl_3 , d_6 -DMSO, d_6 -acetone, or D_2O and were generally 10 to 20% concentration.

Figure 9. Thermogravimetric Analysis (TGA) of Poly(Methyl Styrenesulfonate)

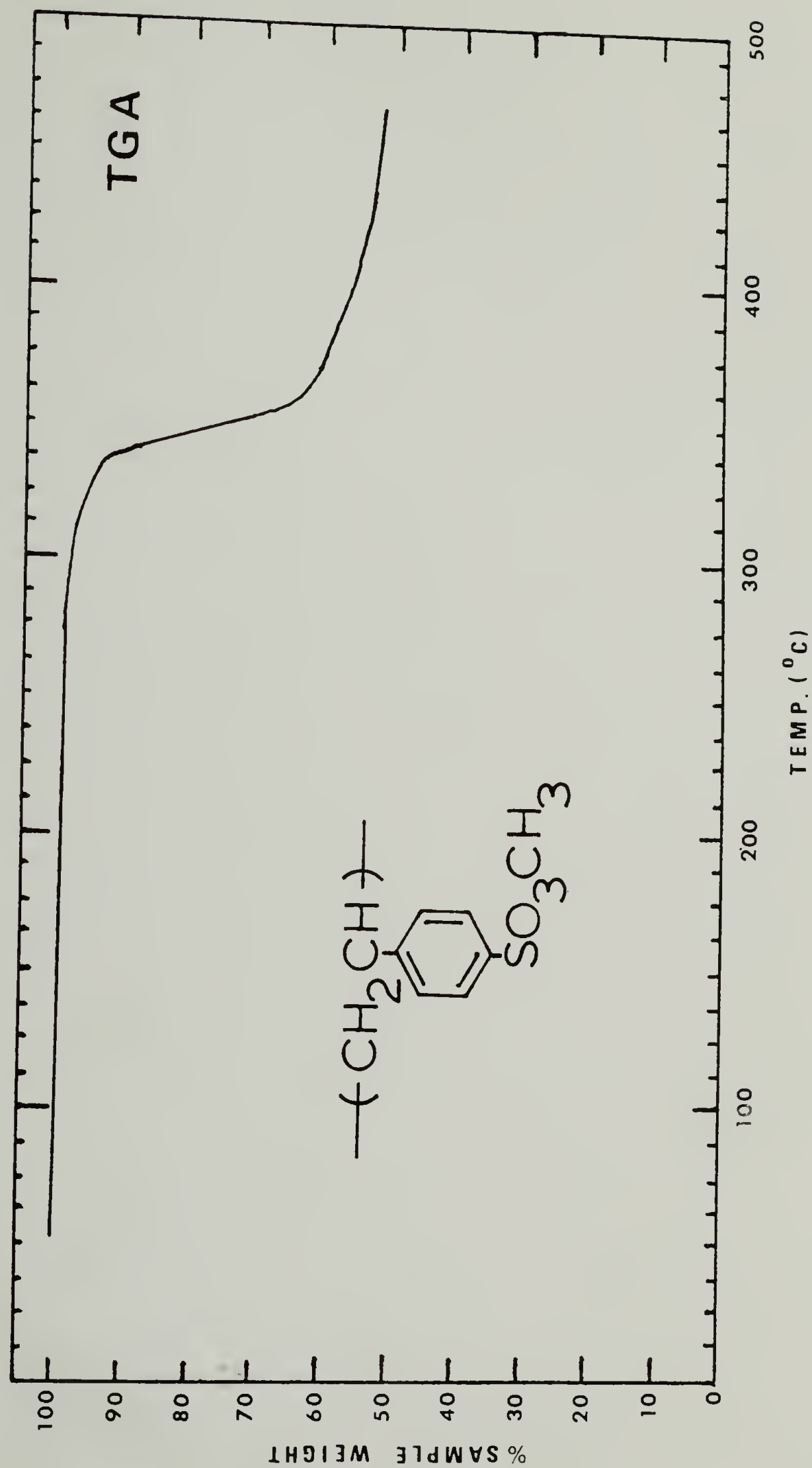
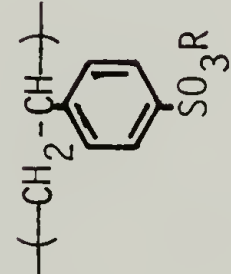


Table 21. Thermogravimetric Analysis (TGA)

	R	T _d onset (°C)	% Residual (@500°C)
	Methyl	325	51
	Ethyl	270	49
	n-Propyl	225	49
	Isopropyl	300	31

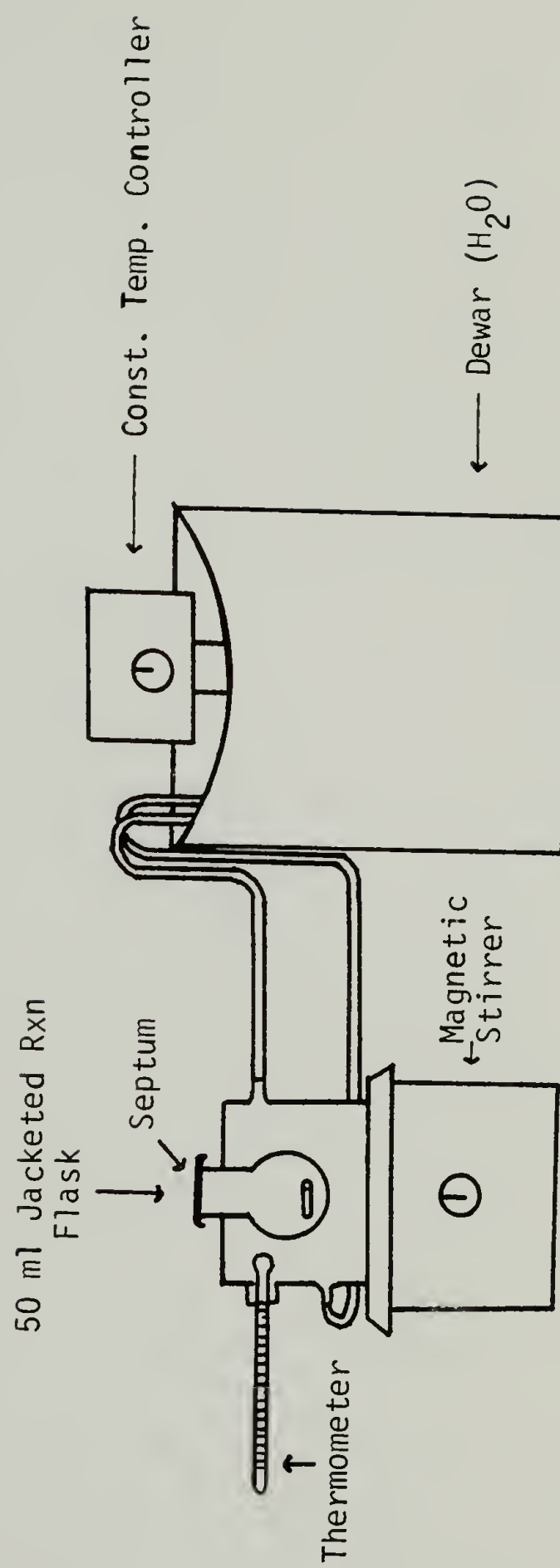
Typical spectra are presented in the appendix.

4. Elemental analysis. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Massachusetts.

J. Hydrolysis Studies

1. General procedure. Kinetic experiments were performed in the apparatus shown in Figure 10. To the appropriate volume of water [5.0 ml for 90/10 (v/v) DMSO/H₂O] was added sufficient DMSO to make a total of 49.0 ml of solution. The solution was allowed to cool to room temperature and the volume adjusted to 49.0 ml with additional DMSO. The DMSO/H₂O solution was added to the reaction flask and allowed to reach reaction temperature (controlled to $\pm 0.05^{\circ}\text{C}$). The sulfonate ester (0.50 mmol) was dissolved in 1.0 ml DMSO and added quickly to the reaction flask. At suitable time intervals a 2.00 ml sample was withdrawn (syringe), quenched with ice, and titrated quickly with 0.200 N NaOH, bromothymol blue being used as indicator. In the case of basic hydrolysis studies, the sample was quenched with excess 1.00 N HCl and back titrated with 0.200 N NaOH as above. In cases where extremely viscous polymer solutions in DMSO were formed (e.g. PMSS/NaSS copolymers), the polymer was added directly to the reaction flask containing 50.0 ml

Figure 10. Hydrolysis Apparatus



of the DMSO/H₂O solution at the reaction temperature.

2. Neutral hydrolysis of alkyl toluenesulfonates in 90/10 (v/v) DMSO/H₂O. Experimental data for the neutral hydrolysis of methyl, ethyl, n-propyl, and isopropyl toluenesulfonates is tabulated in the appendix and summarized in Figures 11-14.
3. Neutral hydrolysis of poly(alkyl styrenesulfonates) in 90/10 (v/v) DMSO/H₂O. Experimental data for the neutral hydrolysis of poly(methyl p-styrenesulfonate), poly(ethyl p-styrenesulfonate), poly(n-propyl p-styrenesulfonate), and poly(isopropyl p-styrenesulfonate) is tabulated in the appendix and summarized in Figures 15-18.
4. Neutral hydrolysis of poly(methyl p-styrenesulfonate-co-styrene) in 90/10 (v/v) DMSO/H₂O. Experimental data for the neutral hydrolysis of poly(methyl p-styrenesulfonate-co-styrene) (50/50 copolymer) is tabulated in the appendix and summarized in Figure 19.
5. Neutral hydrolysis of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O. Experimental data for the neutral hydrolysis of poly(methyl p-styrene-sulfonate-co-sodium styrenesulfonate) (57/43 copolymer) is tabulated in the appendix and summarized in Figure 20.

Figure 11. Neutral Hydrolysis of Methyl Toluene-sulfonate in 90/10 (v/v) DMSO/H₂O

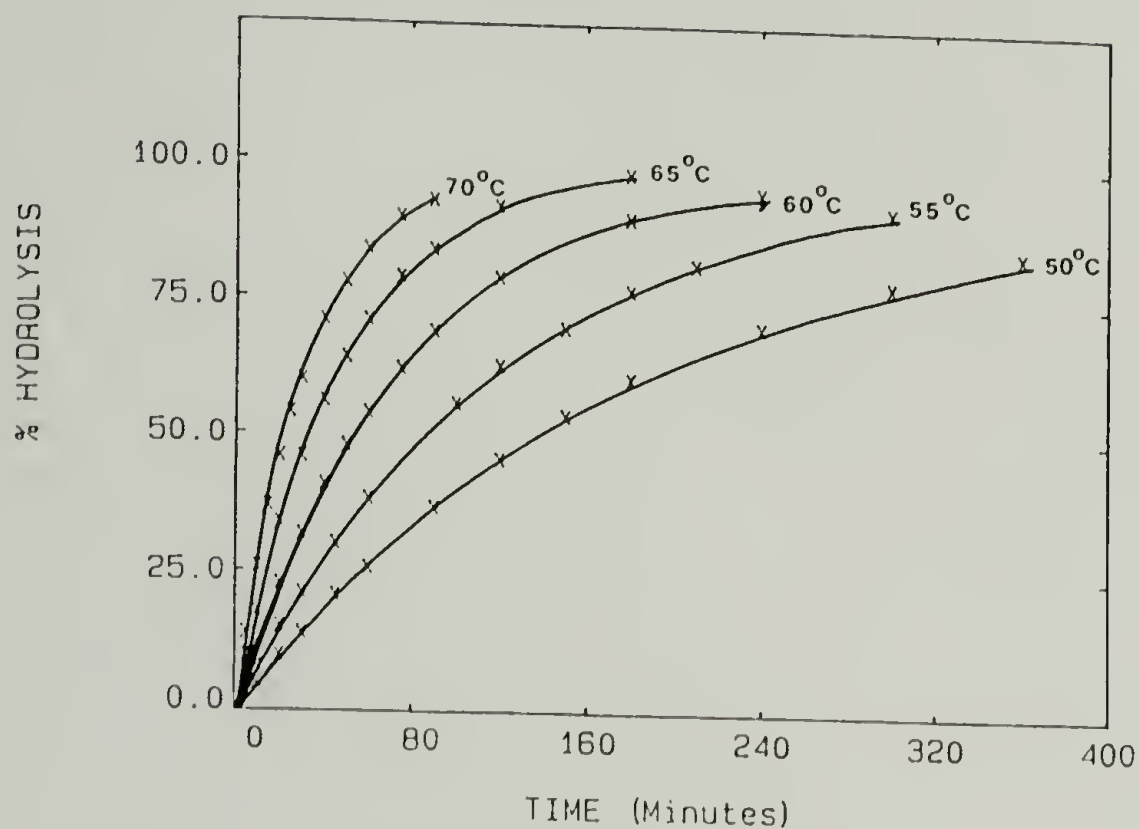


Figure 12. Neutral Hydrolysis of Ethyl Toluene-sulfonate in 90/10 (v/v) DMSO/H₂O

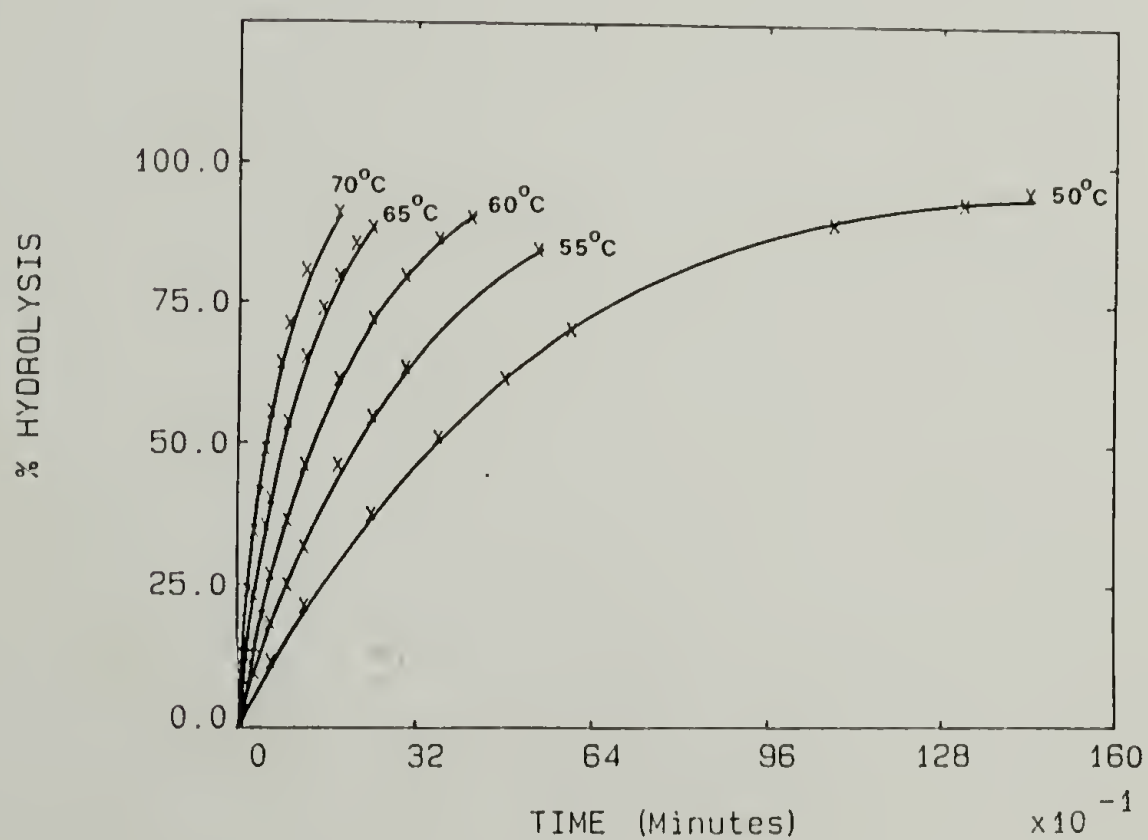


Figure 13. Neutral Hydrolysis of n-Propyl Toluene-sulfonate in 90/10 (v/v) DMSO/H₂O

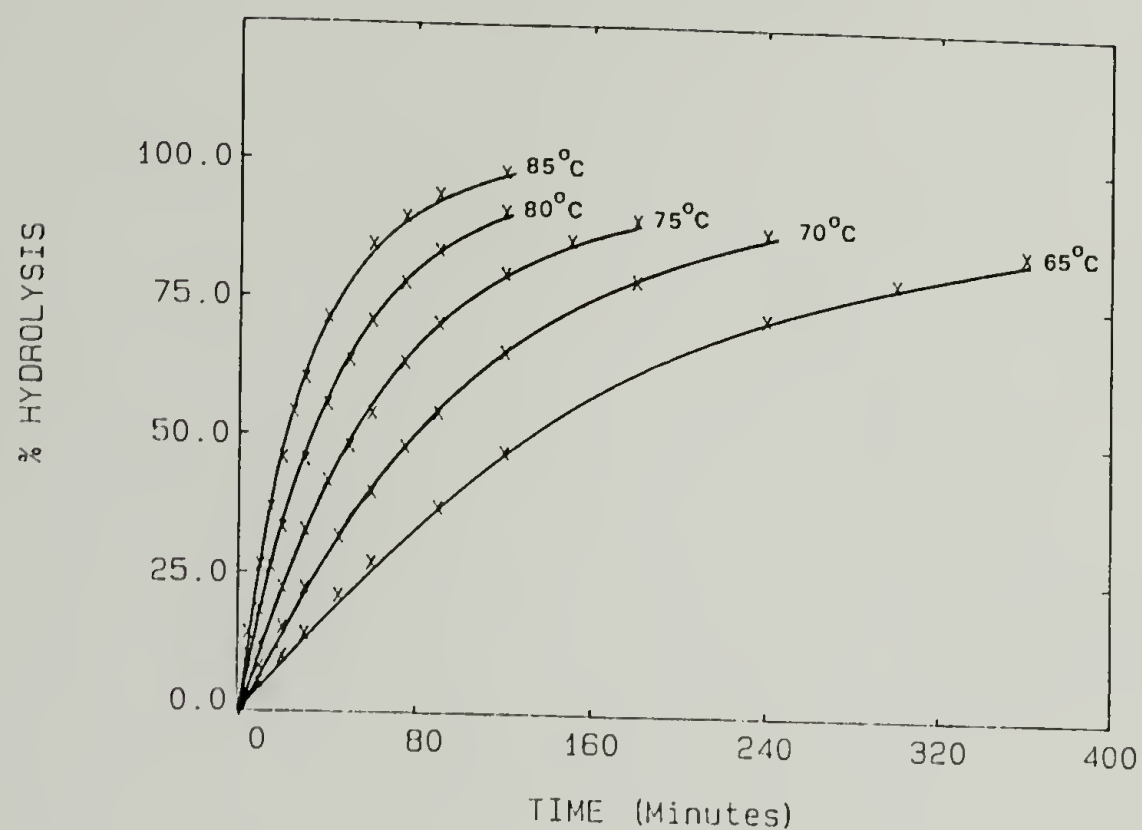


Figure 14. Neutral Hydrolysis of Isopropyl Toluene-sulfonate in 90/10 (v/v) DMSO/H₂O

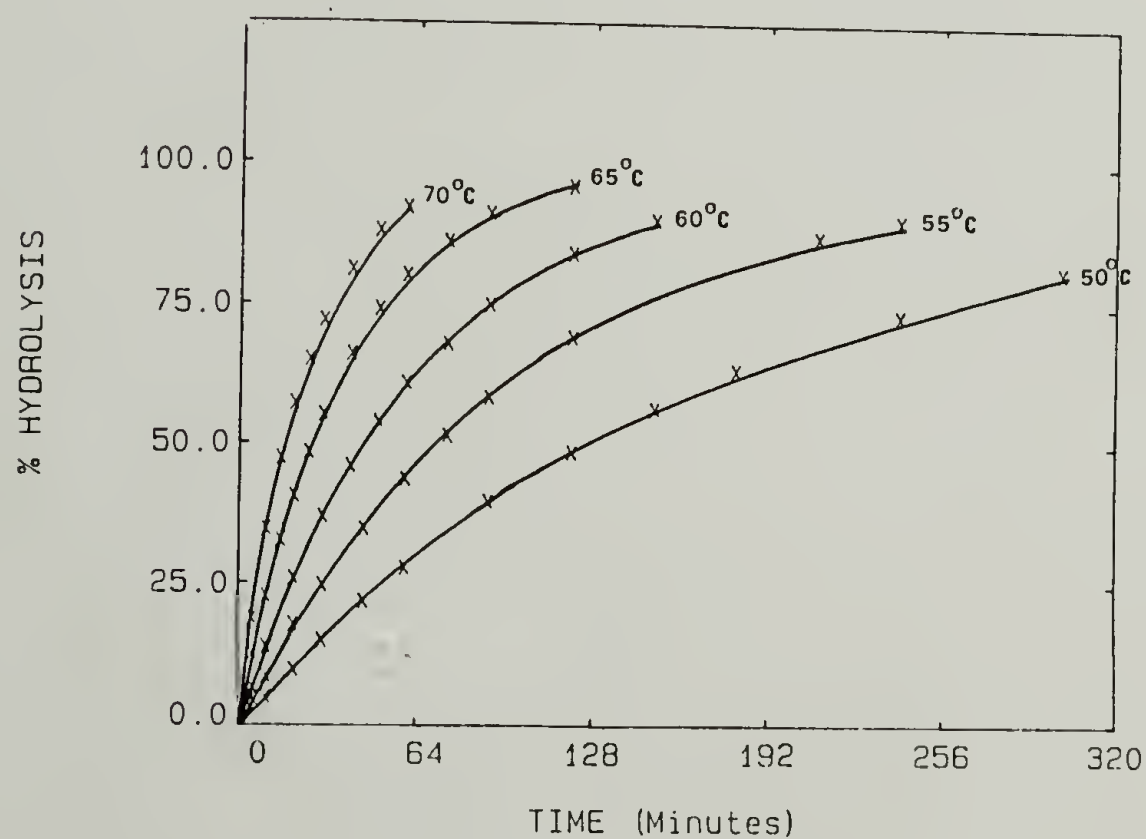


Figure 15. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate) in 90/10 (v/v) DMSO/H₂O

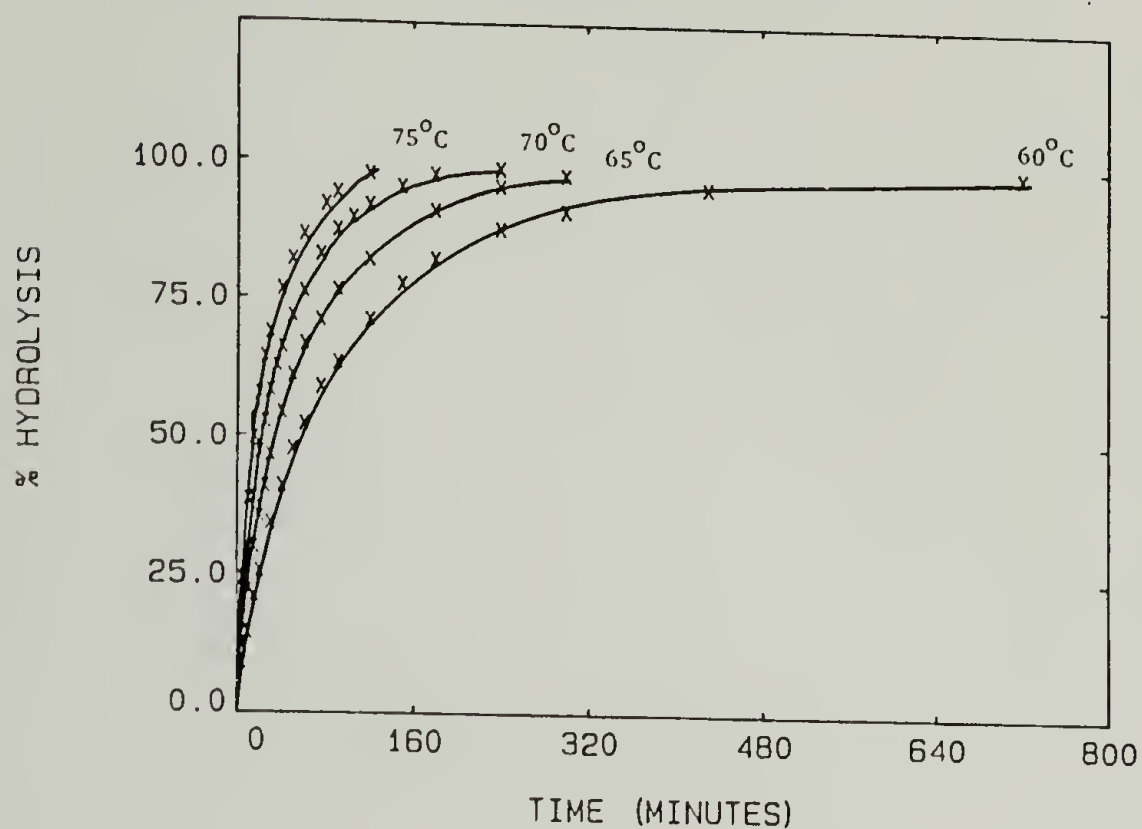


Figure 16. Neutral Hydrolysis of Poly(Ethyl Styrene-sulfonate) in 90/10 (v/v) DMSO/H₂O

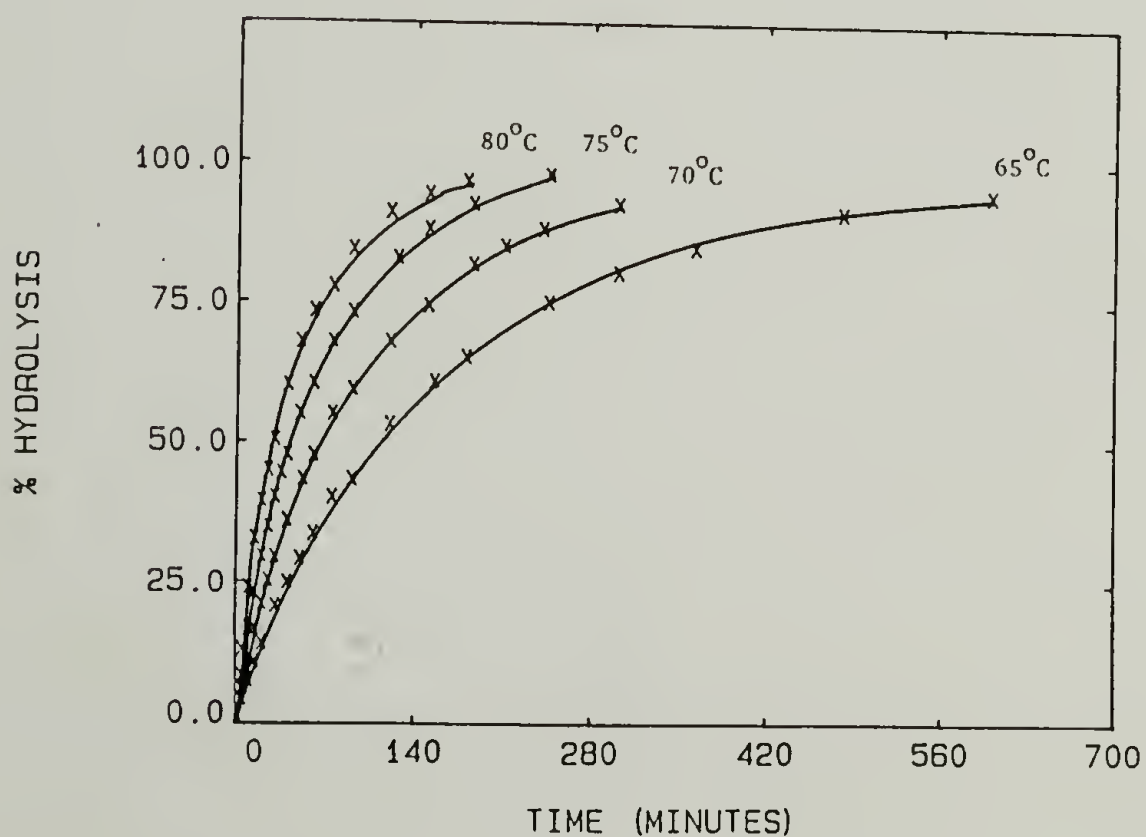


Figure 17. Neutral Hydrolysis of Poly(n-Propyl Styrene-sulfonate) in 90/10 (v/v) DMSO/H₂O

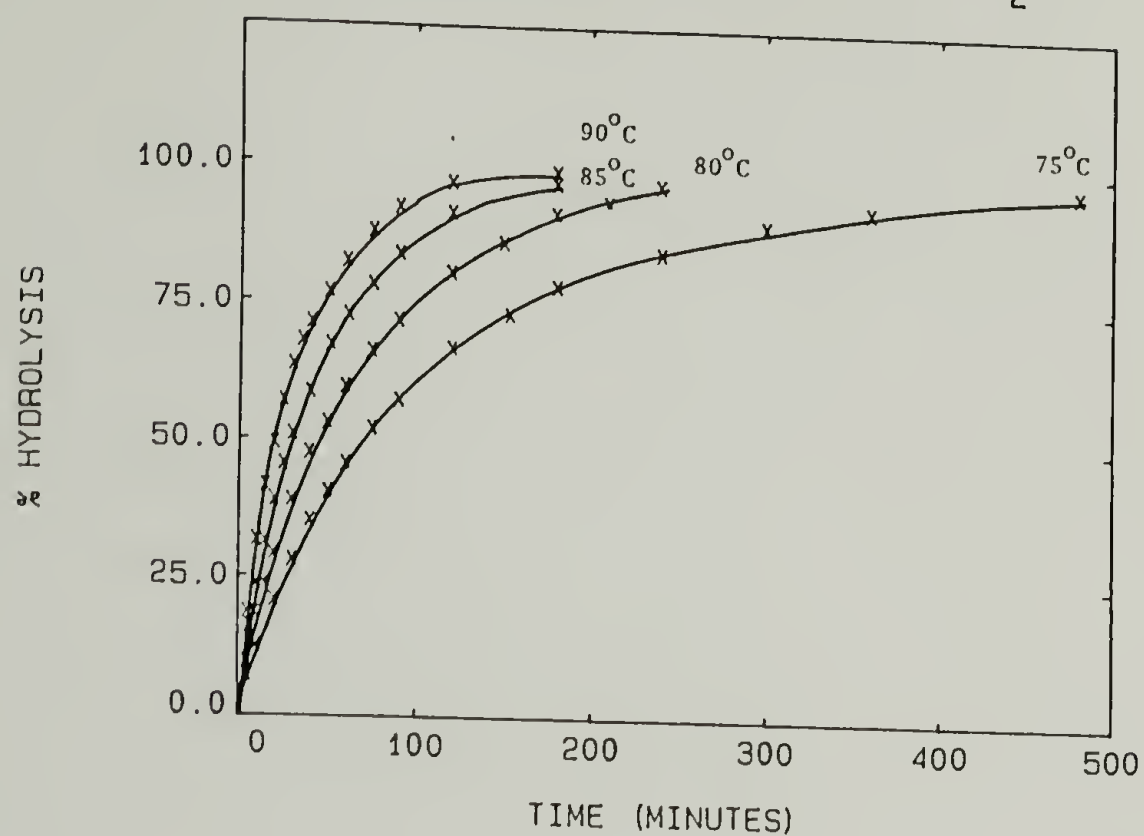


Figure 18. Neutral Hydrolysis of Poly(Isopropyl Styrene-sulfonate) in 90/10 (v/v) DMSO/H₂O

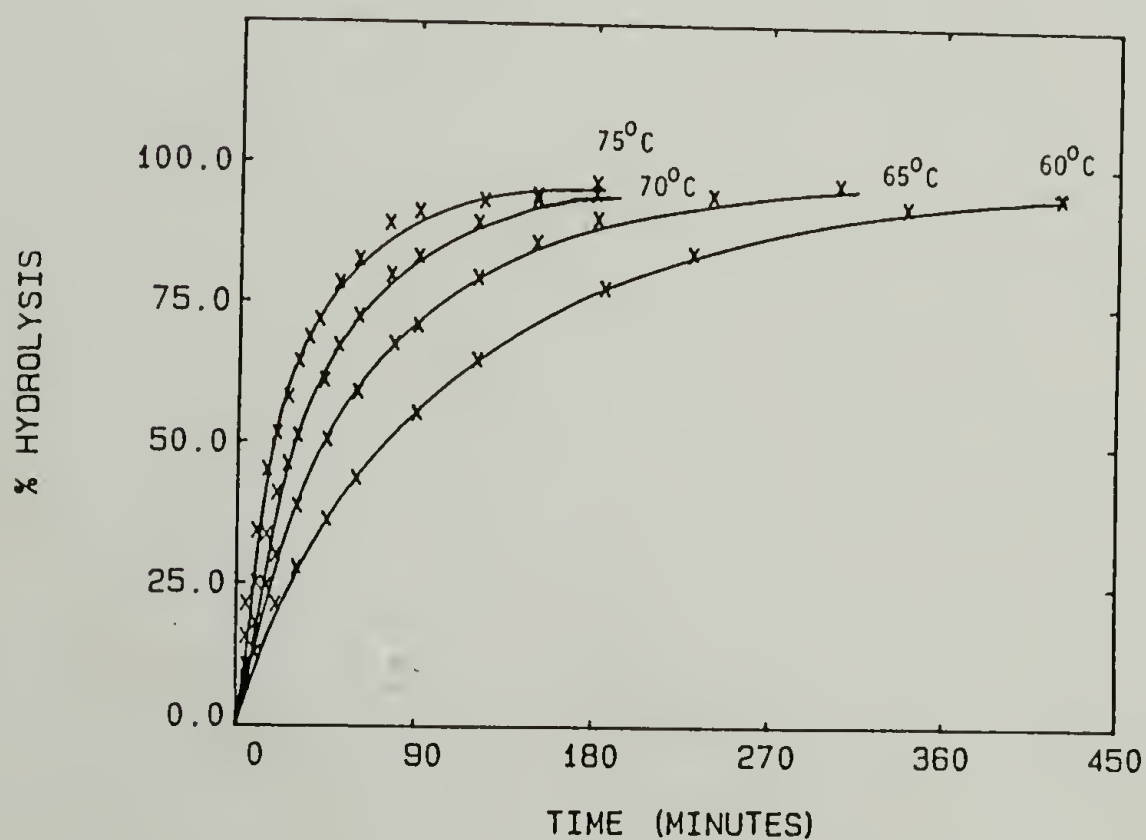


Figure 19. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate-co-Styrene) in 90/10 (v/v) DMSO/ H_2O

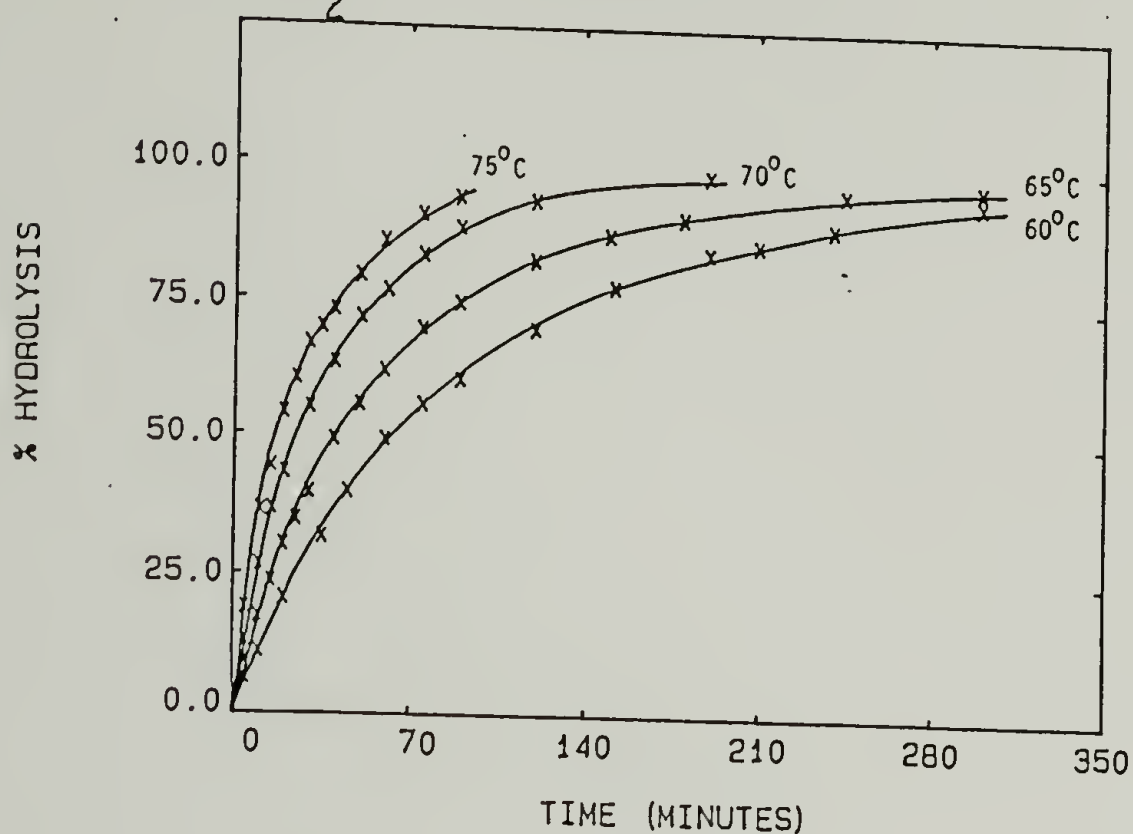
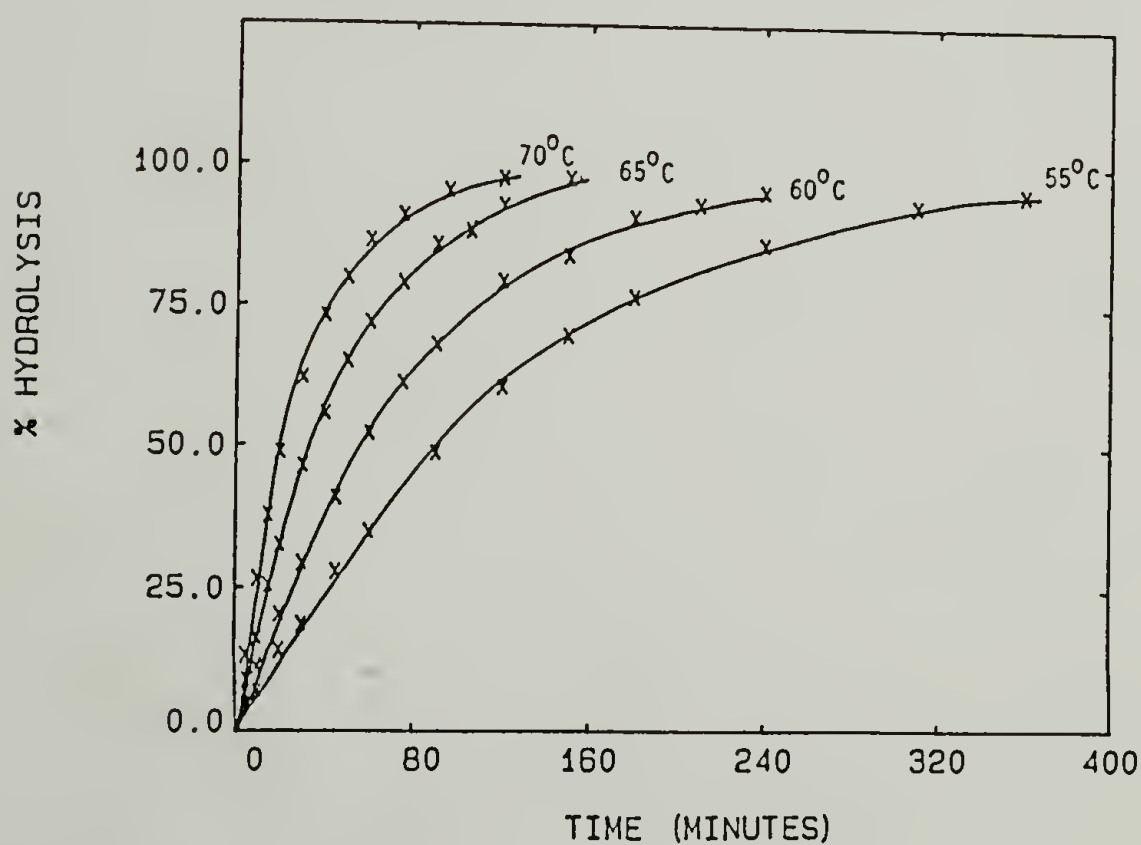


Figure 20. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate-co-Sodium Styrenesulfonate) in 100% H_2O



6. Neutral hydrolysis of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v), 50/50 (v/v), and 0/100 (v/v) DMSO/H₂O. Experimental data for the neutral hydrolysis of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) (57/43 copolymer) in various solvent systems at 70.0°C is tabulated in the appendix and summarized in Figure 21.
7. Basic hydrolysis of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O. Experimental data for the basic hydrolysis (2:1 NaOH:ester) of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) (57/43 copolymer) at 70.0°C is tabulated in the appendix and summarized in Figure 22.
8. Acidic hydrolysis of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O. Experimental data for the acidic hydrolysis (1:1 HCl:ester) of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) (57/43 copolymer) at 70.0°C is tabulated in the appendix and summarized in Figure 22.
9. Neutral hydrolysis of poly(methyl p-styrenesulfonate) in 90/10 (v/v) DMSO/H₂O: effect of molecular weight. Experimental data for the neutral hydrolysis of various molecular weight samples of poly(methyl p-styrenesulfonate)

Figure 21. Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) in Various Solvent Systems at 70°C

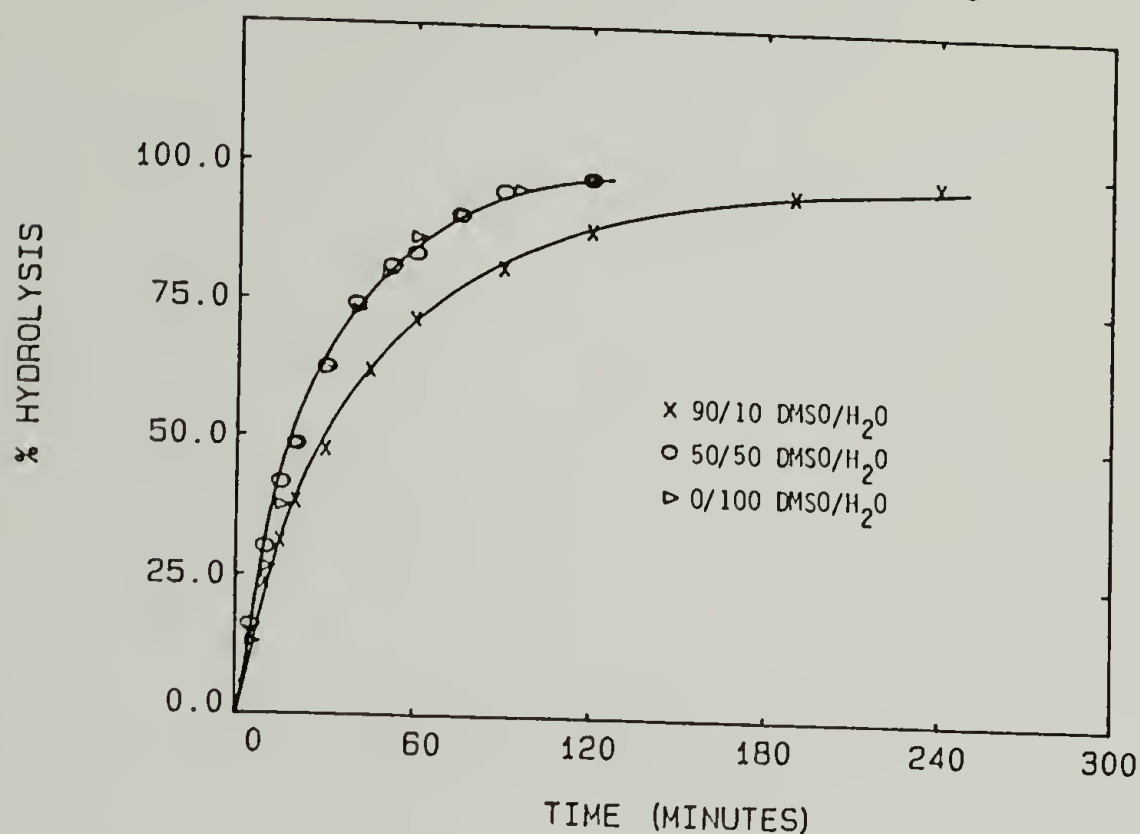
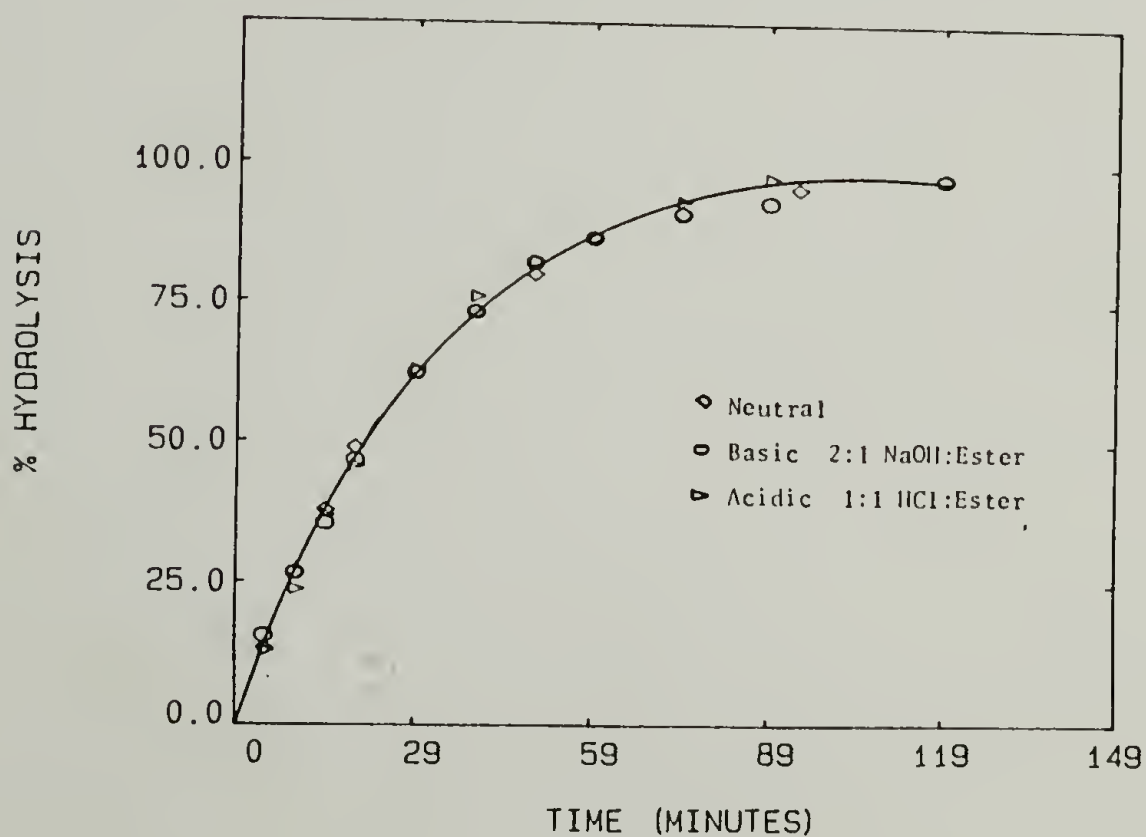


Figure 22. Acidic and Basic Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) in 100% H₂O at 70°C



at 70°C is tabulated in the appendix and summarized in Figure 23.

10. Neutral hydrolysis of poly(methyl p-styrenesulfonate) emulsion in 100% H₂O. Experimental data for the neutral hydrolysis of a poly(methyl styrenesulfonate) emulsion, prepared as described previously, in water (1.0 ml emulsion in 50.0 ml total solution) at 80°C is tabulated in the appendix and summarized in Figure 24.

11. Neutral hydrolysis of poly(methyl p-styrenesulfonate) in 80/20 (v/v) DMSO/H₂O: solution viscosity versus % hydrolysis. A Ubbelohde-type viscometer in a thermostated bath at 50.0°C was charged with 10.0 ml of distilled water and 39.0 ml of DMSO. After 30 minutes, 0.0991g (0.50 mmol) of poly(methyl p-styrenesulfonate) in 1.0 ml of DMSO was added. At suitable time intervals the viscosity of the solution was measured and 2.00 ml samples withdrawn (syringe), quenched with ice, and titrated with 0.200 N NaOH to determine % hydrolysis. A duplicate experiment in 0.5 M NaCl solution [80/20 (v/v) DMSO/H₂O] was run. Experimental results are tabulated in the appendix and summarized in Figure 25.

Figure 23. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate) in 90/10 (v/v) DMSO/H₂O: Effect of Molecular Weight

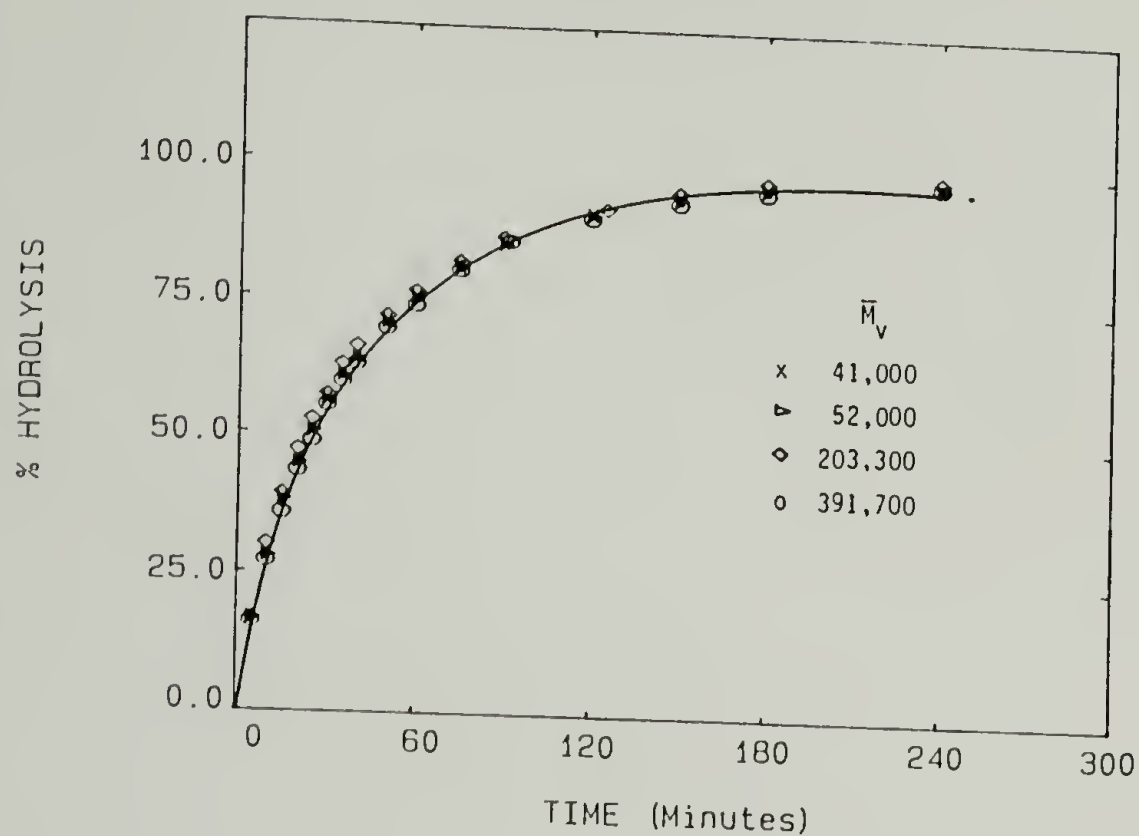


Figure 24. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate) Emulsion in 100% H₂O

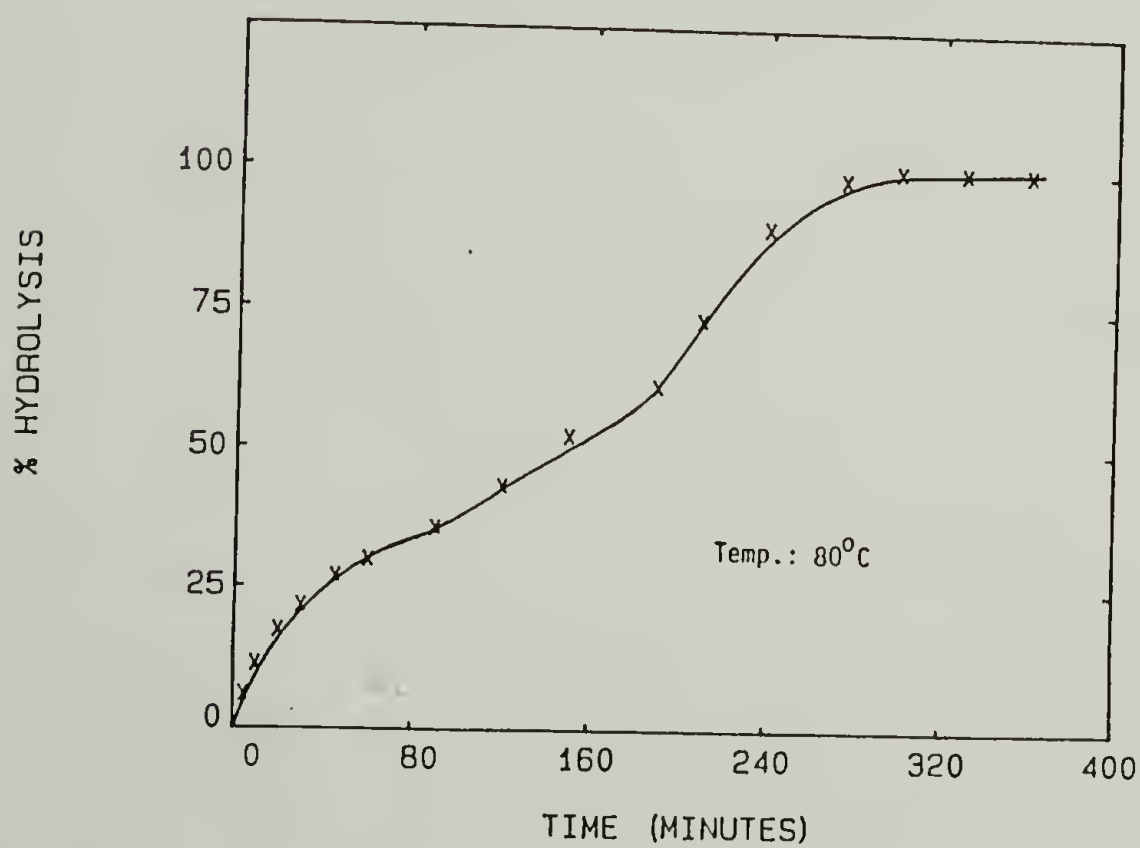
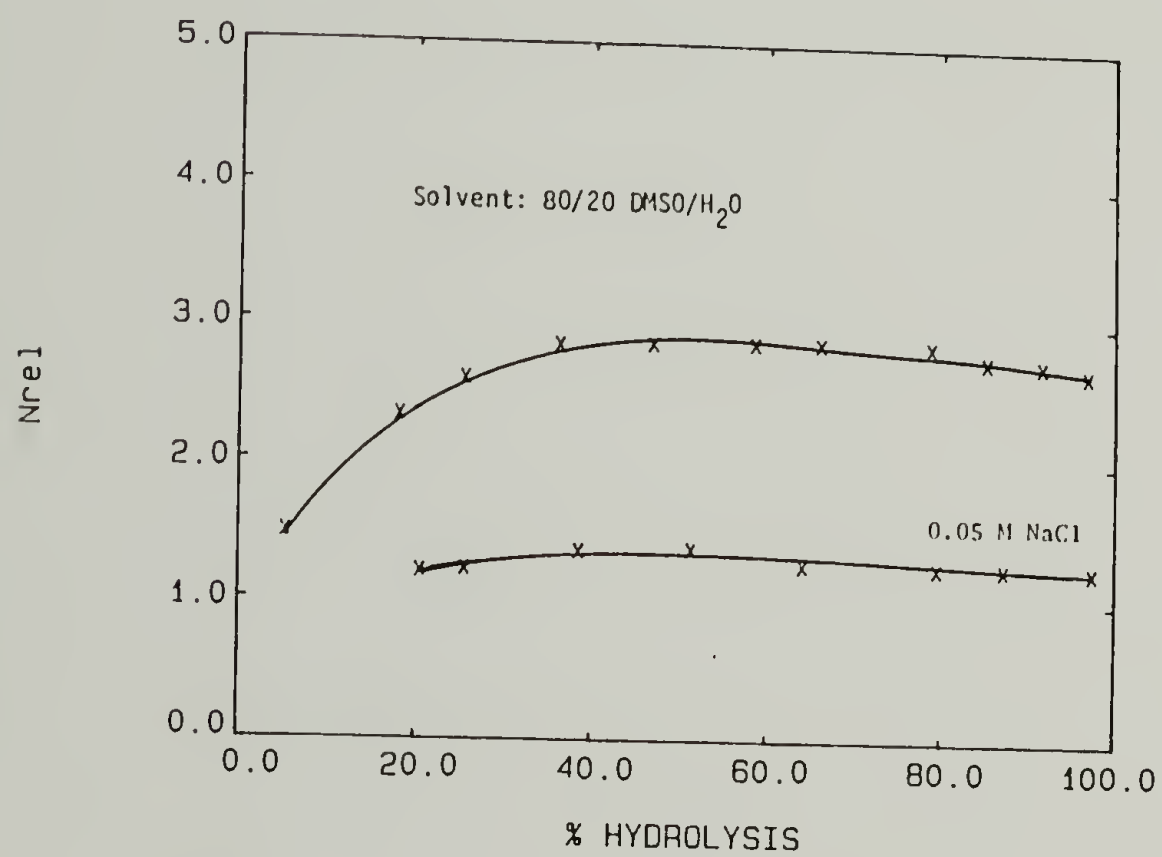


Figure 25. Neutral Hydrolysis of Poly(Methyl Styrene-sulfonate): Solution Viscosity versus % Hydrolysis



12. Attempted hydrolysis of poly(methyl p-styrenesulfonate-co-acrylic acid) in 100% H₂O. Due to the weak acidity of acrylic acid comonomer, determination of equivalence points with visual indicators (e.g. bromothymol blue) in systems containing acrylic acid is difficult. No sharp titration endpoints could be discerned in methyl p-styrenesulfonate/acrylic acid copolymers so that determination of % hydrolysis via titration by the aforementioned procedure was not possible. Construction of titration curves, as detailed below, confirmed this difficulty.

K. Miscellaneous

1. Titration curves for poly(styrenesulfonic acid-co-acrylic acid), poly(styrenesulfonic acid) and poly(acrylic acid). Poly(methyl p-styrenesulfonate-co-acrylic acid) (0.0991g of 26/74 copolymer) was completely hydrolyzed in 50.0 ml distilled water (2 hours at 70°C) and the pH of the solution as a function of 1.00 N NaOH addition was recorded. pH determinations were made on a Fisher Accumet 825P pH meter. Similar curves were recorded in 0.1 M NaCl as well as for poly(styrenesulfonic acid) and poly(acrylic acid). The results are summarized in Figures 26-28.

Figure 26. Titration Curves for Poly(Styrenesulfonic Acid-co-Acrylic Acid)

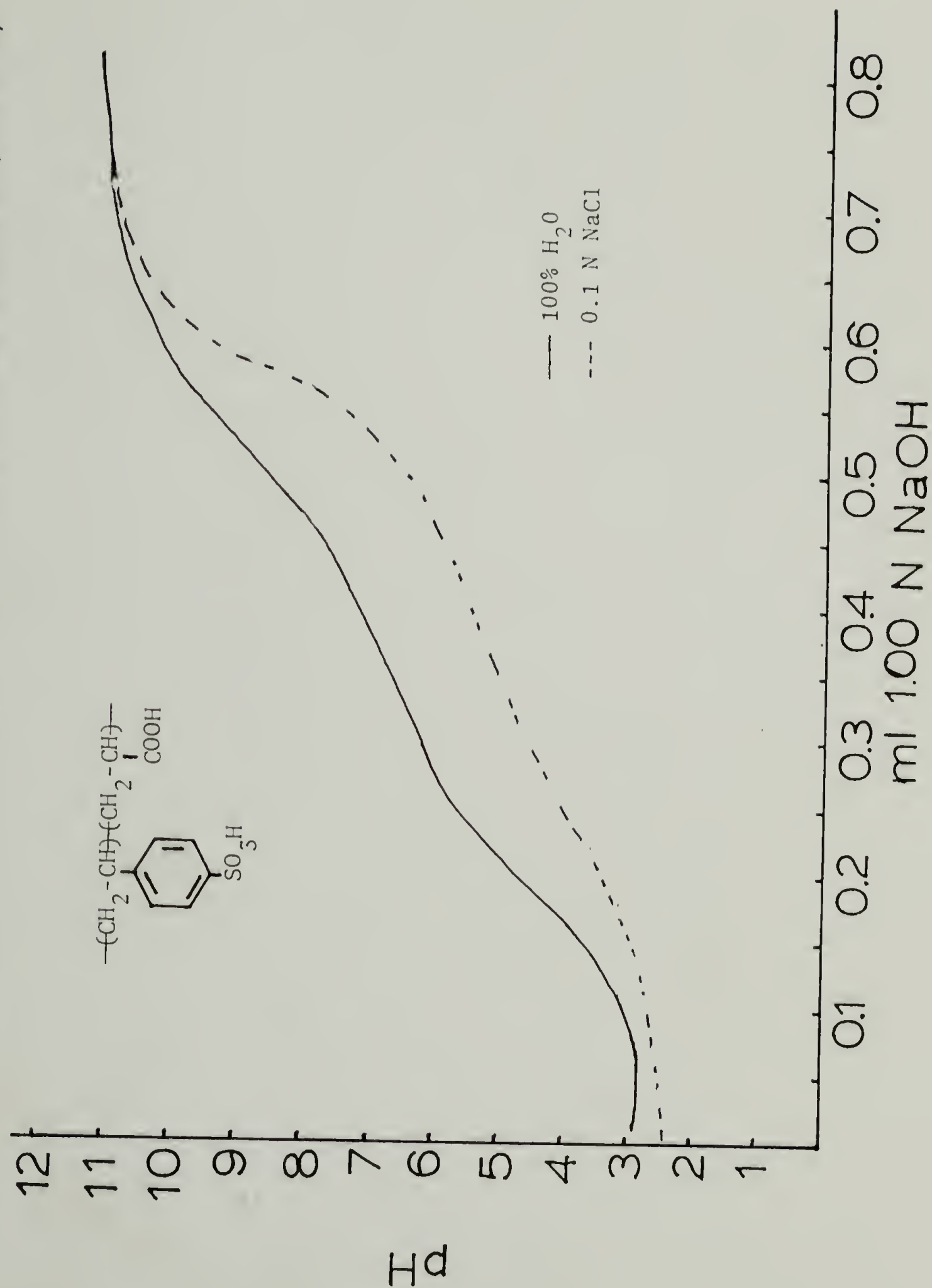
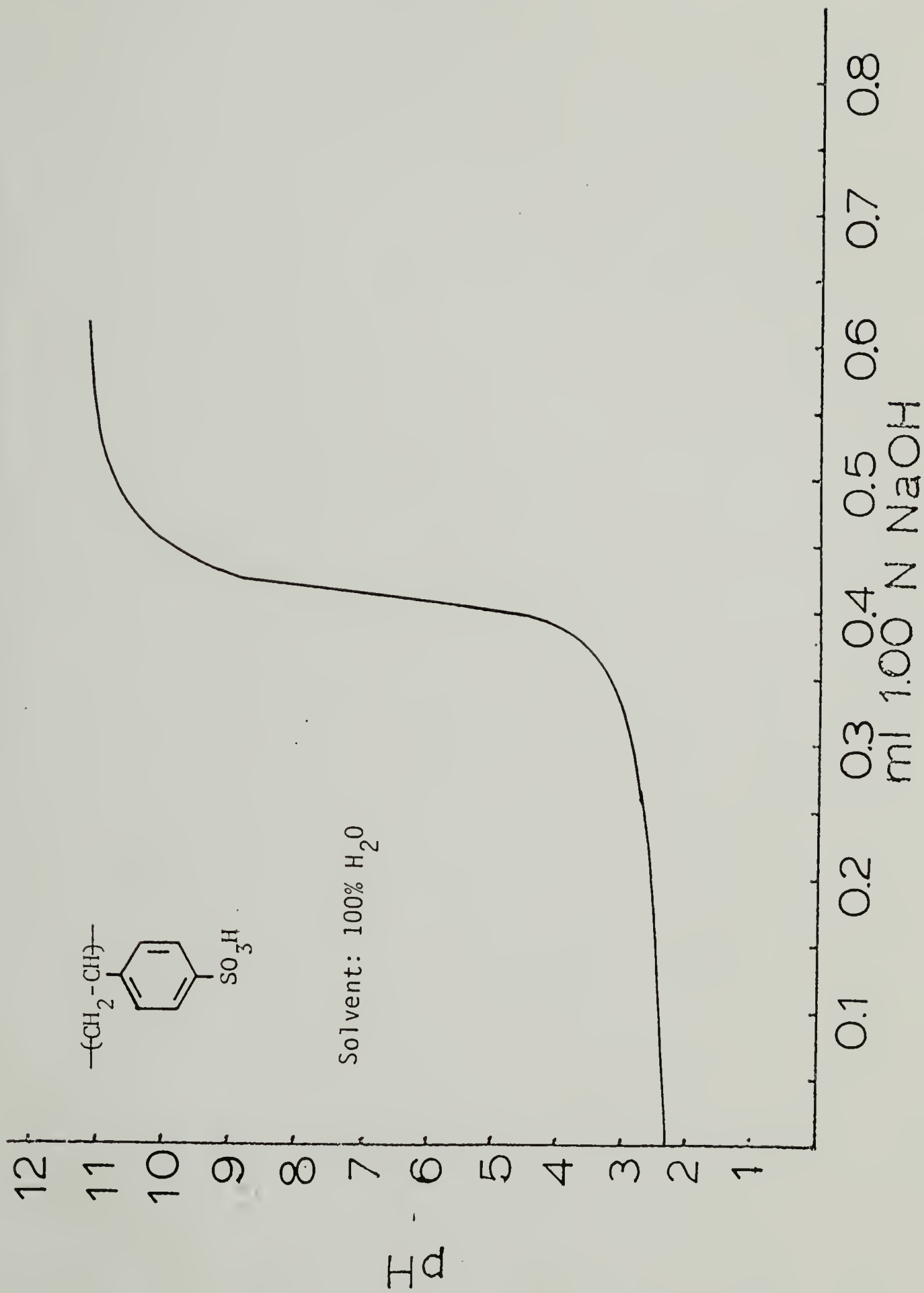


Figure 27. Titration Curve for Poly(Styrenesulfonic Acid)



2. Conductiometric titration of poly(styrenesulfonic acid-co-acrylic acid). Conductiometric titrations were performed on poly(styrenesulfonic acid-co-acrylic acid) solutions, prepared as described above, using a Philscope Phillips conductometer G.M. 4249. Conductance of the aqueous solution was measured as a function of 1.00 N NaOH addition and the results are summarized in Figure 29.

3. Viscosity of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v) DMSO/H₂O and 100% H₂O. Reduced viscosities of poly(methyl p-styrenesulfonate-co-sodium styrenesulfonate) (57/43 copolymer) in 90/10 (v/v) DMSO/H₂O and 100% H₂O were determined at 30.0°C in a Ubbelohde-type viscometer. The polymer concentration in both cases was 0.01 M. The results are summarized in Table 22.

Figure 29. Conductiometric Titration Curve for Poly(Styrene-sulfonic Acid-co-Acrylic Acid) in 100% H₂O

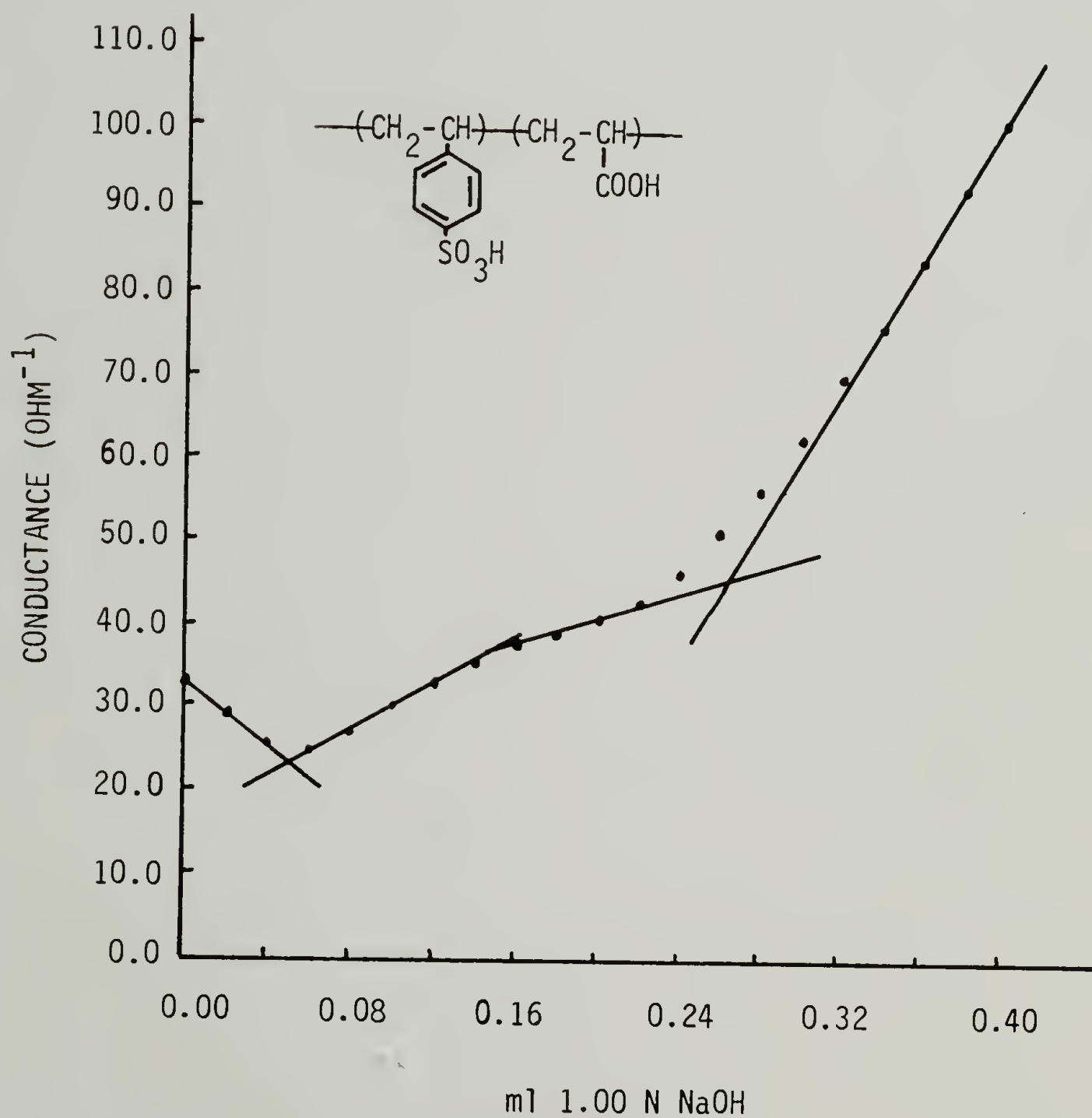


Table 22. Viscosity of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) Solutions in Water and Aqueous DMSO*

Polymer	Solvent	η_{red}
PMSS-CO-NaSS	100% H ₂ O	1.957
PMSS-CO-NaSS	90/10 (v/v) DMSO/H ₂ O	4.929

* Reduced Viscosities determined at 30°C. Polymer concentration 0.0991g/50 ml solvent. Copolymer 57 mole % methyl styrenesulfonate.

CHAPTER III

RESULTS AND DISCUSSION

A. Objectives

The objectives of this work were the synthesis, homopolymerization, and copolymerization of styrenesulfonic acid esters. Specifically, the methyl, ethyl, n-propyl, and isopropyl esters of styrenesulfonic acid were synthesized and homopolymers and copolymers containing these monomers evaluated with respect to hydrolysis behavior. Comonomers chosen for consideration included styrene, acrylamide, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), maleic anhydride, sodium acrylate, sodium styrenesulfonate, and 2-sulfoethyl methacrylate (NaSEM). The effect of a variety of variables, including molecular weight, copolymerization, ester length and branching, solvents, temperature, and pH, on the kinetics of hydrolysis was investigated.

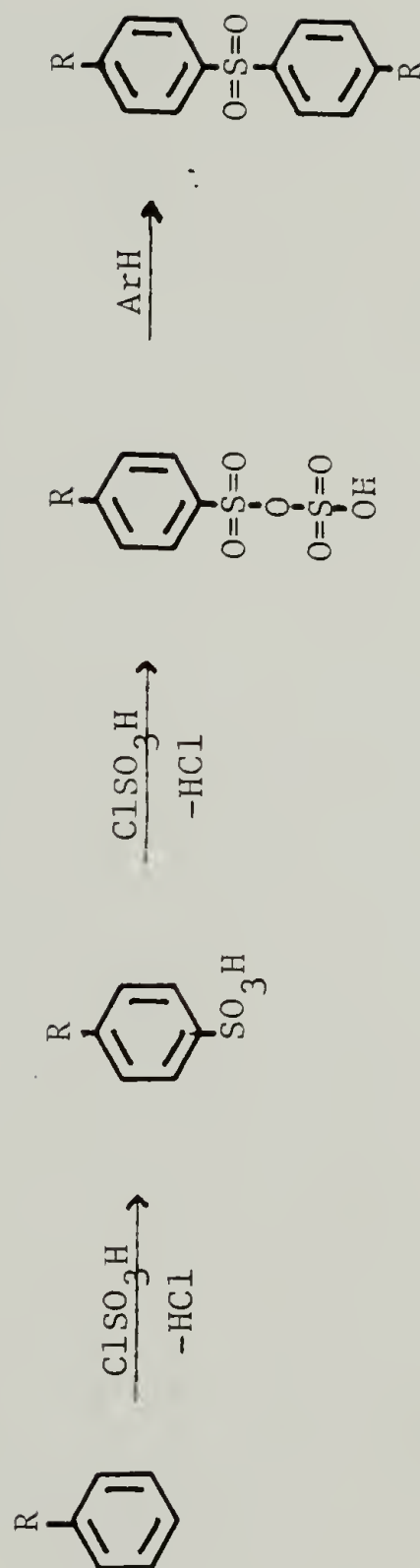
B. Preparation of Alkyl Styrenesulfonates

Two approaches for the synthesis of styrenesulfonic acid esters were investigated. These include (1) synthesis via (2-bromoethyl)benzene, and (2) synthesis via sodium styrenesulfonate. The results of these syntheses are discussed below.

1. Synthesis of Alkyl Styrenesulfonates via (2-bromoethyl)benzene. The method of Spinner, Ciric, and Graydon (6) was used for the preparation of methyl styrenesulfonate. Sulfochlorination of (2-bromoethyl)benzene with chlorosulfonic acid yielded (2-bromoethyl)benzenesulfonyl chloride (60%) which was subsequently esterified with sodium methoxide to yield methyl (2-bromoethyl)benzenesulfonate (60% yield). Dehydrohalogenation with potassium t-butoxide in the presence of 18-crown-6 yielded methyl styrenesulfonate (60%).

Homopolymerization of methyl styrenesulfonate, prepared according to the above procedure, yielded insoluble, cross-linked products. This can be attributed to the presence of sulfone which is a common by-product during sulfochlorination of aromatic compounds (Figure 30). In the current investigation this sulfone represents a difunctional monomer (divinylbenzenesulfone) which accounts for the crosslinking observed. The presence of sulfone was confirmed by

Figure 30. Mechanism of Sulfone Formation (17).



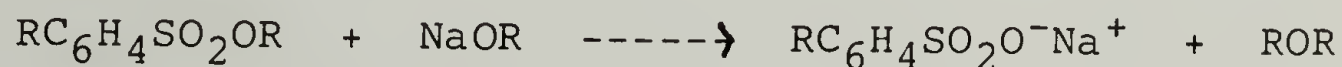
analytical high performance liquid chromatography (See Figure 3).

Several methods were investigated for reduction of sulfone content in order to obtain linear, soluble polymers. Although distillation of p-styrenesulfonate esters has been reported by several investigators using specially designed stills and high vacuums (9,11,12), the distillation is difficult and yields low because of polymerization and degradation which occur at elevated temperatures. As a result, two alternative methods for reducing the sulfone content were investigated; recrystallization and purification by preparative high performance liquid chromatography (HPLC). While recrystallization proved unsuccessful in reducing the sulfone content, purification by preparative HPLC achieved partial success. Purification using this method was shown to be effective in reducing sulfone content (Figure 5). Although repeated purification (2x) enabled reduction of sulfone content to less than 0.5%, polymerization still led to insoluble, crosslinked products. Due to the time-consuming nature of preparative HPLC purification, alternative methods for preparation of sulfone-free monomers were investigated.

2. Synthesis of alkyl styrenesulfonates via sodium styrenesulfonate. The method of Gritsai and Prib (14),

employing sodium styrenesulfonate as a starting material, was investigated for the preparation of styrenesulfonic acid esters. Use of sodium styrenesulfonate as a starting material is advantageous in that it can be obtained sulfone-free due to its water solubility and the inherent insolubility of divinylbenzenesulfone in water. Thus, the problem of crosslinking resulting from sulfone impurities, as in the case of monomer preparation via (2-bromoethyl)benzene as previously described, is conveniently circumvented.

Sodium styrenesulfonate was converted to the acid chloride (87% yield) by reaction with phosphorous pentachloride. Subsequent esterification with suitable excesses of the appropriate alcohol and sodium hydroxide in ether solution (Table 8) yielded the corresponding styrenesulfonic acid esters. In this manner the methyl (67% yield), ethyl (55% yield), n-propyl (50% yield), and isopropyl (40% yield) esters of styrenesulfonic acid were prepared. Yields in the esterification reaction are limited due to attack of alkoxide ions on previously formed ester moieties:

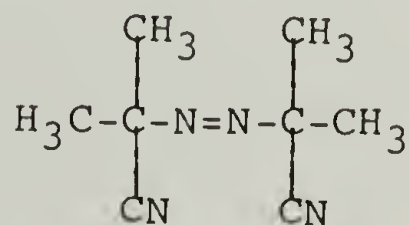


In general, it was observed that as the size (bulkiness) of the ester increased (i.e. in the series methyl, ethyl, n-propyl, and isopropyl) monomer yields decreased. This observed behavior is inherently due to steric factors and increasing contributions from side reactions as described above.

C. Homopolymerization of Alkyl Styrenesulfonates

Solution, emulsion, and bulk polymerization systems were investigated for the homopolymerization of alkyl styrenesulfonates. All three systems were found to be applicable for the preparation of high molecular weight homopolymers in good yields and at reasonable rates. The results are summarized in Table 23.

Bulk polymerizations were carried out in sealed tubes at 60°C with azobisisobutyronitrile



as the free radical initiator. Polymerization times were generally 16-24 hours and yields of 50-70% were obtained (Table 23). Low yields in the case of isopropyl styrene-

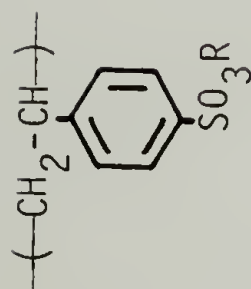


Table 23. Homopolymer Synthesis Results

R	Polymerization	Temp. (°C)	Time (hrs)	Yield (%)	\bar{M}_v
Methyl	Bulk	60	18	63	391,700
"	Solution (DMF)	60	18	70	-
"	Emulsion	60	2	72	-
Ethyl *	Bulk	60	18	70	676,000
n-Propyl	Bulk	60	16	50	175,000
Isopropyl	Bulk	60	24	30	96,000

* Distilled monomer

sulfonate homopolymerization are possibly due to chain transfer (either to monomer or polymer) which is enhanced by the presence of a secondary hydrogen atom in the ester moiety. When reinitiation by a chain transfer-formed radical is much less than that of the original propagating radical, the overall polymerization rate is lowered (95). A lowered polymerization rate would account for the low yields obtained. The presence of chain transfer in the polymerization reaction is supported by the relatively low molecular weight obtained (Table 23).

Solution polymerization of methyl styrenesulfonate was carried out in N,N-dimethylformamide which is a solvent for both the monomer and homopolymer. As indicated in Table 23, slightly higher yields (70%) were obtained than in bulk homopolymerization (63%). Optimization of reaction conditions could, undoubtedly, improve yields even further.

Emulsion polymerization of methyl styrenesulfonate was carried out in water (dispersant) with sodium lauryl sulfate (emulsifier) at 60°C. A potassium persulfate/sodium bisulfite redox initiator system was used for the production of free radicals which initiate polymerization (Equations 6,7). Comparison of the data in

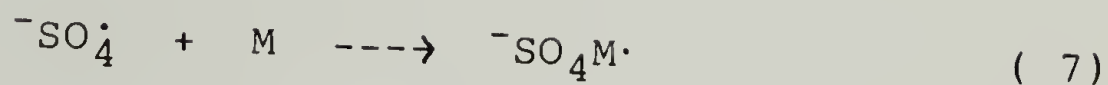
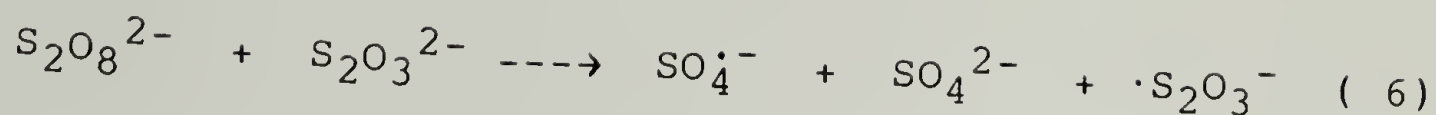


Table 23 indicates that emulsion polymerization proved to be the best method for the production of homopolymers in good yields (72%) in the shortest period of time (2 hours). Titration of the resultant homopolymer with 0.200N sodium hydroxide indicated less than 1% sulfonic acid content, thus demonstrating that negligible hydrolysis had occurred during polymerization.

Solubility studies on the various homopolymers indicated that poly(alkyl styrenesulfonates) are insoluble in common organic solvents for polystyrene (e.g. benzene, toluene, xylene, tetrahydrofuran, and methyl ethyl ketone) but were soluble in highly polar aprotic solvents such as N,N-dimethylformamide, dimethyl sulfoxide, and N-methyl pyrrolidinone. Thus, introduction of the highly polar sulfonate group ($-\text{SO}_3^-$) was found to greatly affect solubility behavior.

D. Copolymerization of Alkyl Styrenesulfonates

Alkyl styrenesulfonates were found to readily copolymerize with a variety of comonomers. Comonomers investigated include styrene and various water-soluble comonomers such as acrylic acid, acrylamide, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), maleic anhydride, sodium acrylate, sodium styrenesulfonate, and sodium 2-sulfoethyl methacrylate (NaSEM). These water-soluble comonomers were chosen so as to allow for the preparation of water-soluble copolymers which are desirable in many applications.

1. Copolymerization with styrene. Methyl, ethyl, n-propyl, and isopropyl styrenesulfonates were found to readily copolymerize with styrene in the bulk at 60°C with azobisisobutyronitrile (AIBN) as the free radical initiator. Results are summarized in Table 10. Reasonable yields were obtained (63-71%) in 24 hours or less. Elemental analysis indicated considerable incorporation of styrene into the copolymer (50 mole %).

2. Copolymerization with acrylic acid. Methyl, ethyl, n-propyl, and isopropyl styrenesulfonates were also found to readily copolymerize with acrylic acid. However, in this case, bulk polymerization systems led to insoluble, cross-

linked products. Such results are typical of acrylic acid polymerizations in concentrated solutions and is possibly due to the formation of anhydride linkages resulting from the high heat of polymerization (96). As a result, polymerization in solution (N-methyl pyrrolidinone) was necessary in order to prepare linear, soluble copolymers. Results are summarized in Table 11. Reasonable yields were obtained (54-87%) in 24 hours. Again, optimization of reaction conditions could improve yields even further. Elemental analysis indicated considerable incorporation of acrylic acid into the copolymer (59 mole %).

3. Copolymerization with maleic anhydride. Copolymerization of methyl, ethyl, n-propyl, and isopropyl styrene-sulfonates with maleic anhydride occurred readily at 60°C in the bulk with azobisisobutyronitrile (AIBN). Relatively good yields were obtained (50-70%) as summarized in Table 12. Elemental analysis indicated a 40 mole % maleic anhydride content in the copolymer (50/50 mole % feed). As maleic anhydride is well known not to homopolymerize under these conditions, this high incorporation of maleic anhydride indicates a strong tendency for alternation. Similar behavior is observed in styrene-maleic anhydride systems (97).

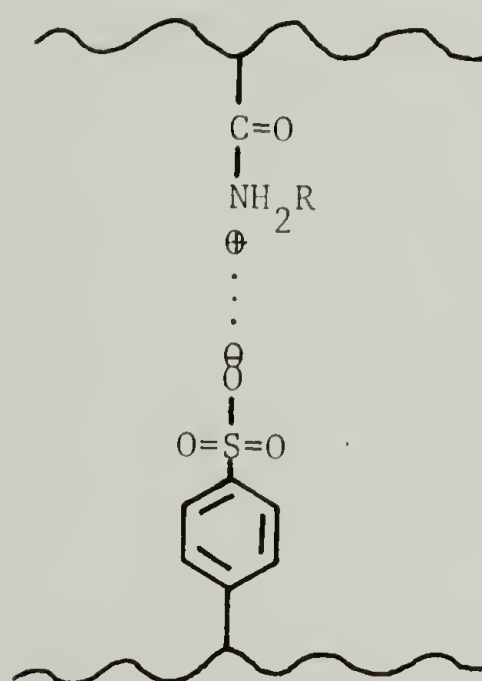
4. Copolymerization with 2-acrylamido-2-methyl-propanesulfonic acid (AMPS). 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) was insoluble in methyl styrene-sulfonate, thereby preventing use of bulk copolymerization techniques. However, AMPS proved to be soluble in highly polar aprotic solvents, thus enabling solution polymerization techniques to be employed. Methyl styrenesulfonate readily copolymerized with AMPS (50/50 mole % feed) in N,N-dimethylformamide (20% solids) at 60°C with azobisisobutyronitrile. Reaction for 24 hours yielded 67% of a water-soluble copolymer. Elemental analysis indicated significant incorporation of AMPS into the copolymer (50 mole %).
5. Copolymerization with sodium 2-sulfoethyl methacrylate (NaSEM). As in copolymerization with AMPS, sodium 2-sulfoethyl methacrylate (NaSEM) was insoluble in methyl styrenesulfonate thereby preventing copolymerization in the bulk. However, methyl styrenesulfonate was readily copolymerized with NaSEM in N-methyl pyrrolidinone solution (10% solids) to yield 86% of a water-soluble copolymer. Again, elemental analysis indicated significant incorporation of NaSEM into the copolymer (50 mole %).
6. Attempted copolymerization with acrylamide. Copolymerization of alkyl styrenesulfonates with acrylamide in

either N-methyl pyrrolidinone, N,N-dimethylformamide, or dimethyl sulfoxide solution led to insoluble gels. As sulfonic acid esters are known to be strong alkylating agents (98,99), the most probable explanation for this involves the presence of ionic crosslinks formed by alkylation of the amide functionality by the sulfonate ester (Figure 31).

7. Attempted copolymerization with sodium acrylate.

While the preceding work illustrates the high reactivity of alkyl styrenesulfonates toward copolymerization, limitations do exist in choice of comonomers, the major factor being availability of a reaction medium. When the comonomers are immiscible in one another, the preferred method for copolymerization involves the use of a solution process carried out in a common solvent for both comonomers. In the case of oil-insoluble comonomers, such as sodium acrylate, choice of a common solvent for copolymerization with alkyl styrenesulfonates proved to be an insurmountable problem. Numerous copolymerization solvents were investigated including methanol, ethanol, N,N-dimethylformamide, dimethyl sulfoxide, acetonitrile, and N-methyl pyrrolidinone, but none was found which would dissolve sodium acrylate to any appreciable extent. Thus, although there is no doubt that this comonomer would readily

Figure 31. Ionic Crosslinks in Alkyl Styrenesulfonate-Acrylamide Copolymers.



copolymerize with alkyl styrenesulfonates, copolymer preparation is hampered, not by reactivity considerations, but by physical considerations (i.e. choice of common reaction solvent).

8. Attempted copolymerization with sodium styrenesulfonate.

As in the case of sodium acrylate, sodium styrenesulfonate could not be directly copolymerized with alkyl styrenesulfonates due to mutual insolubility and unavailability of a suitable reaction medium. Numerous solvents were investigated, including methanol, ethanol, N,N-dimethylformamide, dimethyl sulfoxide, acetonitrile, and N-methyl pyrrolidinone, for applicability as a copolymerization medium, but none was found which would dissolve sodium styrenesulfonate to any appreciable extent.

9. Preparation of alkyl styrenesulfonate-sodium styrene-

sulfonate copolymers. While, as described above, alkyl styrenesulfonates and sodium styrenesulfonate could not be directly copolymerized due to reaction medium limitations, a procedure was developed which circumvented this problem. Reaction of a suitable homopolymer with a carefully measured amount of sodium hydroxide in dimethyl sulfoxide solution allows for the preparation of alkyl styrenesulfonate-sodium-styrenesulfonate copolymers of any desired composition (Figure 32). In this manner a water-soluble methyl styrene-

Figure 32. Preparation of Alkyl Styrenesulfonate-Sodium Styrenesulfonate Copolymers

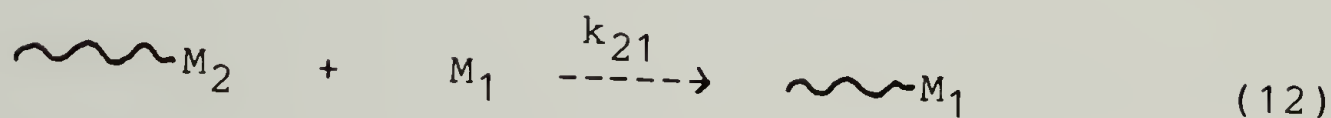
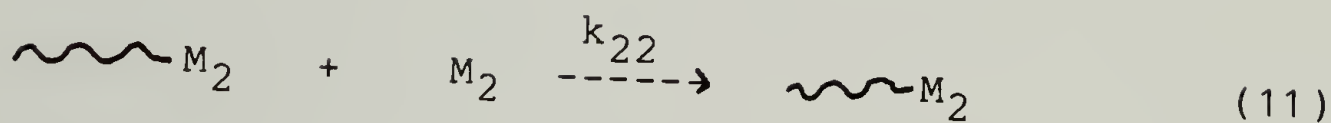
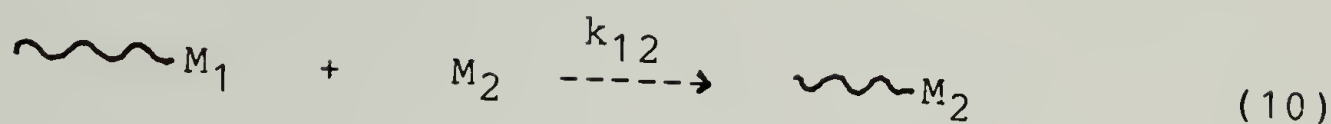
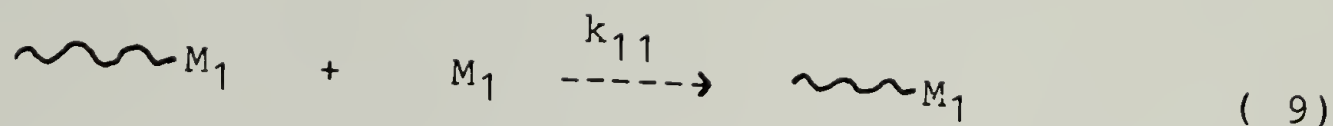


sulfonate-sodium styrenesulfonate copolymer containing 43 mole % sodium styrenesulfonate was successfully prepared.

10. Copolymerization reactivity ratios. The composition of a copolymer, in most instances, is found to be different than that of the copolymer feed from which it is produced. In other words, different monomers have differing tendencies to undergo copolymerization. The composition of a copolymer being formed, at any given instant, is given by Equation 8, known as the copolymerization equation or the

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + r_1([M_1]/[M_2])}{1 + r_2([M_1]/[M_2])} \quad (8)$$

copolymer composition equation where $d[M_1]/d[M_2]$ is the molar ratio of the two monomers, M_1 and M_2 , in the copolymer and $[M_1]/[M_2]$ is the molar ratio of the two monomers in the feed (100). The monomer reactivity ratios, r_1 and r_2 , are the ratios of the rate constant for a given radical adding to its own monomer to that for its adding to the other monomer (Equations 9-14).



$$r_1 = \frac{k_{11}}{k_{12}} \quad (13)$$

$$r_2 = \frac{k_{22}}{k_{21}} \quad (14)$$

The tendency of two monomers to copolymerize is noted by r values between zero and unity. An r_1 value of greater than unity means that M_1 preferentially adds M_1 instead of M_2 , while an r_1 value of less than unity means that M_1 preferentially adds M_2 . An r_1 value of zero would mean that M_1 is incapable of undergoing homopolymerization.

Experimentally, determination of r_1 and r_2 values

involves copolymerization to low conversion (< 10%) for a variety of feed compositions. The copolymers are isolated and their compositions determined (e.g. by elemental analysis). The copolymerization equation (Equation 8) can be rearranged into the form

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_2 + \frac{f_1^2(F_1-1)}{F_1(1-2f_1)^2} r_1 \quad (15)$$

where f_1 and F_1 are defined by Equations 16 and 17 (101). The left side of Equation 15

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad (16)$$

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (17)$$

is plotted against the coefficient of r_1 (for a variety of feed compositions f_1) to yield a straight line with slope r_1 and intercept r_2 .

Experimental results for the copolymerization of methyl styrenesulfonate with styrene, acrylic acid, and maleic anhydride are summarized in Tables 13, 14, and 15. A Fineman-Ross treatment of the data, according to Equation

15, for copolymerization of methyl styrenesulfonate with styrene and acrylic acid yields plots given in Figures 33 and 34 respectively. In the case of maleic anhydride, which does not homopolymerize (i.e. $r_2 = 0$), Equation 8 reduces to

$$\frac{d[M_1]}{d[M_2]} - 1 = r_1 \frac{[M_1]}{[M_2]} \quad (18)$$

where r_1 can be determined as the slope of a plot of the left side versus various monomer feed ratios ($[M_1]/[M_2]$). Such a treatment of the methyl styrenesulfonate-sodium styrenesulfonate data summarized in Table 15 is given in Figure 35.

Experimentally determined r_1 and r_2 values for copolymerization of methyl styrenesulfonate with styrene, acrylic acid, and maleic anhydride are summarized in Table 24. Results from the literature for the copolymerization of various styrenesulfonic acid derivatives are summarized in Table 25 for comparison. Analysis of the data in Tables 24 and 25 indicates that alkyl styrenesulfonates are highly reactive monomers with a tendency towards self-propagation in copolymerization (i.e. r_1 values > 1.0). By virtue of

Figure 33. Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Styrene (Equation 15)

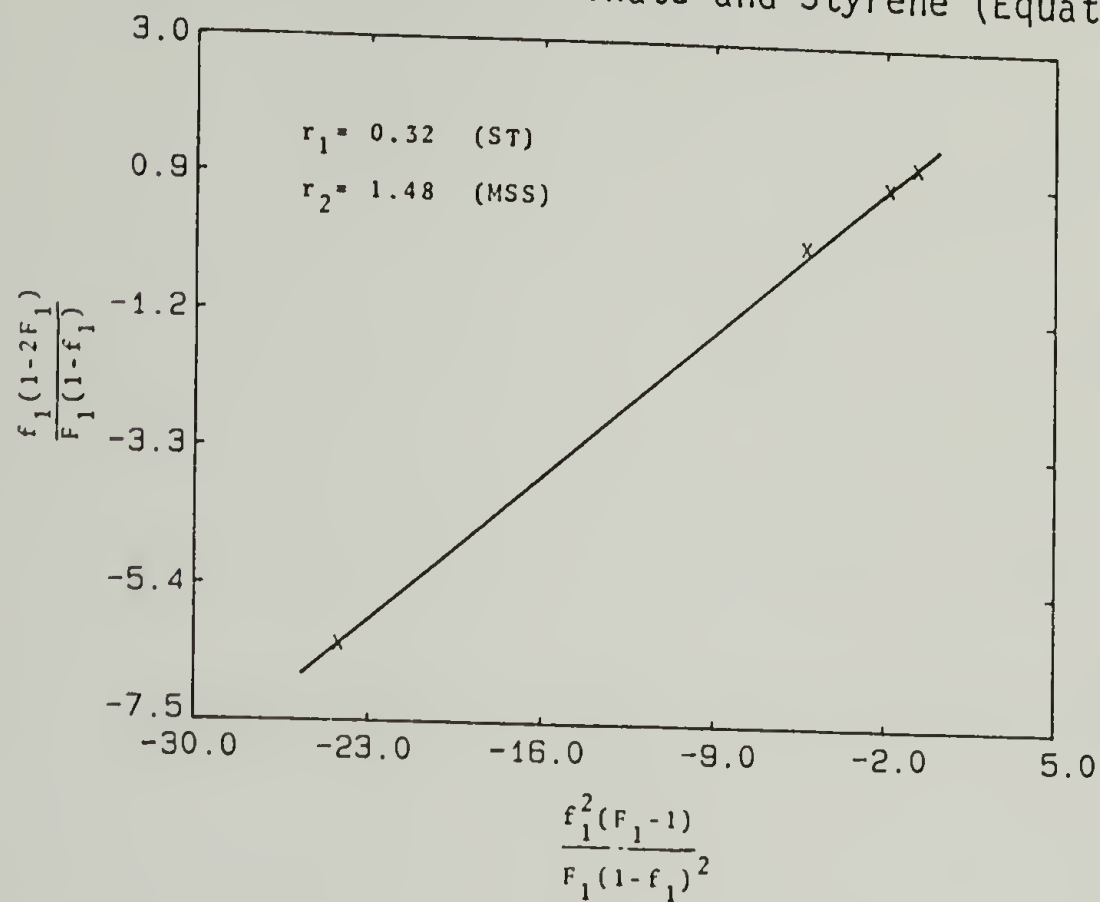


Figure 34. Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Acrylic Acid (Equation 15)

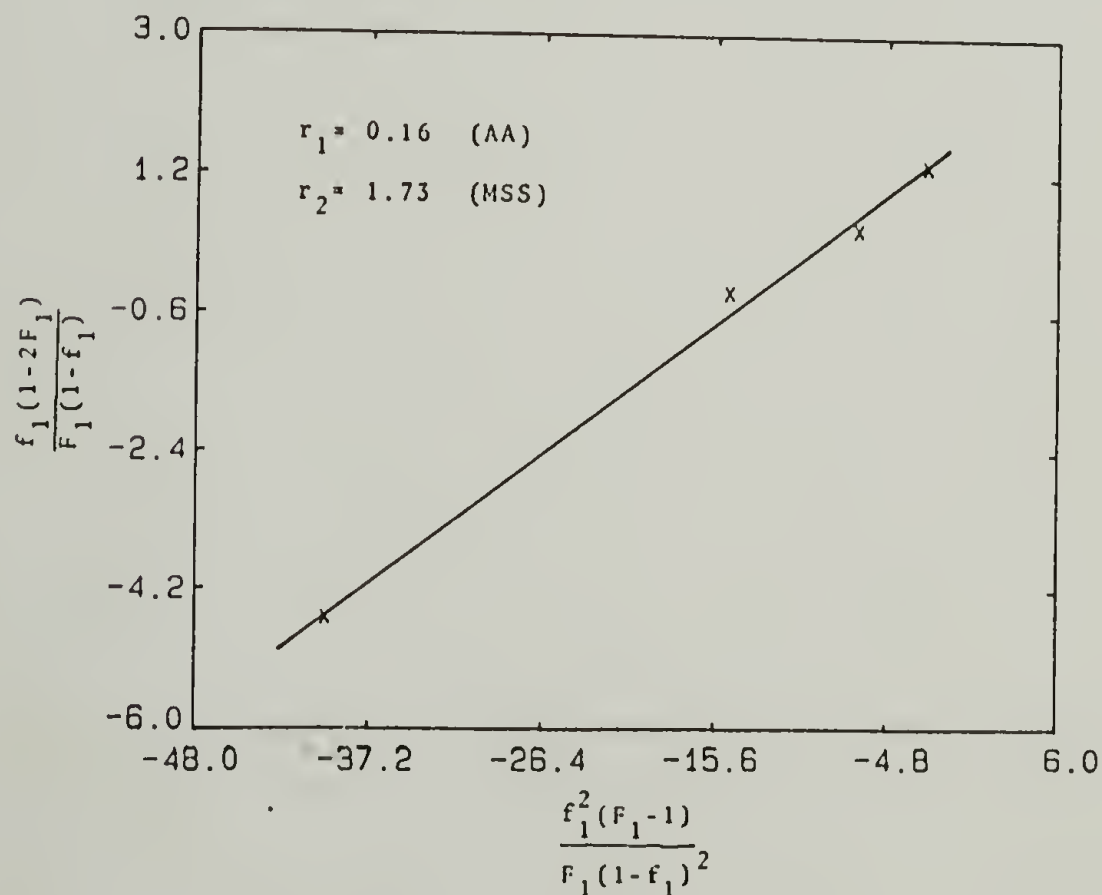


Figure 35. Reactivity Ratio Determination for Copolymerization of Methyl Styrenesulfonate and Maleic Anhydride (Equation 18)

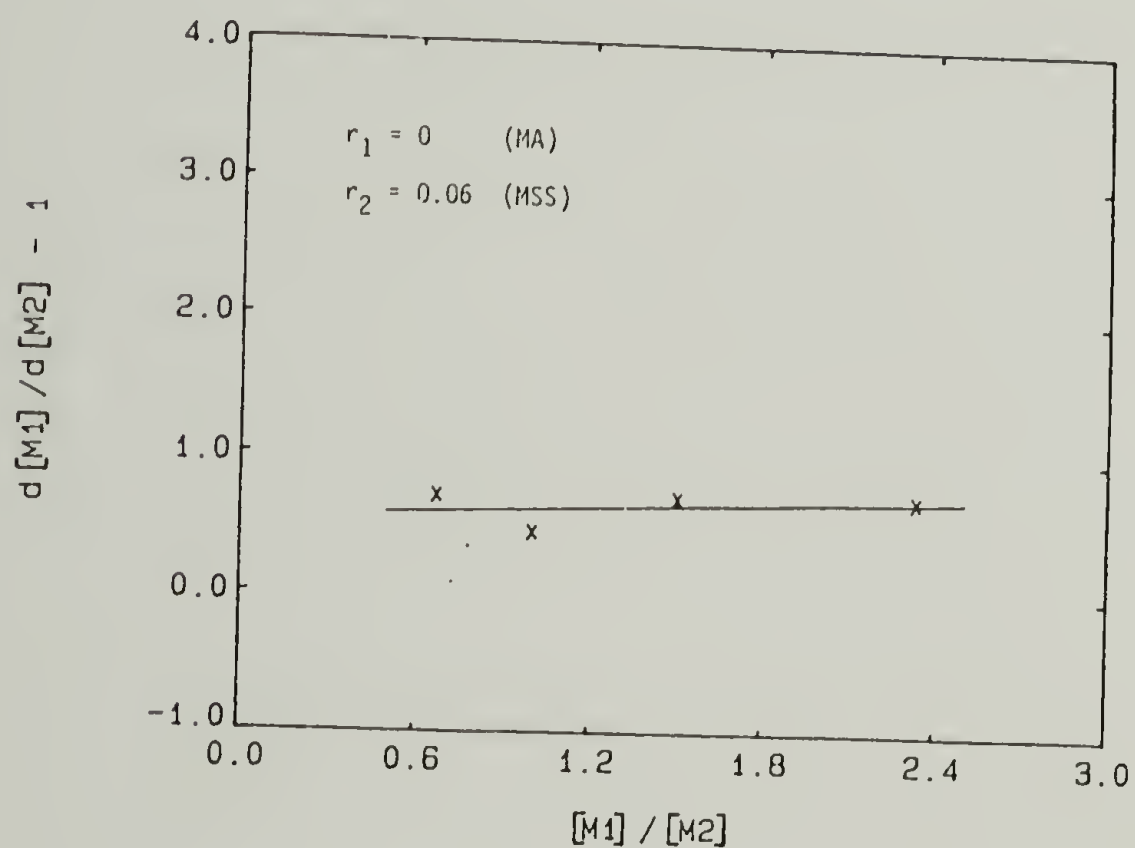


Table 24. Copolymerization Reactivity Ratios

M_1	M_2^*	Temp. ($^{\circ}\text{C}$)	r_1	r_2
Styrene	MSS	50	0.32	1.48
Acrylic Acid	MSS	50	0.16	1.73
Maleic Anhydride	MSS	50	0	0.06

* MSS = Methyl styrenesulfonate

Table 25. Reactivity Ratios of Styrenesulfonic Acid Derivatives

M_1	M_2	r_1	r_2	Temp. ($^{\circ}\text{C}$)	Ref.
Sodium Styrene-sulfonate	Acrylic Acid	1.0	0.10	70	102
Potassium Styrene-sulfonate	Acrylonitrile	1.5	0.02	70	102
Potassium Styrene-sulfonate	Styrene	0.56	0	90	103
Styrenesulfonic Acid	Acrylonitrile	1.20	0.10	45	104
Styrenesulfonyl Fluoride	Styrene	1.30	0.25	75	105
Styrenesulfonyl Fluoride	Acrylic Acid, Methyl Ester	4.0	0.20	75	105
Styrene	Acrylic Acid	0.25	0.07	50	106
Styrene	Maleic Anhydride	0.019	0	50	107

the large reactivity ratios observed for methyl styrene-sulfonate in copolymerizations with styrene and acrylic acid it is reasonable to assume that these copolymers are somewhat blocky in nature. As described previously, the data for copolymerization with maleic anhydride indicates a highly alternating copolymer structure ($r_1, r_2 \ll 1.0$). A more quantified treatment of monomer reactivity, according to the Alfrey-Price Q-e scheme, is discussed below.

11. Q-e scheme. Each copolymerization reactivity ratio r describes the relative tendency of two monomers to add to a particular growing chain. The reactive end of the growing chain is a free radical derived from one of the two monomers. Obviously, two types of reactive ends can exist and for this reason reactivity ratios must be determined in pairs. Moreover, because the values obtained experimentally are relative values, they pertain to only one particular pair of monomers. A much more useful measure of copolymerization behavior would be one which placed the radical-monomer reaction on a quantitative basis in terms of correlating structure and reactivity. Such a correlation is the Q-e scheme of Alfrey and Price (108,109). They proposed that there existed two parameters for each monomer and corresponding radical: Q , a measure of resonance stabilization of monomer and corresponding radical, and e , a

measure of polarity of monomer and corresponding radical. The relationship between these parameters and the actual reactivity ratios was proposed to be:

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (19)$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (20)$$

where the subscripts correspond to monomers 1 and 2.

Experimentally, Q and e values are determined based on reactivity ratio values and the arbitrarily chosen reference values of $Q = 1.0$ and $e = -0.80$ for styrene. Using reactivity ratio data obtained for copolymerization of monomer M_2 with styrene, Q and e values for M_2 can be determined according to Equations 21 and 22.

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2} \quad (21)$$

$$Q_2 = \frac{Q_1}{r_1} \exp[-e_1(e_1 - e_2)] \quad (22)$$

Results for methyl styrenesulfonate, calculated from reactivity ratio data summarized in Table 24, are summarized in Table 26. Q and e values reported in the literature for various styrenesulfonic acid derivatives are summarized in Table 27 for comparison.

The Q value of a monomer is at least a crude indication of the resonance effect (e.g. conjugated monomers have high Q values) and the e value is related to the electron-donating or electron-withdrawing character of the substituent. In the case of most ring-substituted styrenes, the Q values are very close to styrene itself (usually slightly larger) and the principal effect of ring substituents is to change the e value from that of the parent styrene (1.09). The Q value for methyl styrenesulfonate (1.56) is comparable to those for styrene (1.00) and other styrenesulfonic acid derivatives (Table 27) and indicates a large resonance stabilization in the monomer and corresponding radical. The experimentally determined e value for methyl styrenesulfonate (+0.07) is slightly positive and indicates that the sulfonate ester substituent is electron-withdrawing when compared to styrene ($e = -0.80$) which is electron-donating. Comparison with the literature values reported in Table 27 indicate that the e value for methyl styrenesulfonate is comparable to those for styrenesulfonyl fluoride (+0.200) and p-sulfamidostyrene (+0.370)

Table 26. Alfrey-Price Q-e Values for Methyl Styrenesulfonate

Monomer	r	Q	e
Styrene (M_1)	0.32	(1.00)	(-0.80)
Methyl Styrenesulfonate (M_2)	1.48	1.56	0.07

Table 27. Alfrey-Price Q-e Values for Styrenesulfonic Acid Derivatives (122)

Monomer	Q	e
Styrenesulfonic Acid	1.040	-0.260
Styrenesulfonic Acid, Potassium Salt	1.140	-0.300
Styrenesulfonic Acid, Sodium Salt	2.490	-0.590
Styrenesulfonyl Fluoride	1.640	0.200
p-Sulfonamidostyrene	1.620	0.370
Vinyl Sulfonic Acid, Sodium Salt	0.410	0.064
Vinyl Sulfonic Acid, Propyl Ester	1.760	0.270
Vinyl Sulfonyl Fluoride	1.390	0.120

and the sulfonate ester group has slightly more electron-withdrawing character than either the acid ($e = -0.260$), potassium salt ($e = -0.300$) or sodium salt ($e = -0.590$) forms. Similar results are observed in vinyl sulfonates (Table 27).

12. Copolymer water solubility studies. Copolymers of alkyl styrenesulfonates with maleic anhydride, acrylic acid, and sodium styrenesulfonate were tested for water solubility. While copolymers containing maleic anhydride were insoluble in water, as are styrene-maleic anhydride copolymers (110), copolymers containing acrylic acid and sodium styrenesulfonate were prepared which were water-soluble. Studies were initiated involving these two comonomers to determine the comonomer content necessary to impart water solubility. Copolymers of various compositions were prepared and the experimental results are summarized in Tables 16 and 17.

Experimental observations indicate that approximately 70 mole % of acrylic acid is necessary to impart water solubility whereas only approximately 40 mole % of sodium styrenesulfonate is necessary to achieve the same goal. As sodium styrenesulfonate is expected to be much more fully ionized in solution as compared to the weak acrylic acid moieties, these observations are consistent with

expectations.

E. Hydrolysis Studies

The mechanism and kinetics of sulfonic acid ester hydrolysis was reviewed in Chapter I. In the absence of bases, the hydrolysis of alkyl sulfonates obeys the following first order rate law:

$$\frac{d[x]}{dt} = k_1([x]_0 - [x]) \quad (23)$$

where $[x]_0 - [x]$ is the concentration of the ester at time t and k_1 is the first order rate constant. Solving for $k_1 t$ one obtains:

$$k_1 t = \ln(100/100-p) \quad (24)$$

where p is defined as the extent of reaction or percent hydrolysis. Thus, k_1 can be experimentally determined, according to Equation 24, by measuring the extent of reaction, p , at various times, t . Construction of a plot of t versus $\ln(100/100-p)$ yields a straight line from which k_1 is obtained as the slope.

In the presence of bases the hydrolysis of alkyl

sulfonates obeys the following kinetic equation:

$$\frac{d[x]}{dt} = k_1([x]_0 - [x]) + k_2([x]_0 - [x])([OH]_0 - [x]) \quad (25)$$

where $[OH]_0 - [x]$ is the concentration of base at time t and k_2 is the second order rate constant. In the presence of a large excess of base the first term (i.e. neutral hydrolysis) can be neglected and Equation 25 reduces to

$$k_2 t = \frac{1}{[OH]_0 - [x]_0} \ln \left(\frac{100[OH]_0 - p[x]_0}{[OH]_0(100 - p)} \right) \quad (26)$$

where $[OH]_0$ and $[x]_0$ are the initial concentrations of base and ester respectively. Thus, k_2 can be experimentally determined, according to Equation 26, by measuring the extent of reaction, p , at various times, t . Plotting the right-hand side of Equation 26 versus t , one obtains a straight line of slope k_2 .

Determination of the rate constants, either k_1 or k_2 , at various temperatures allows for determination of activation energies (E) and frequency factors (A) for hydrolysis according to the Arrhenius equation

$$k = Ae^{-E/RT} \quad (27)$$

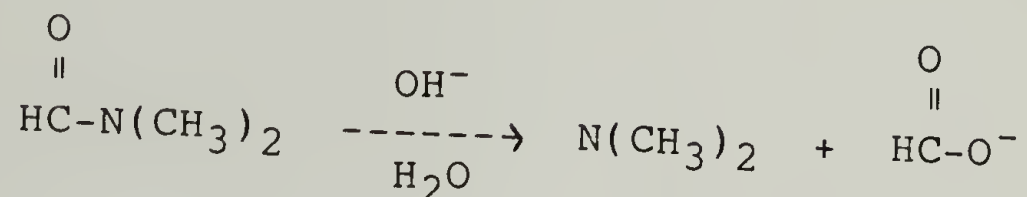
where R is the universal gas constant (1.9872 cal./deg. mol.). Experimentally, the activation energy and frequency factor are determined according to Equation 28 by plotting $\ln k$ vs $1/T$. The slope of the

$$\ln k = \ln A - E/RT \quad (28)$$

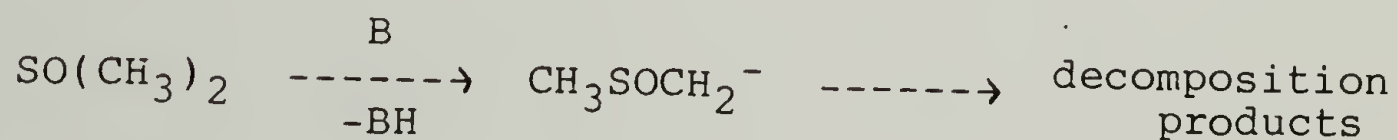
line yields E while $\ln A$ is obtained as the y intercept.

Hydrolysis studies of low molecular weight aromatic sulfonic acid esters (methyl, ethyl, n-propyl, and isopropyl toluenesulfonates) were undertaken for comparison with polymer hydrolysis studies. Results for the hydrolysis of alkyl toluenesulfonates as well as the analogous styrene-sulfonic acid ester-containing homopolymers and copolymers are discussed below. The majority of hydrolysis studies were performed in 90/10 (v/v) dimethyl sulfoxide/water solutions. This solvent system was chosen as it is a solvent for both the ester-containing and hydrolyzed (sulfonic acid-containing) forms of the polymer, thus providing a homogeneous system throughout the hydrolysis reaction. Dimethyl sulfoxide was chosen as a co-solvent in that it provides a convenient solvent for the unreacted homopolymer and is inherently more stable in the presence of

base than dimethylformamide which reacts readily in aqueous solution (111). However, in the course of this work, it has



been found that aqueous solutions containing dimethyl sulfoxide, although much more stable than dimethylformamide, slowly decompose in the presence of base. Although very little has been reported in the literature concerning this reaction, the base catalyzed decomposition most probably centers around the formation and known instability of the dimsyl ion in solution (112).



As a result of the instability of alkaline, aqueous dimethyl sulfoxide solutions, investigation of the hydrolysis behavior of the various homopolymers was limited to neutral hydrolysis studies in aqueous dimethyl sulfoxide. However, preparation of water-soluble copolymers, specifically alkyl styrenesulfonate-sodium styrenesulfonate copolymers, allowed for investigation of acidic and basic hydrolysis in

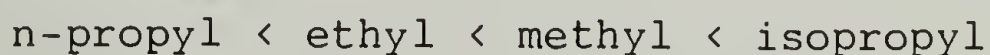
100% H₂O without complications introduced by the presence of dimethyl sulfoxide.

1. Neutral Hydrolysis of Alkyl Toluenesulfonates.

Experimental results for the neutral hydrolysis of methyl toluenesulfonate (MTS), ethyl toluenesulfonate (ETS), n-propyl toluenesulfonate (NPTS), and isopropyl toluenesulfonate (IPTS) in 90/10 (v/v) DMSO/H₂O are presented in Figures 11-14. For comparison purposes, hydrolysis curves for the various esters at 70°C are shown together in Figure 36.

Plots of t versus $\ln(100/100-p)$, according to Equation 24, are presented in Figures 37-40. First order rate constants (k_1) obtained from these plots are summarized in Table 28. Arrhenius plots of the data from Table 28, according to Equation 28, are presented in Figures 41-44. Values of E and $\log A$, obtained from these plots, are summarized in Table 28.

The experimental results for the neutral hydrolysis of methyl, ethyl, n-propyl, and isopropyl toluenesulfonates (see Figure 36 and Table 28) show that the reaction velocity for hydrolysis increases in the order:



Since alkyl groups are electron-repelling groups, the

Figure 36. Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Alkyl Toluenesulfonates at 70°C in 90/10 (v/v) DMSO/H₂O

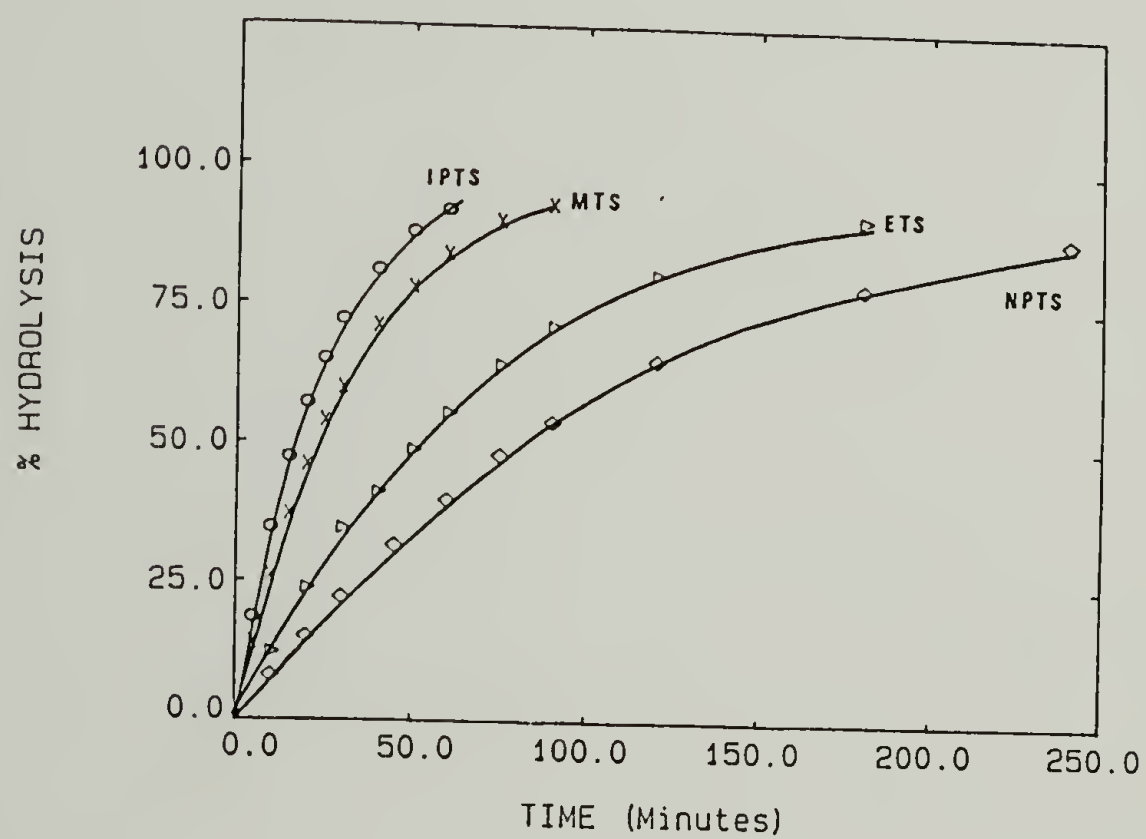


Figure 37. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

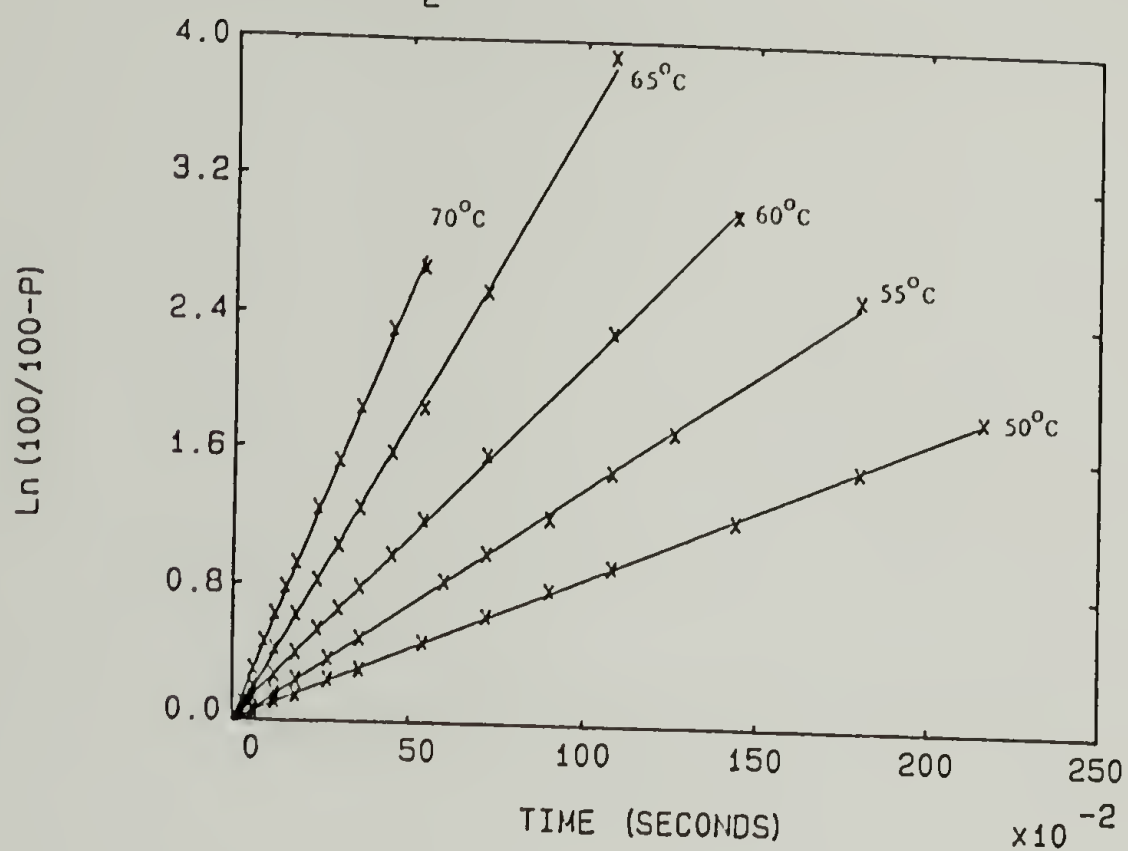


Figure 38. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Ethyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

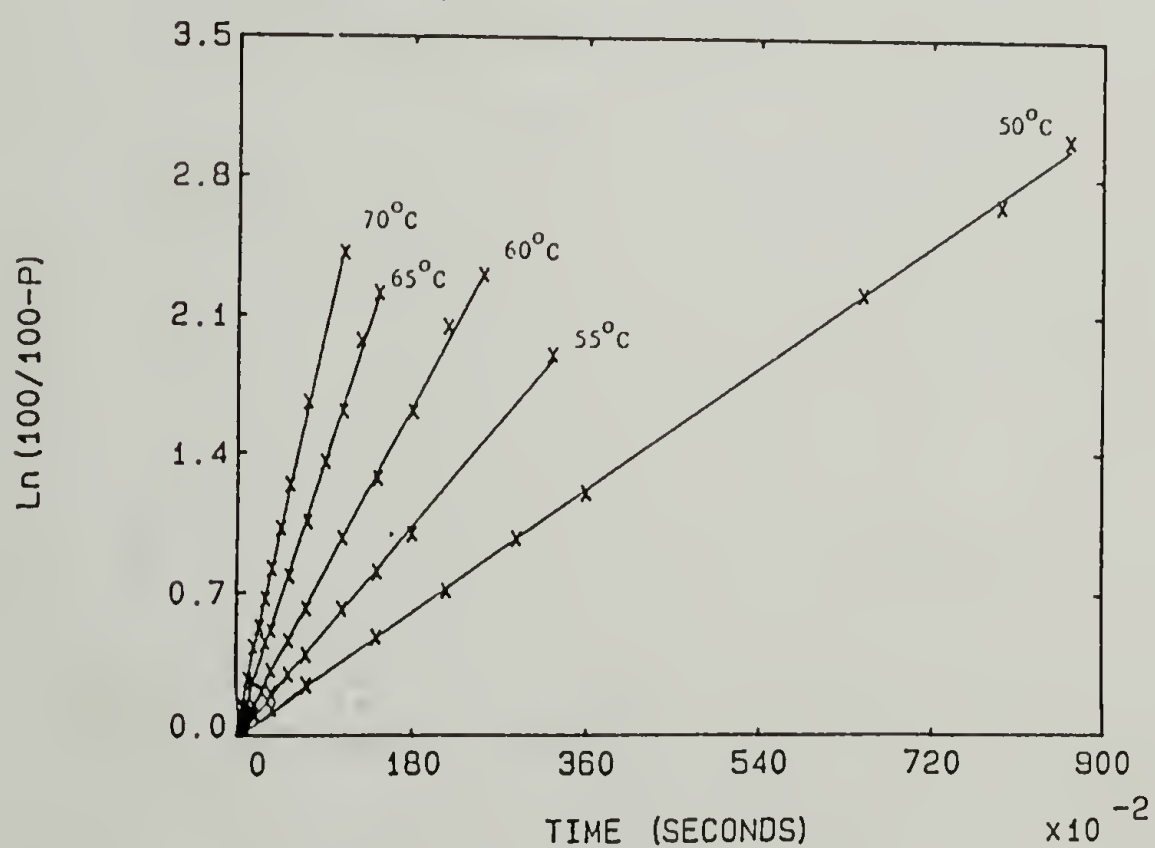


Figure 39. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of n-Propyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

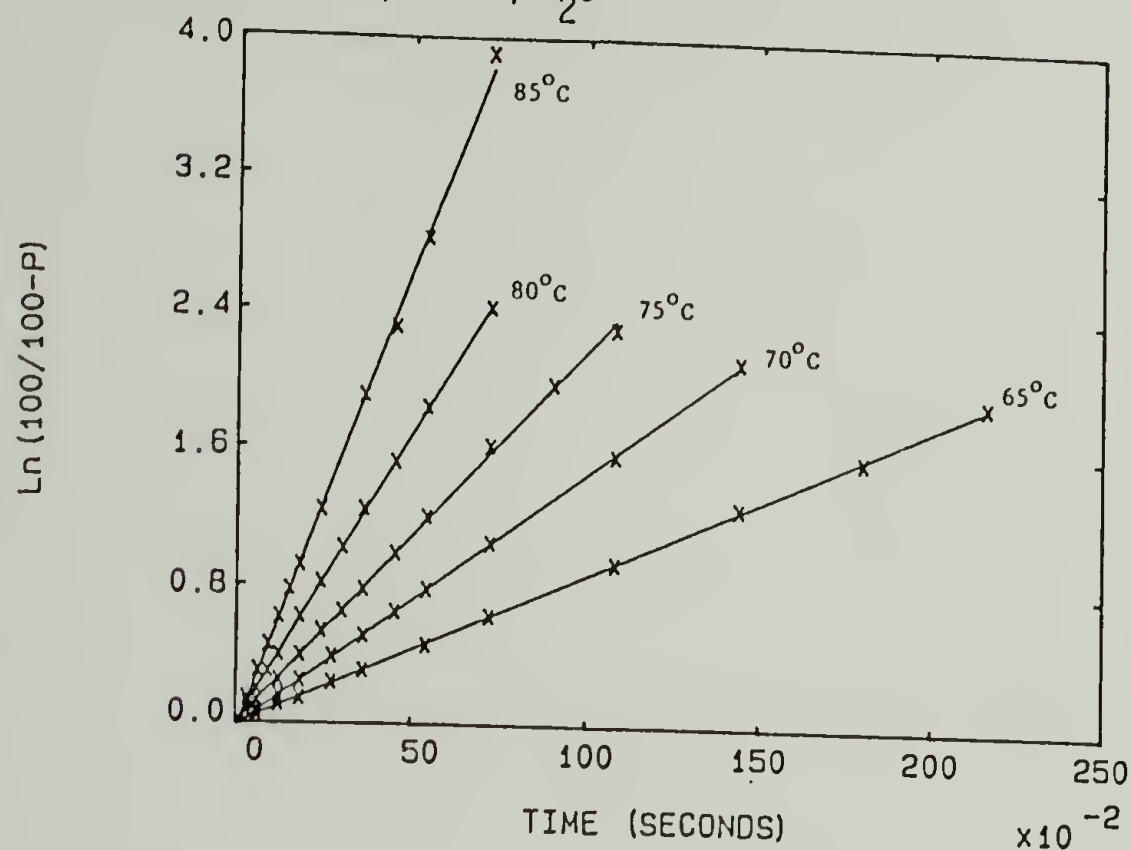


Figure 40. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Isopropyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

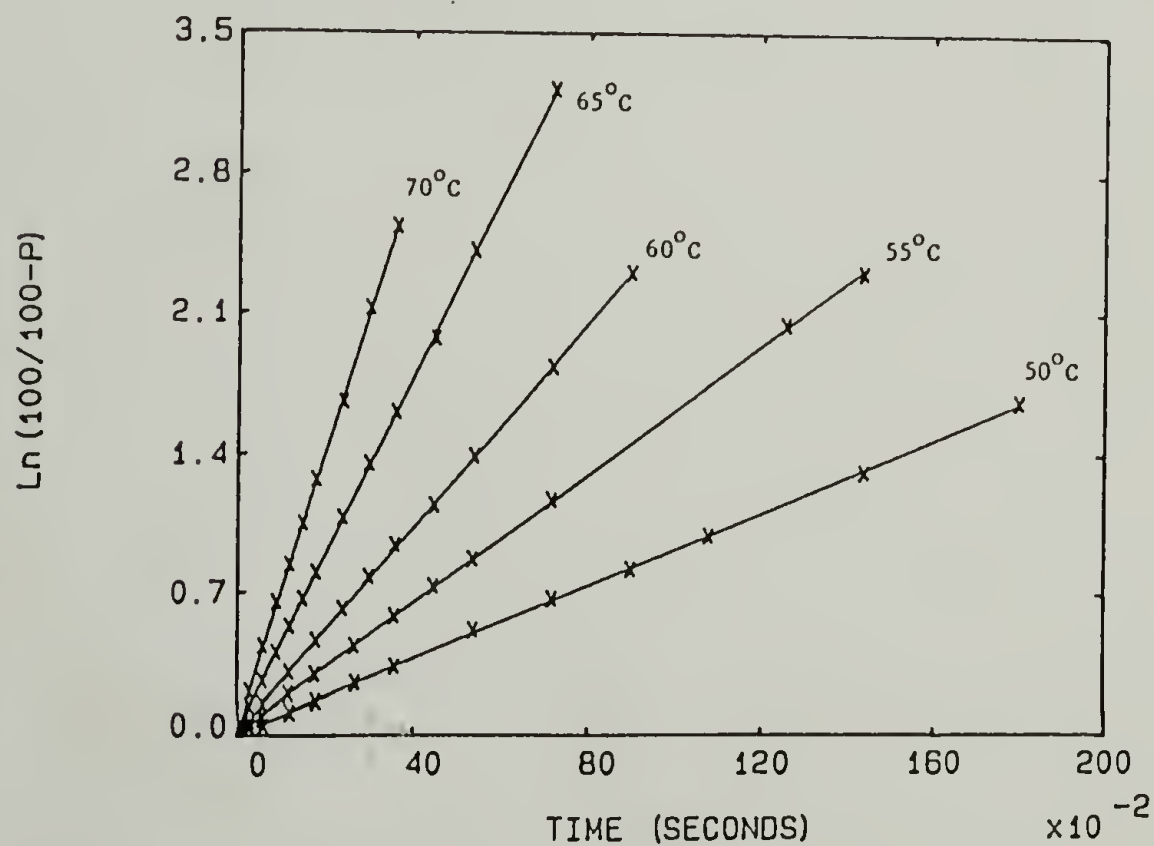


Figure 41. Arrhenius Plot for the Neutral Hydrolysis of Methyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

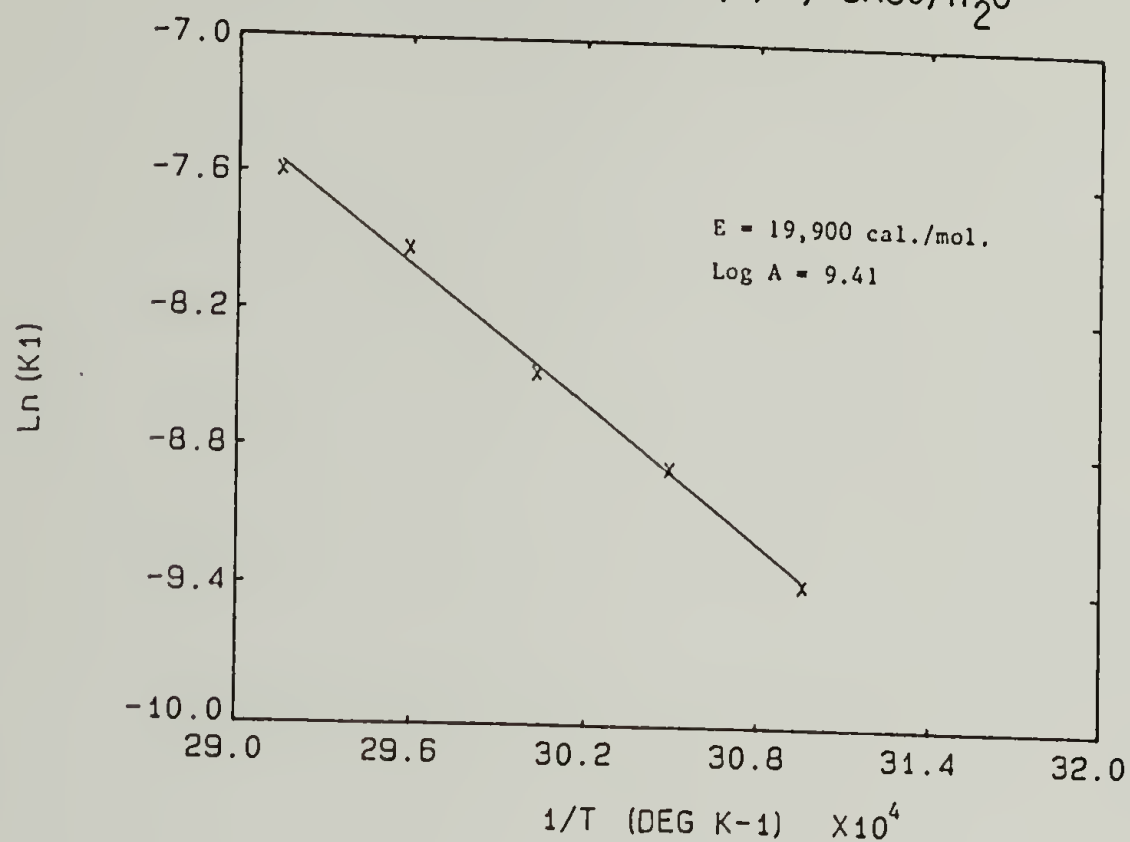


Figure 42. Arrhenius Plot for the Neutral Hydrolysis of Ethyl Toluenesulfonate in 90/10 (V/v) DMSO/H₂O

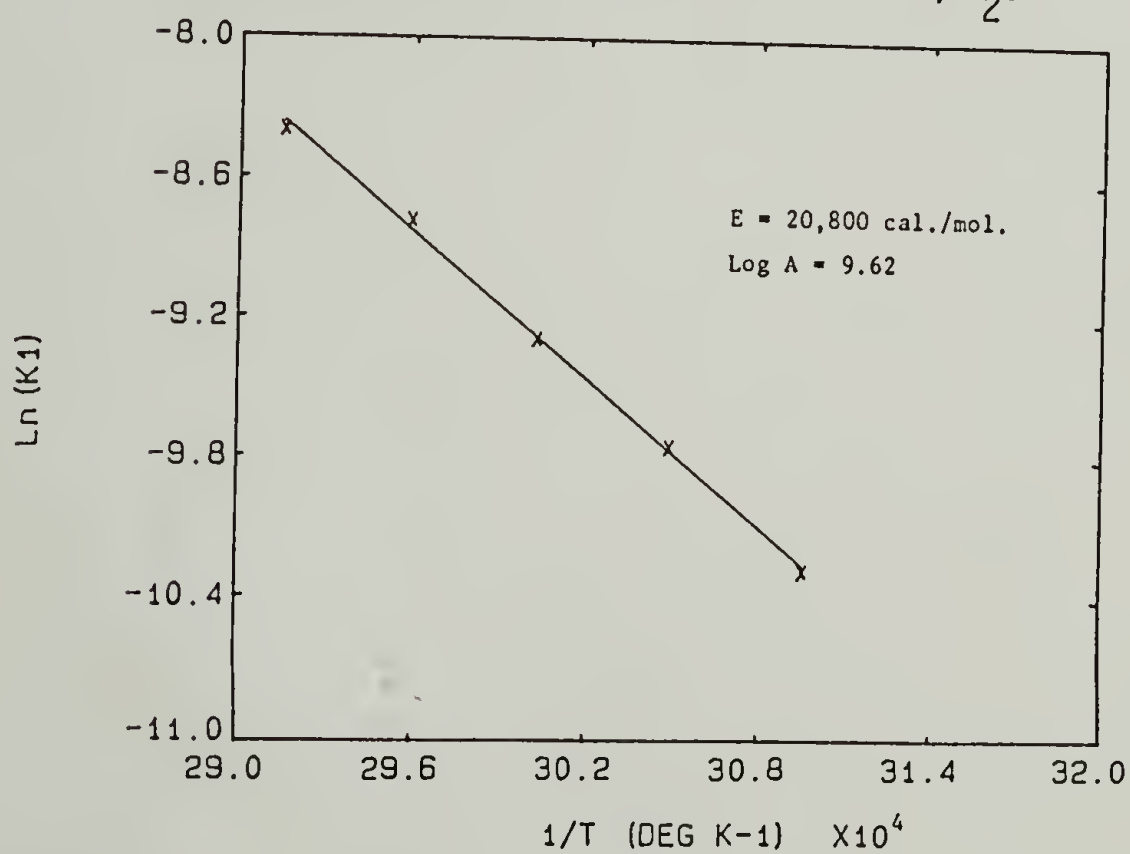


Figure 43. Arrhenius Plot for the Neutral Hydrolysis of n-Propyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O

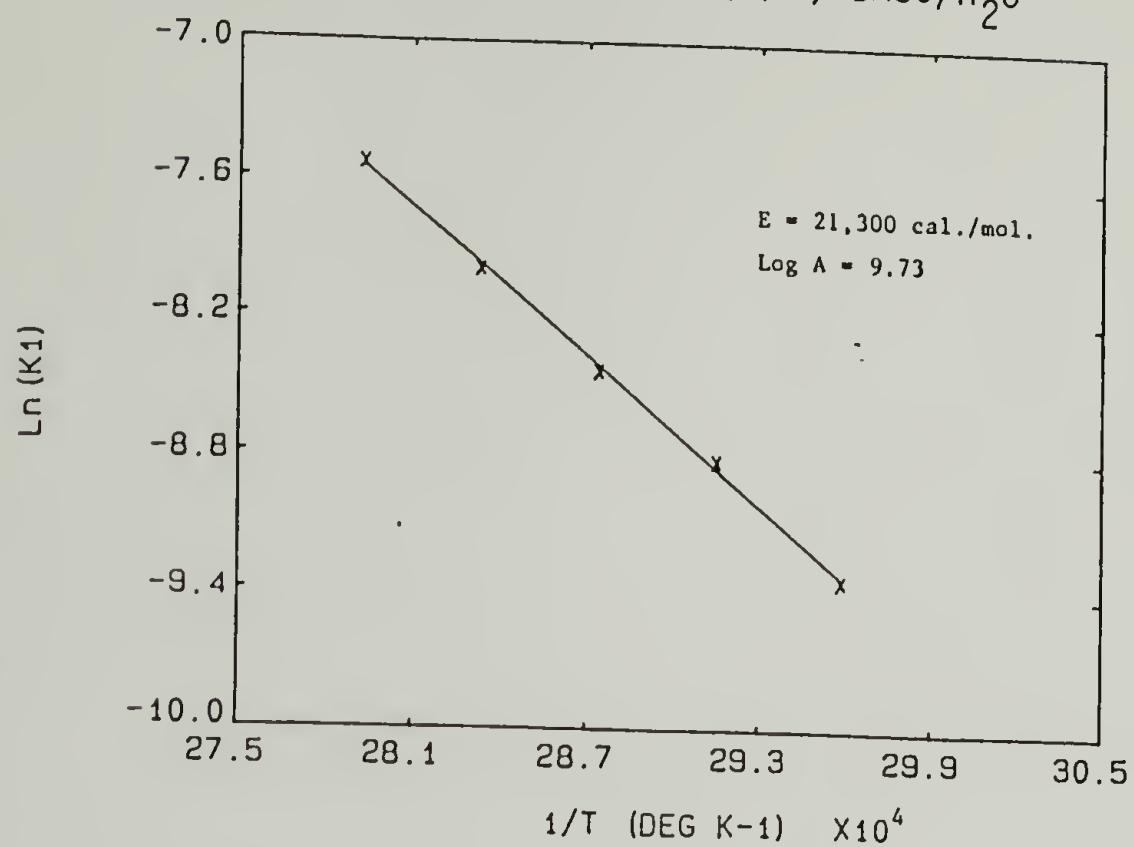
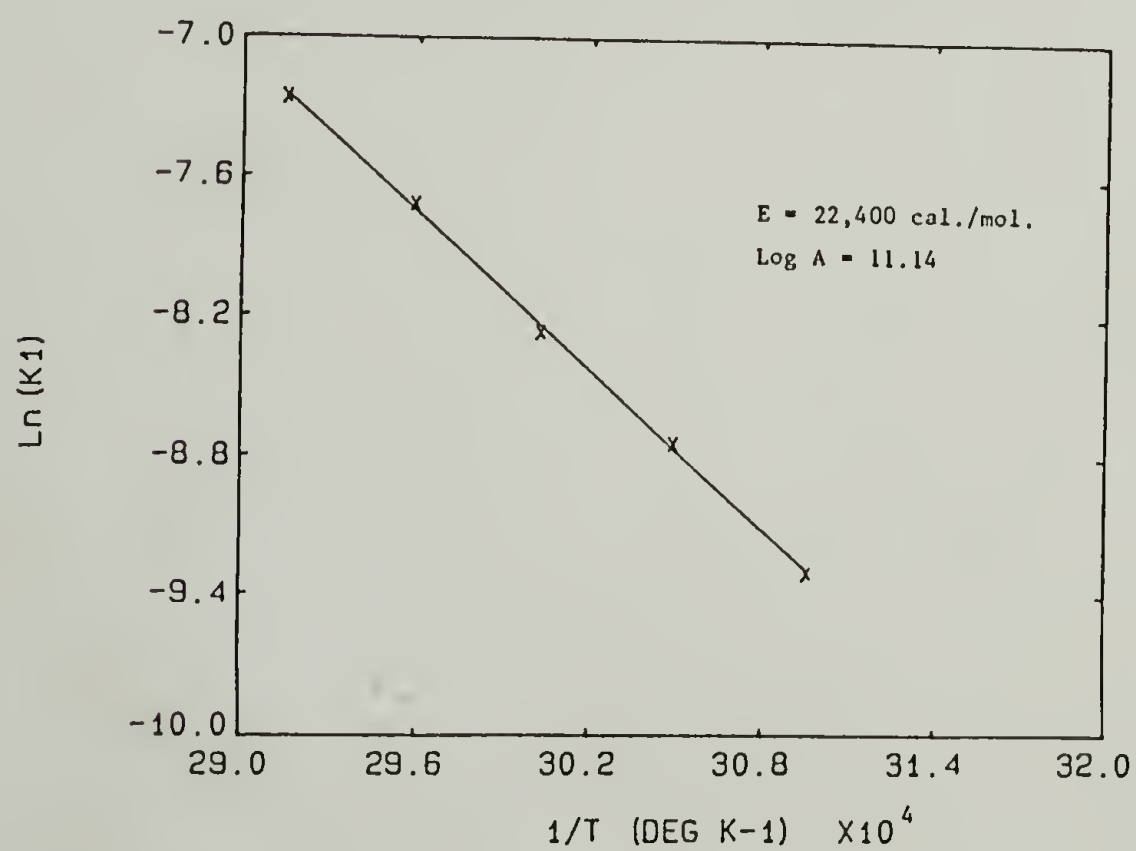


Figure 44. Arrhenius Plot for the Neutral Hydrolysis of Iso-propyl Toluenesulfonate in 90/10 (v/v) DMSO/H₂O



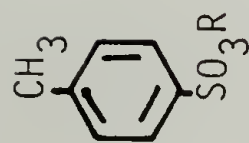


Table 28. Values of k_1 , E , and $\text{Log } A$ for the Neutral Hydrolysis of Alkyl Tofuenesulfonates in 90/10 DMSO/ H_2O

R	$10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$							E (cal./mol.)	Log A
	50°	55°	60°	65°	70°	75°	80°	85°	
Methyl	0.84	1.4	2.1	3.6	5.1				9.41
Ethyl	0.34	0.59	0.93	1.5	2.2				9.62
n-Propyl				0.88	1.5	2.2	3.4	5.4	9.73
Isopropyl	0.92	1.6	2.6	4.5	7.0				11.14

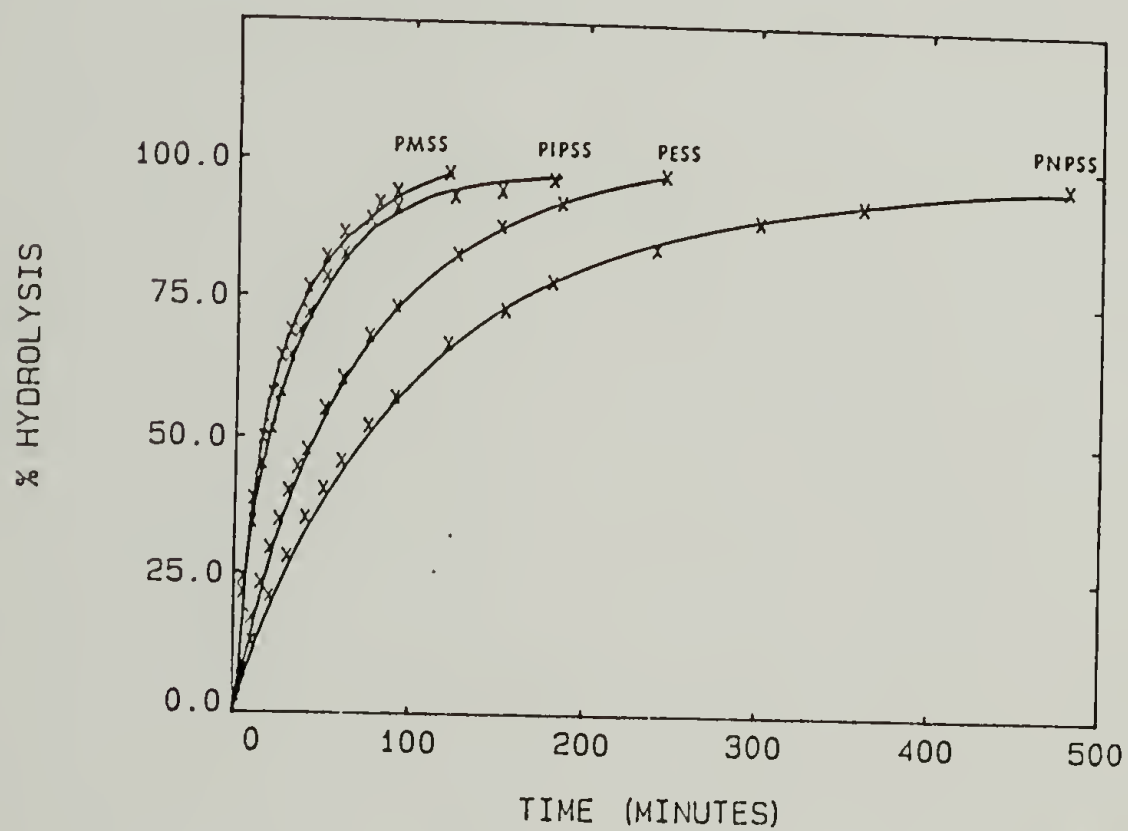
sequence of influence being methyl < ethyl < n-propyl, repulsion of a nucleophilic reagent to the carbon atom in the group $--O--CH_2--$ will be increased in this order. Thus, as discussed in Chapter I, one would anticipate the observed order of reactivity for the hydrolysis of alkyl toluenesulfonates. However, the isopropyl ester reacts much faster than one would anticipate using this ideology. As discussed in Chapter I, this is due to a change in reaction mechanism ($S_N2 \rightarrow S_N1$). S_N1 mechanisms usually exhibit greater activation energies and greater frequency factors than S_N2 mechanisms for similar molecules as substantiated by the data in Table 28. Thus, the relatively high rates observed for the hydrolysis of isopropyl toluenesulfonate arise from an increase in the frequency factor (A) caused by a change in reaction mechanism.

2. Neutral hydrolysis of poly(alkyl styrenesulfonates).

Experimental results for the neutral hydrolysis of poly(methyl styrenesulfonate) (PMSS), poly(ethyl styrenesulfonate) (PESS), poly(n-propyl styrenesulfonate) (PNPSS), and poly(isopropyl styrenesulfonate) (PIPSS) in 90/10 (v/v) DMSO/H₂O are presented in Figures 15-17. For comparison purposes, hydrolysis curves for the various esters at 70°C are shown together in Figure 45.

Comparison of the hydrolysis curves (Figure 45) shows

Figure 45. Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Poly(Alkyl Styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H₂O



the following reactivity:



Qualitatively, this is the same behavior observed for low molecular weight analogs, i.e. reactivity decreases with increasing repulsion towards a nucleophilic reagent. As with low molecular weight sulfonic acid esters the isopropyl ester reacts faster than would be expected based on its electron-donating character. Again, this is due to a change in reaction mechanism ($S_N2 \rightarrow S_N1$) as discussed previously.

While general reactivity appears to be the same for the hydrolysis of poly(alkyl styrenesulfonates) and their low molecular weight analogs, comparison of the hydrolysis curves indicates some striking differences. As seen in Figures 46 and 47, for the case of poly(methyl styrenesulfonate), it is evident that hydrolysis of the polymer begins similarly to that of methyl toluenesulfonate but as the reaction progresses the reaction involving the polymer slows down. Similar behavior is observed for the hydrolysis of homopolymers of ethyl, n-propyl, and isopropyl styrenesulfonates. Kinetic evaluation of the data, according to Equation 24, is shown in Figures 48-51. In all cases the hydrolysis reaction appears to occur in two distinct steps characterized by two rate constants. After a

Figure 46. Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate and Poly(Methyl Styrenesulfonate) at 65°C in 90/10 (v/v) DMSO/H₂O

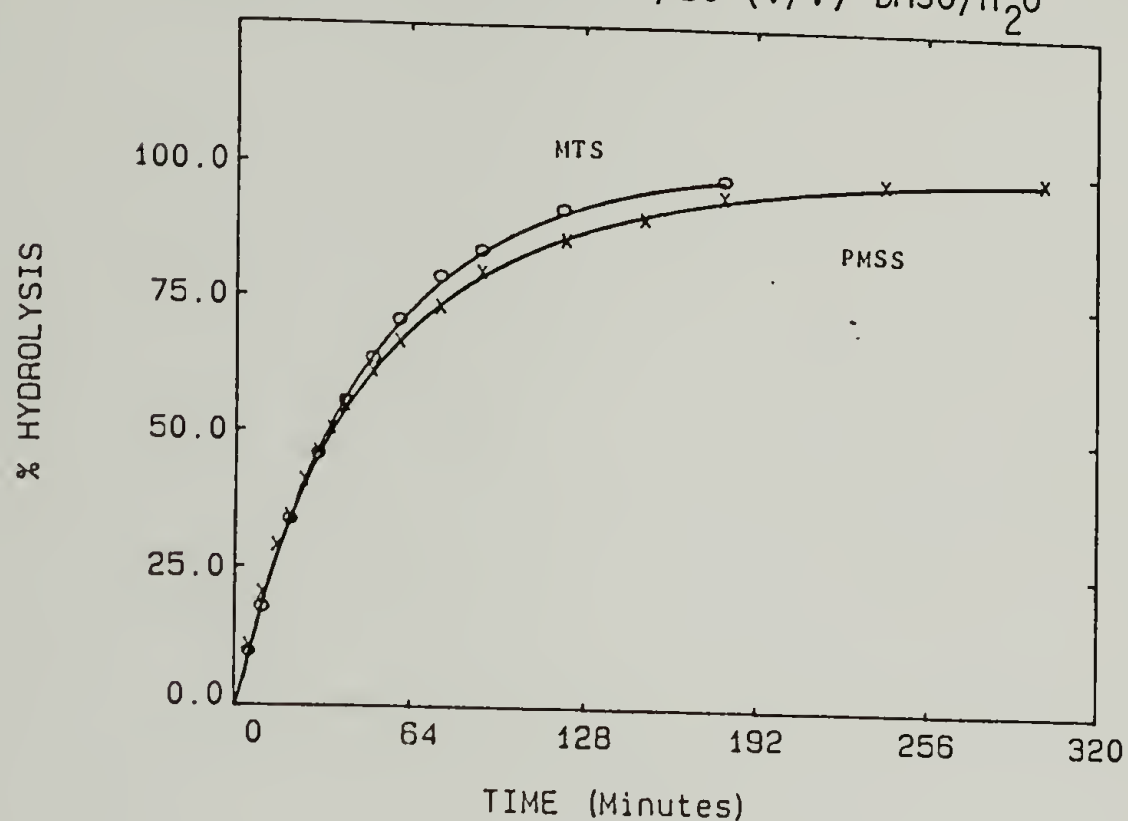


Figure 47. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate and Poly(methyl Styrenesulfonate) at 65°C in 90/10 (v/v) DMSO/H₂O

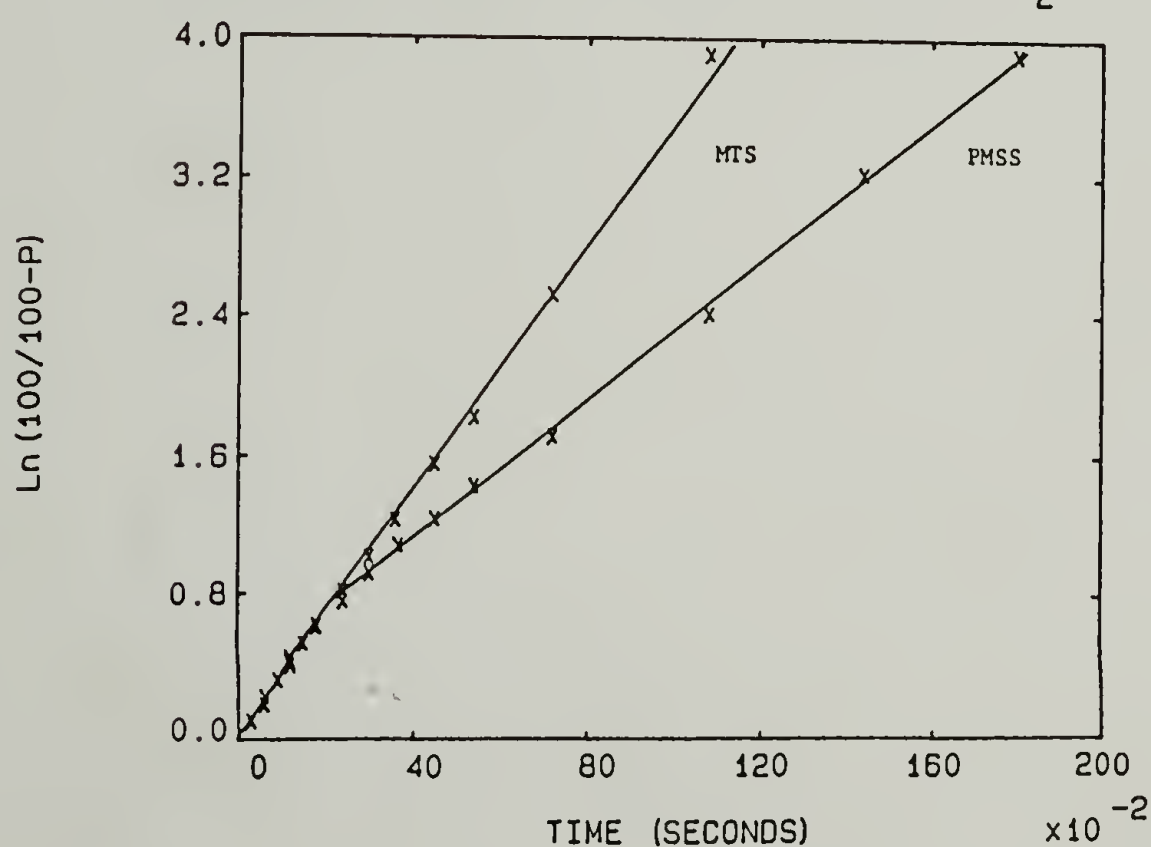


Figure 48. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O

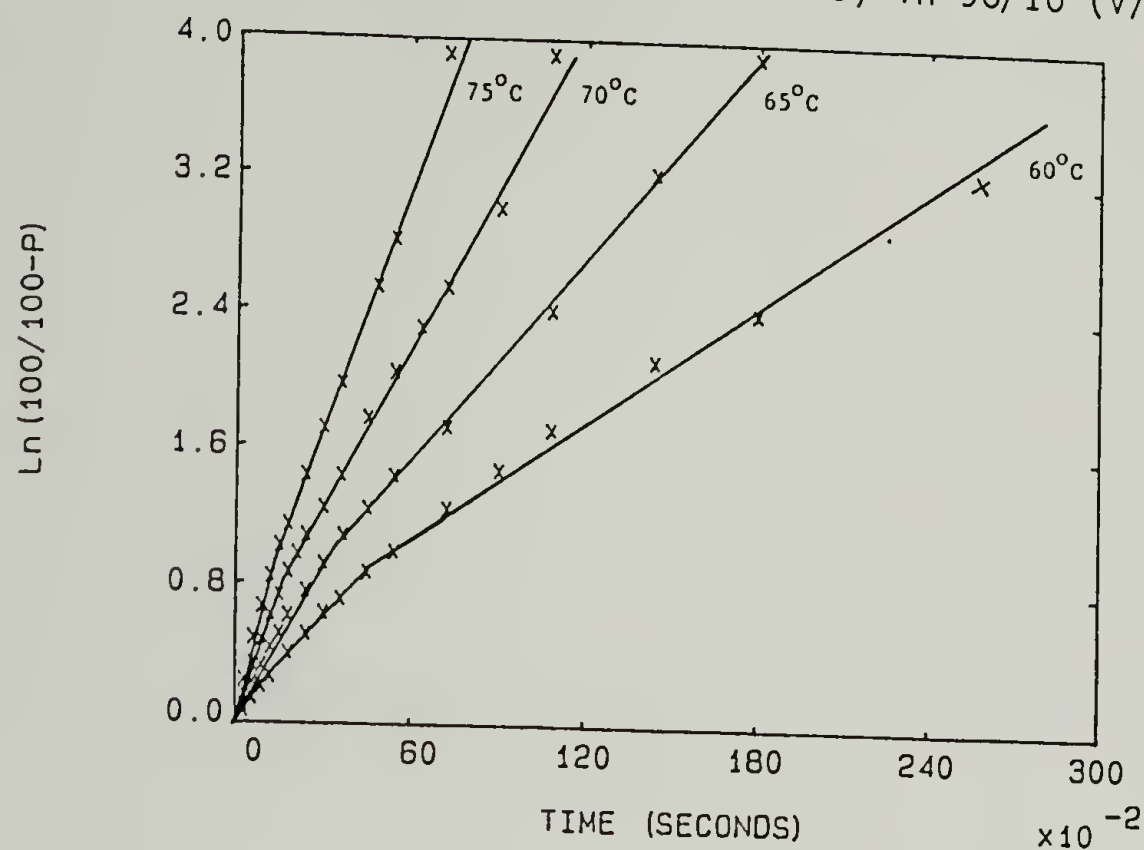


Figure 49. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Ethyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O

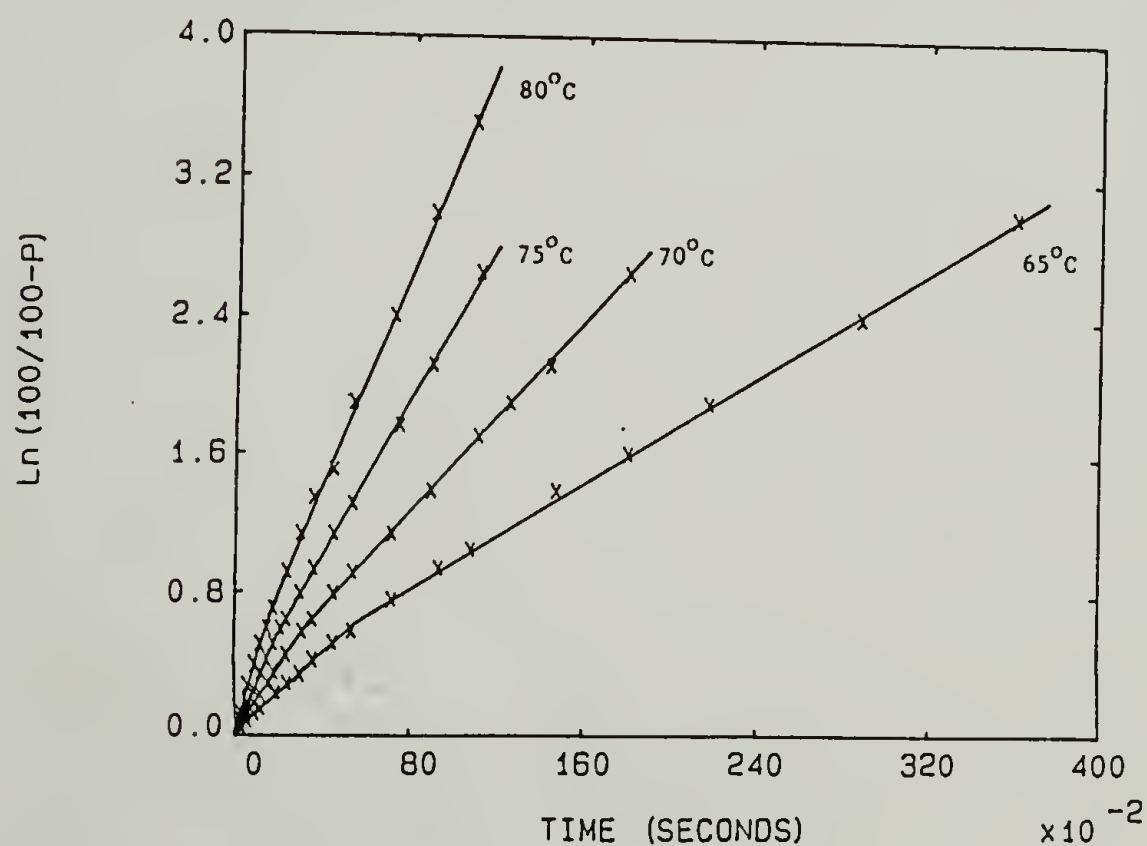


Figure 50. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(n-Propyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O

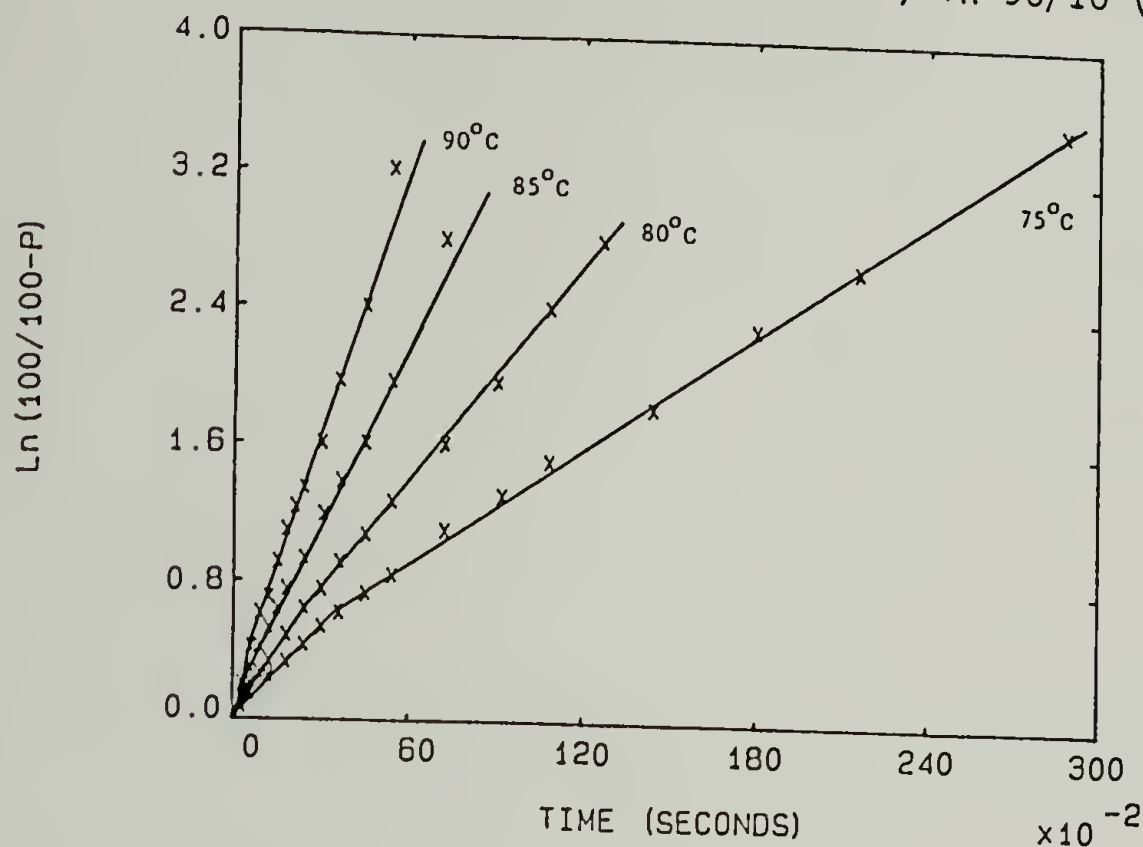
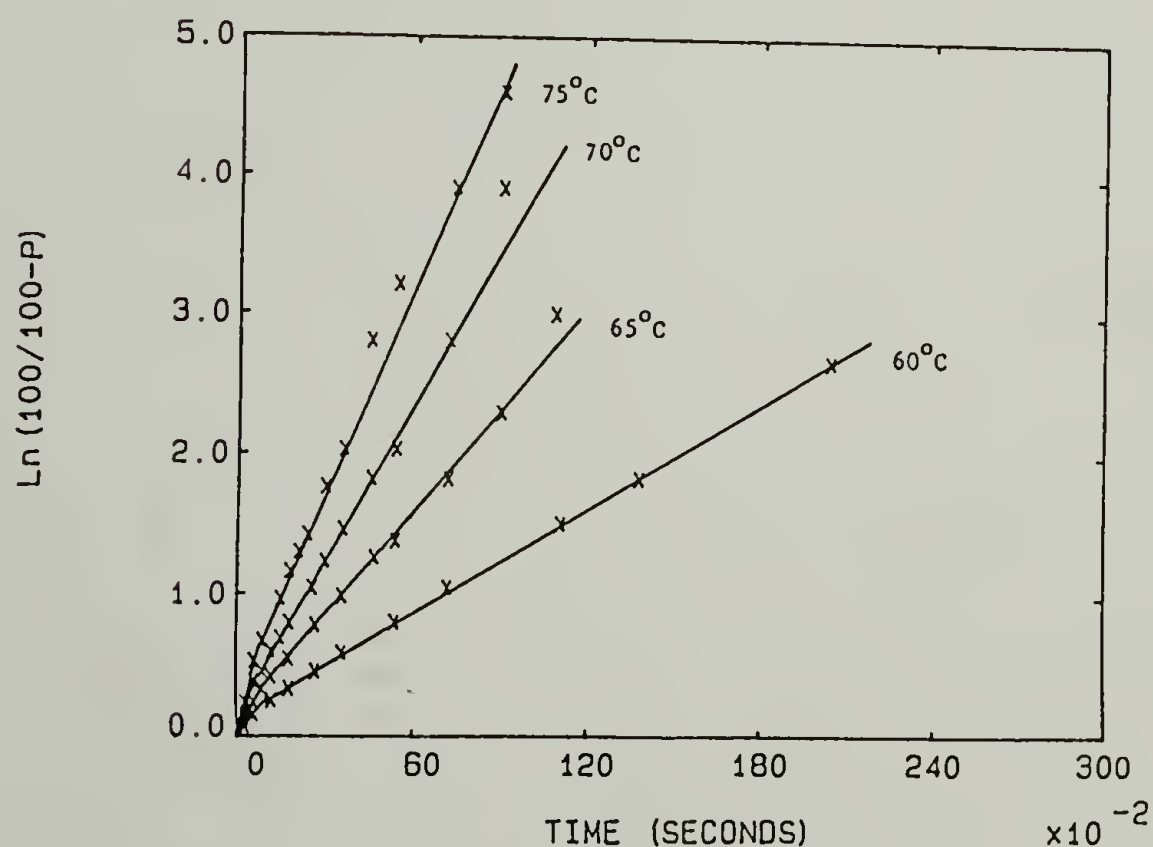
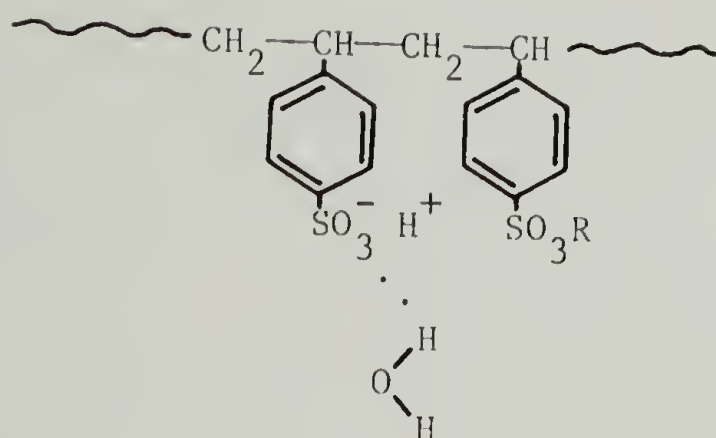


Figure 51. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Isopropyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O



first period (up to approximately 40% reaction), during which the reaction proceeds rapidly, the rate slows down somewhat abruptly. Similar behavior has been observed in the alkaline hydrolysis of poly(acrylamide) (79). The existence of two steps, which are not observed in similar reactions involving low molecular weight compounds, must be related to the polymeric nature of the substance. The slowdown in rate is not due to a secondary reaction but to an increasing charge on the polymeric chain as the reaction proceeds. In the initial stages the hydrolysis is undoubtedly a random process along a given polymer chain and the probability of reaction of near neighbors is small. This is supported by solution viscosity versus % hydrolysis studies (Figure 25) in which it was found that the maximum viscosity increase (i.e. coil expansion) was observed in the 0-40% hydrolysis range. As the reaction proceeds unhydrolyzed ester groups inevitably must have hydrolyzed neighbors; the results show that the effect of the latter is to slow down the reaction. The retardation behavior observed is undoubtedly not an inductive effect because of the large separation of the reaction centers. Instead, it is proposed that the sulfonic acid groups produced during the course of the hydrolysis reaction "tie" up surrounding water molecules, probably through hydrogen bonding as shown in Figure 52. This interaction effectively reduces the

Figure 52. Neighboring Group Effects in the Hydrolysis of Poly(alkyl styrenesulfonates).



amount of "free" water available for reaction with ester groups in the near vicinity of a sulfonic acid group. Also, the sulfonic acid-water interaction decreases the amount of water available for solvation of the transition complex in the hydrolysis of a neighboring ester moiety. Both of these factors would be expected to contribute to the decreased reaction velocities observed experimentally.

First order rate constants, calculated according to Equation 24, characterizing the first (0-40% hydrolysis) and second (60-100% hydrolysis) steps in the neutral hydrolysis of poly(methyl styrenesulfonate), poly(ethyl styrenesulfonate), poly(n-propyl styrenesulfonate), and poly(isopropyl styrenesulfonate) in 90/10 DMSO/H₂O are summarized in Table 29. Activation energies and frequency factors, determined as in Figures 53-56, are included in Table 29. As can be seen, values of k_1 , E , and $\text{Log } A$ characterizing the first step of the hydrolysis reaction are consistent with those given in Table 28 for the low molecular weight analogs. The second step of the hydrolysis reaction, in each case, is characterized by a rate which is approximately 50% slower than the first step. Consequently, activation energies corresponding to the second step of the hydrolysis reaction are correspondingly higher (Table 29).

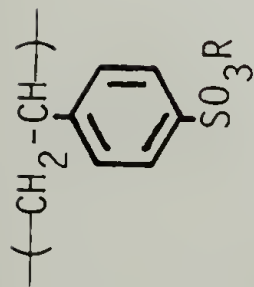


Table 29. Values of k_1 , E , and $\text{Log } A$ for the Neutral Hydrolysis of Poly(alkyl styrenesulfonates) in 90/10 (v/v) DMSO/ H_2O

R	$10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$							E (cal./mol.)	Log A
	60°	65°	70°	75°	80°	85°	90°		
Methyl	2.1	3.6	5.1	8.0				20,400	9.73
	1.1	2.0	3.1	5.0				22,900	11.09
Ethyl		1.3	2.2	2.8	5.3			20,900	9.63
		0.76	1.4	2.3	3.1			22,100	10.23
n-Propyl				1.9	3.3	5.0	6.8	21,600	9.84
				1.1	2.2	3.3	5.1	24,900	11.69
Isopropyl	2.7	4.3	7.3	9.7				22,800	11.39
	1.3	2.7	4.2	5.0				26,400	13.47

Figure 53. Arrhenius Plot for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O

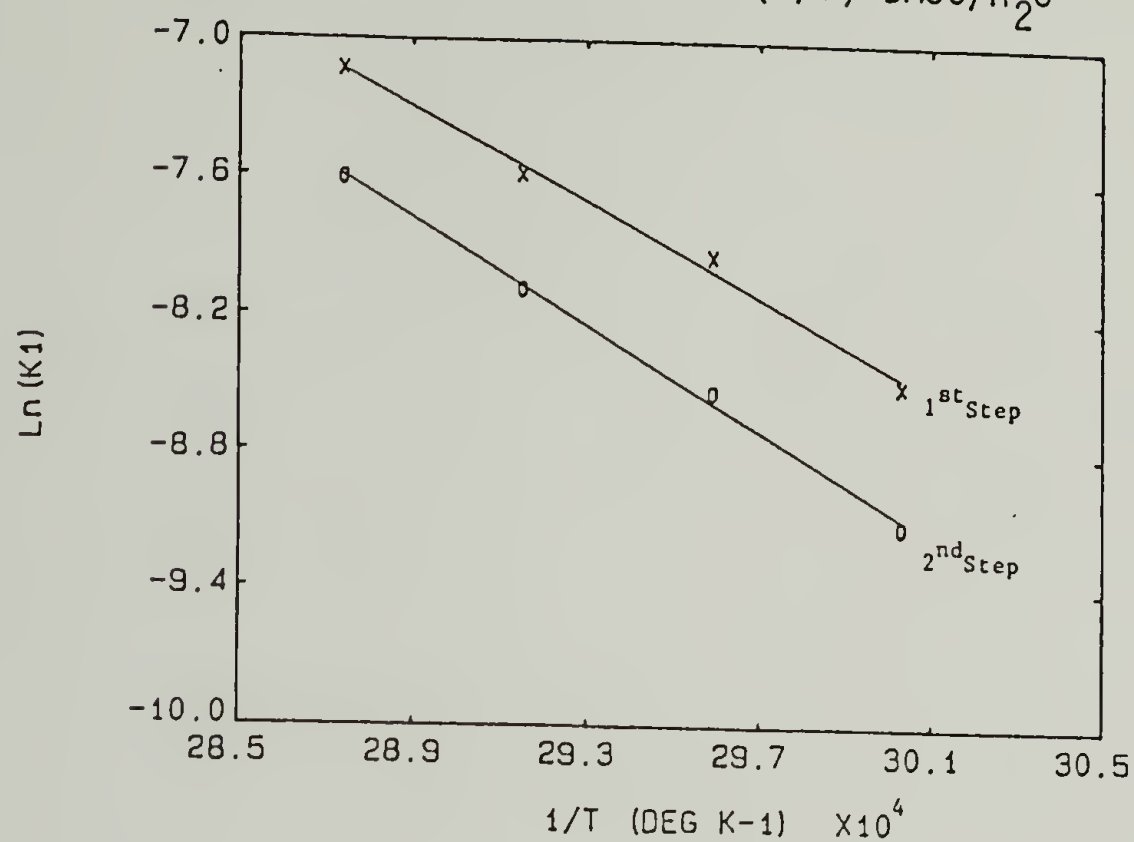


Figure 54. Arrhenius Plot for the Neutral Hydrolysis of Poly(Ethyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O

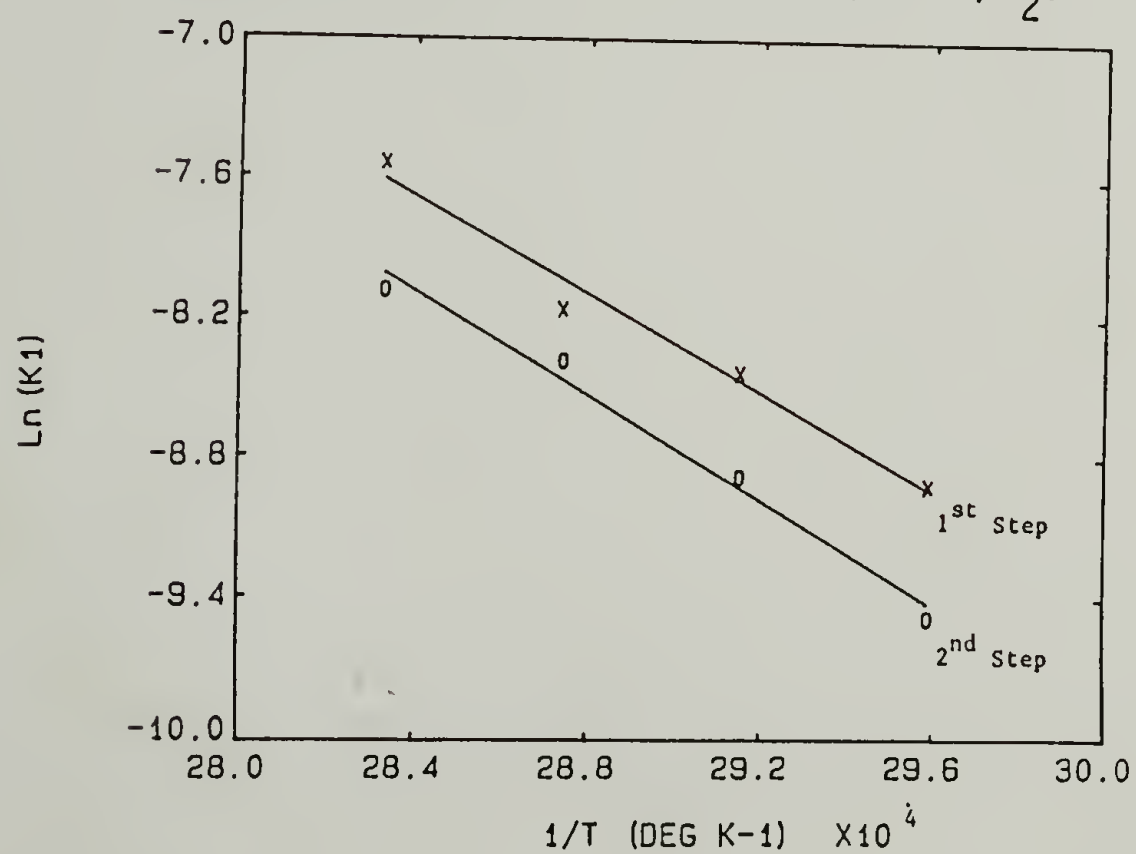


Figure 55. Arrhenius Plot for the Neutral Hydrolysis of Poly-(n-Propyl Strenesulfonate) in 90/10 (v/v) DMSO/H₂O

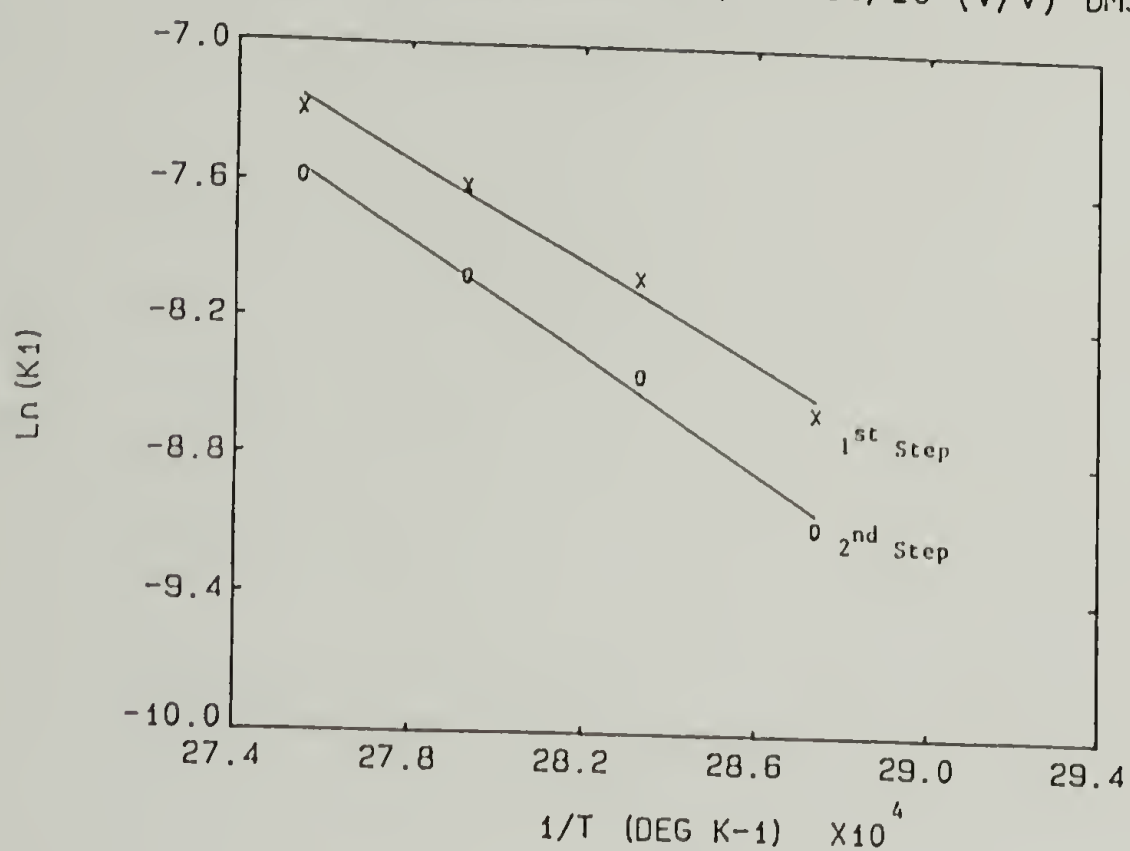
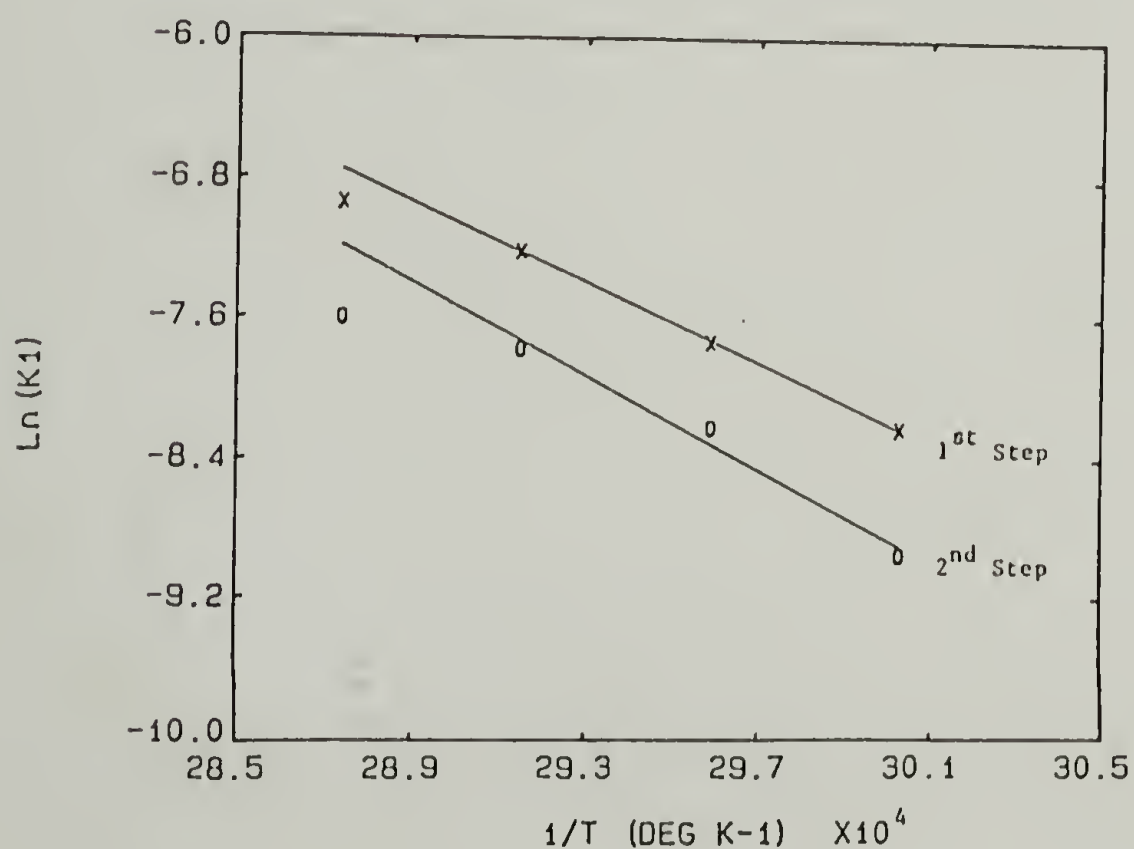


Figure 56. Arrhenius Plot for the Neutral Hydrolysis of Poly-(Isopronyl Styrenesulfonate) in 90/10 (v/v) DMSO/H₂O



3. Neutral hydrolysis of poly(alkyl styrenesulfonate) copolymers.

a. Poly(methyl styrenesulfonate-co-styrene).

Experimental results for the neutral hydrolysis of poly(methyl styrenesulfonate-co-styrene) (50/50 mole % copolymer) in 90/10 (v/v) DMSO/H₂O are presented in Figure 19. For comparison purposes, curves for the hydrolysis of poly(methyl styrenesulfonate-co-styrene), poly(methyl styrenesulfonate) and methyl toluenesulfonate at 65°C are shown together in Figure 57.

Plots of t versus $\ln(100/100-p)$, according to Equation 24, are presented in Figure 58. First order rate constants (k_1) obtained from these plots are summarized in Table 30 along with the corresponding activation energies and frequency factors determined according to Equation 28 (see Figure 59).

As seen in Figure 58 the hydrolysis of poly(methyl styrenesulfonate-co-styrene) is characterized by two individual steps as was observed in the homopolymers discussed previously. Furthermore, comparison of the data in Tables 29 and 30 indicate that the kinetic parameters (k , E , and A) characterizing the two steps in the hydrolysis reaction for poly(methyl styrenesulfonate-co-styrene) are similar to those obtained for poly(methyl styrenesulfonate).

Figure 57. Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Methyl Toluenesulfonate, Poly(Methyl Styrenesulfonate), and Poly(Methyl Styrenesulfonate-co-Styrene) at 70°C in 90/10 (v/v) DMSO/H₂O

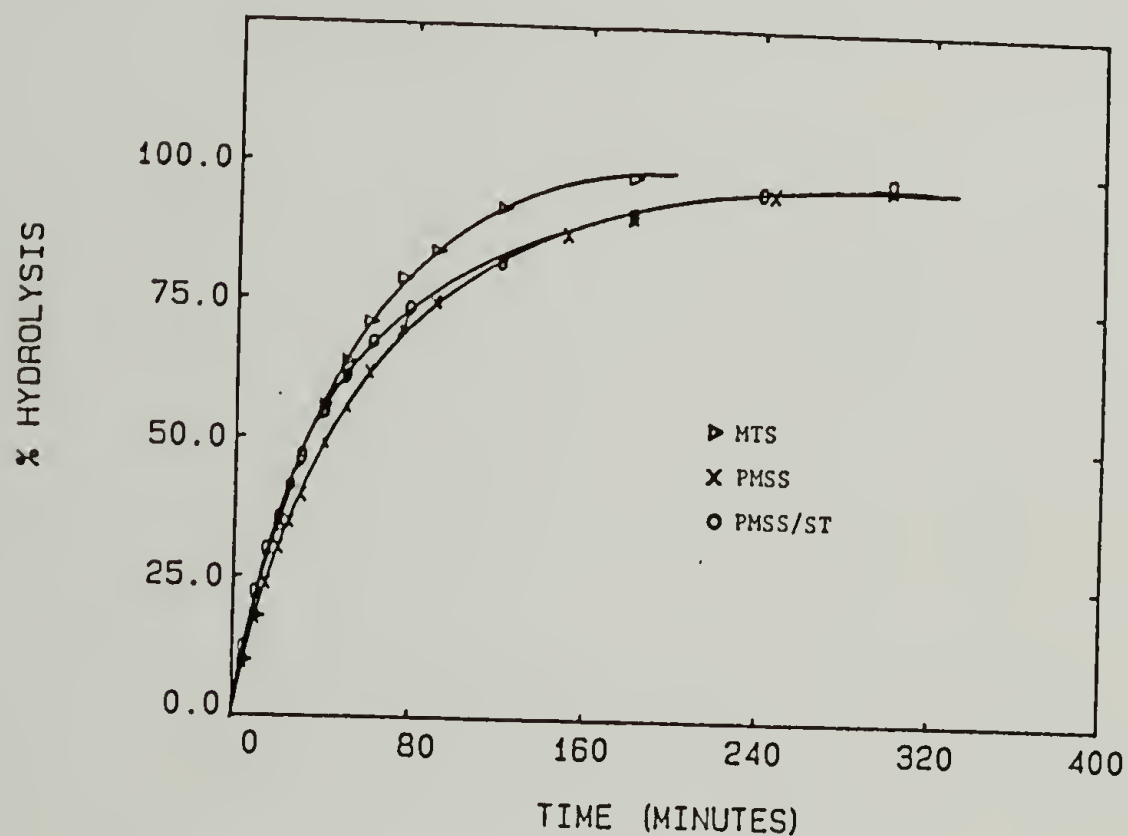


Figure 58. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Styrene) in 90/10 (v/v) DMSO/H₂O

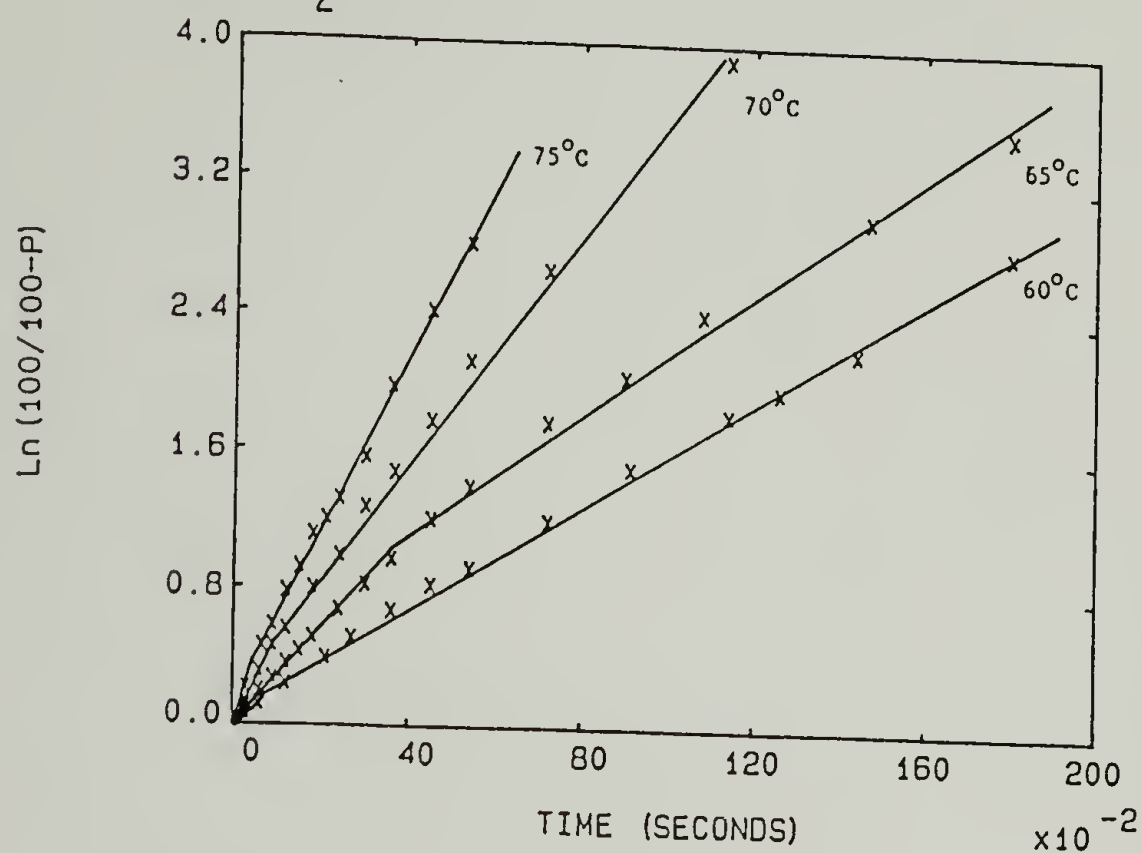
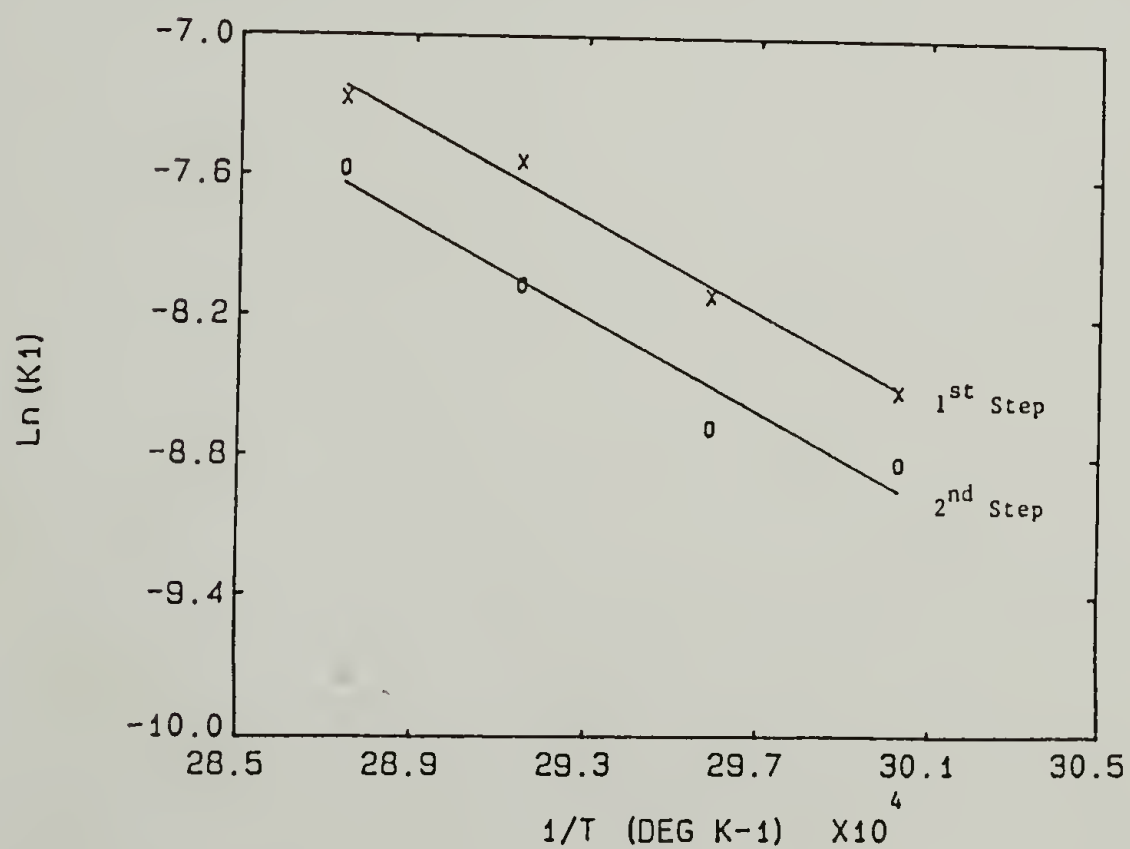


Figure 59. Arrhenius Plot for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Styrene) in 90/10 (v/v) DMSO/H₂O



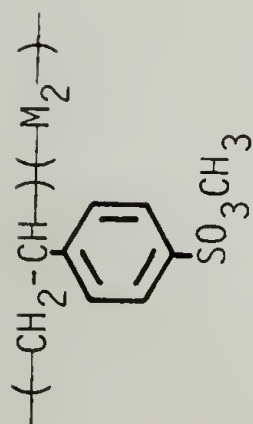


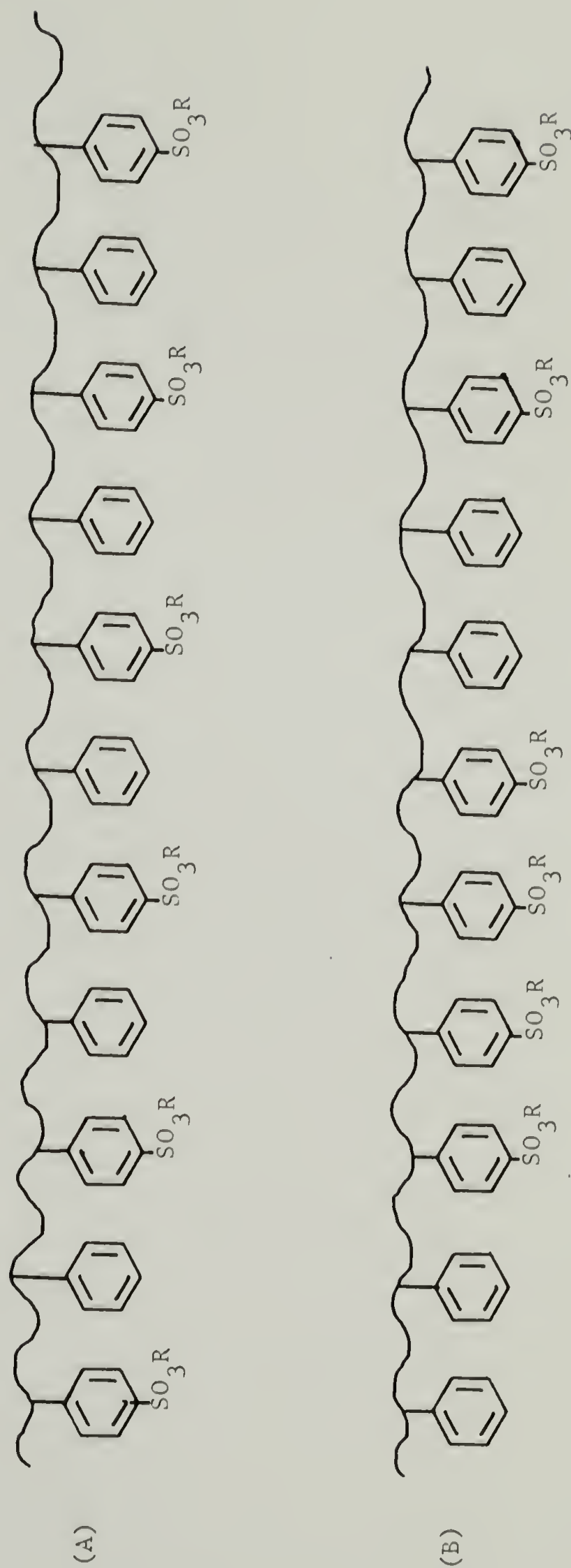
Table 30. Values of k_1 , E , and $\text{Log } A$ for the Neutral Hydrolysis of Methyl Styrenesulfonate Copolymers

Copolymer *	Solvent	$10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$					E (cal./mol.)	Log A
		55°	60°	65°	70°	75°		
Poly(MSS-co-Styrene)	90/10 (v/v) DMSO/H ₂ O							
1st step.....	"		2.0	3.0	5.3	6.9	19,900	9.39
2nd step.....	"		1.5	1.7	3.1	5.0	24,200	11.93
Poly(MSS-co-NaSS) ...	100% H ₂ O	1.4	2.2	4.0	5.5		20,900	10.05

* MSS = Methyl styrenesulfonate
NaSS = Sodium styrenesulfonate

However, consideration of the data in Figure 57 indicates that the onset of observed retardation behavior occurs at later stages in the hydrolysis reaction in the case of the copolymer (approximately 60% hydrolysis). In other words, although two stages are observed in both the hydrolysis of poly(methyl styrenesulfonate) and poly(methyl styrenesulfonate-co-styrene), in the case of the copolymer the first step, characterized by kinetic parameters similar to low molecular weight analogs, extends to later stages in the hydrolysis reaction than observed for the homopolymer. The reason for the observed behavior can be understood by considering the structure of the copolymer. In the copolymer the styrene units are expected to exert a diluting effect in separating the ester functionalities. Since, in the copolymer, many of ester moieties are expected to be neighbored by unsubstituted phenyl groups, one would anticipate an observed suppression of neighboring group effects. In fact, if the copolymer was exactly alternating (see Figure 60) neighboring group effects would be expected to be non-existent. However, reactivity ratios for copolymerization of methyl styrenesulfonate ($r_1 = 1.48$) and styrene ($r_2 = 0.32$) indicate that the copolymer is probably somewhat blocky in nature. Even so, a number of isolated ester groups undoubtedly exist within the copolymer (see Figure 60). The existence of these blocky and isolated ester functionalities within the copolymer would account

Figure 60. Alkyl Styrenesulfonate-Styrene Copolymers: (A) Alternating Copolymer;
(B) Blocky Copolymer.

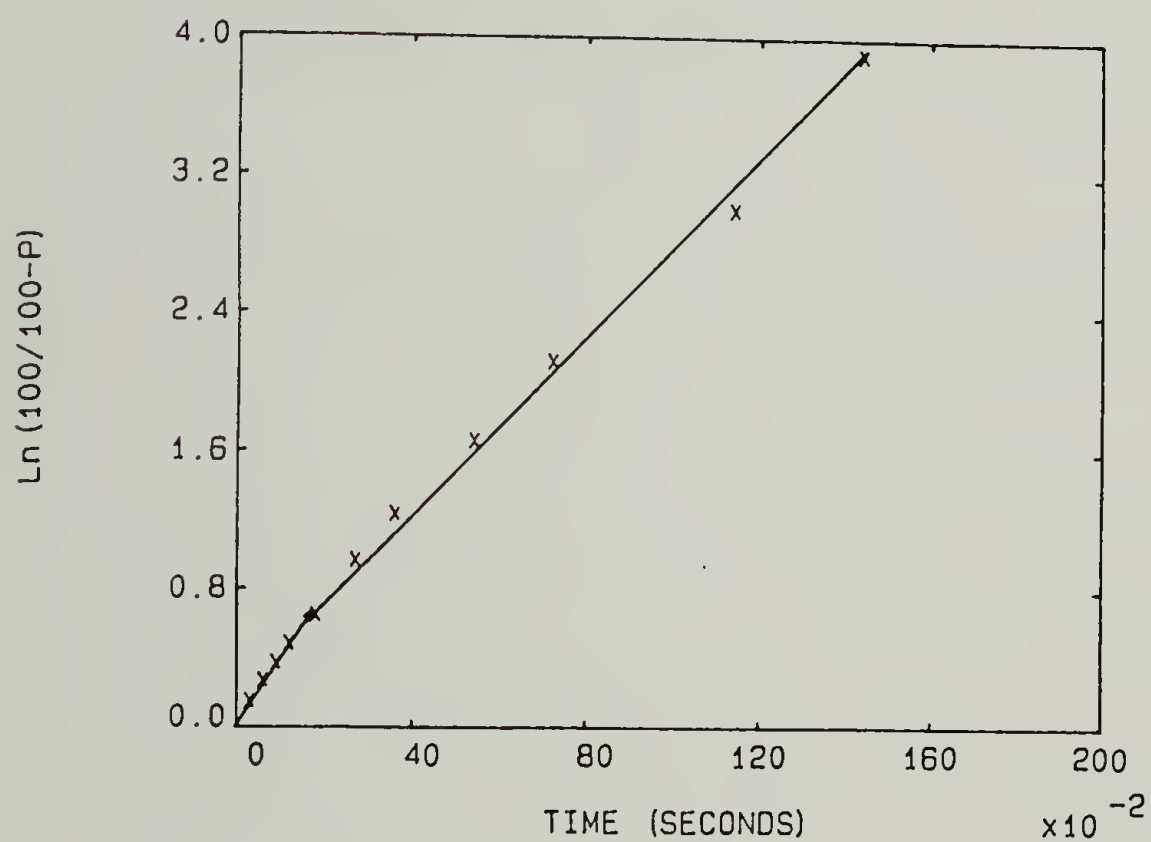


for the observed hydrolysis behavior.

b. Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v) DMSO/H₂O. Experimental results for the neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) (57/43 mole % copolymer) at 70°C in 90/10 DMSO/H₂O are presented in Figure 21. A plot of hydrolysis time (t) versus $\ln(100/100-p)$, according to Equation 24, is shown in Figure 61 and the first order rate constant included in Table 30.

One would anticipate the methyl styrenesulfonate-sodium styrenesulfonate copolymer to behave essentially identical to poly(methyl styrenesulfonate) after a corresponding degree of hydrolysis. Consideration of the data in Table 30 indicates that this indeed is the case. Two steps in the hydrolysis reaction are still observed as would be expected in that the initial copolymer is essentially only 43% hydrolyzed corresponding to the tail end of the first step in the homopolymer hydrolysis. As this degree of hydrolysis corresponds roughly to the transition range between the first and second steps in the hydrolysis reaction (i.e. 40-60% hydrolysis), the experimentally determined rate constant for the initial portion of the hydrolysis reaction ($k_1 = 3.7 \times 10^{-4} \text{ sec}^{-1}$) is intermediate between that of the first ($k_1 = 5.1 \times 10^{-4} \text{ sec}^{-1}$) and second ($k_1 = 3.1 \times 10^{-4} \text{ sec}^{-1}$)

Figure 61. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) at 70°C in 90/10 (v/v) DMSO/H₂O



hydrolysis steps in the hydrolysis of poly(methyl styrenesulfonate). The second linear portion of Figure 61, comprising the majority of the hydrolysis data (30-100% hydrolysis) corresponds to a rate constant ($2.9 \times 10^{-4} \text{ sec}^{-1}$) similar to that for the second step in the homopolymer hydrolysis.

c. Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H_2O . Experimental results for the neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) (57/43 mole % copolymer) in 100% H_2O are summarized in Figure 20. A plot of hydrolysis time (t) versus $\ln(100/100-p)$, according to Equation 24, is shown in Figure 62 and the first order rate constants included in Table 30 along with the corresponding activation energies and frequency factors determined according to Equation 28 (see Figure 63).

The experimental results in Figure 62 indicate that no neighboring group effects are present as linear plots of $\ln(100/100-p)$ versus time are obtained. Furthermore, rate constants, activation energies, and frequency factors characterizing the hydrolysis (Table 30) agree with those corresponding to both the first step in the neutral hydrolysis of the homopolymer (Table 29) and the hydrolysis of methyl toluenesulfonate (Table 28). Obviously, the

Figure 62. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) in 100% H_2O

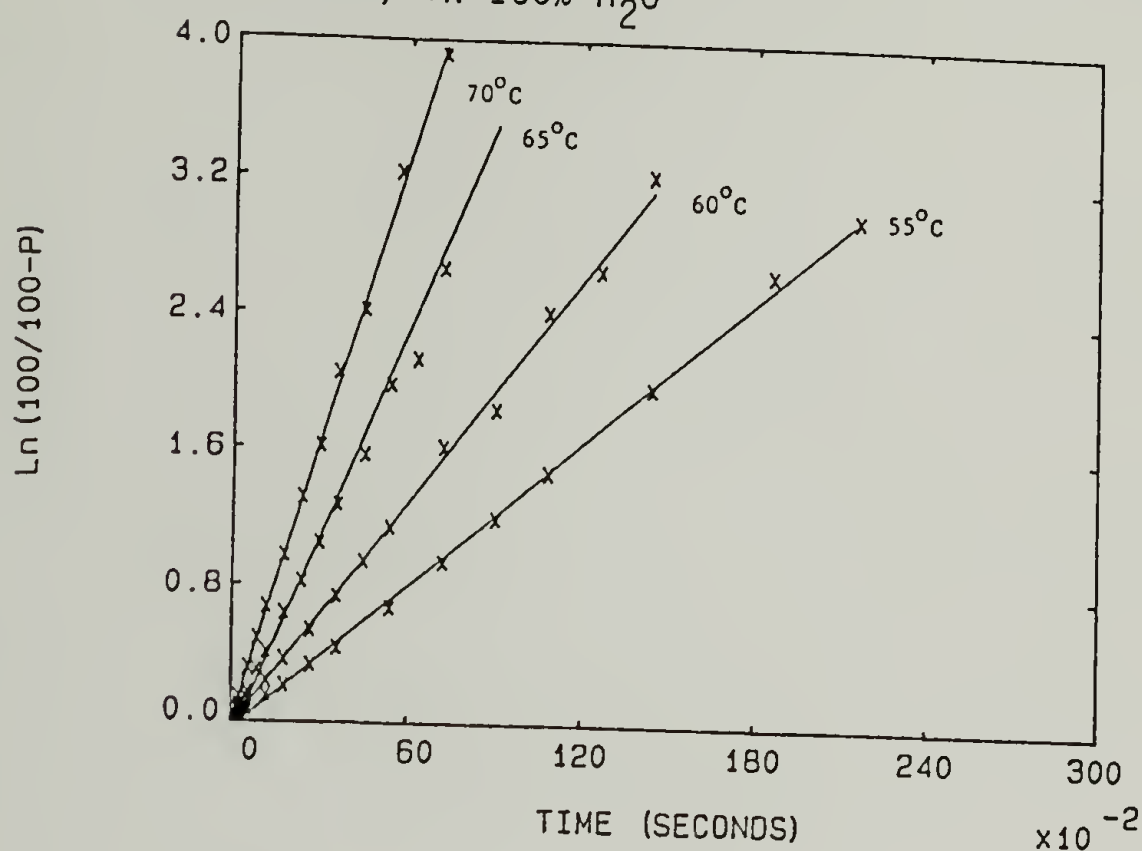
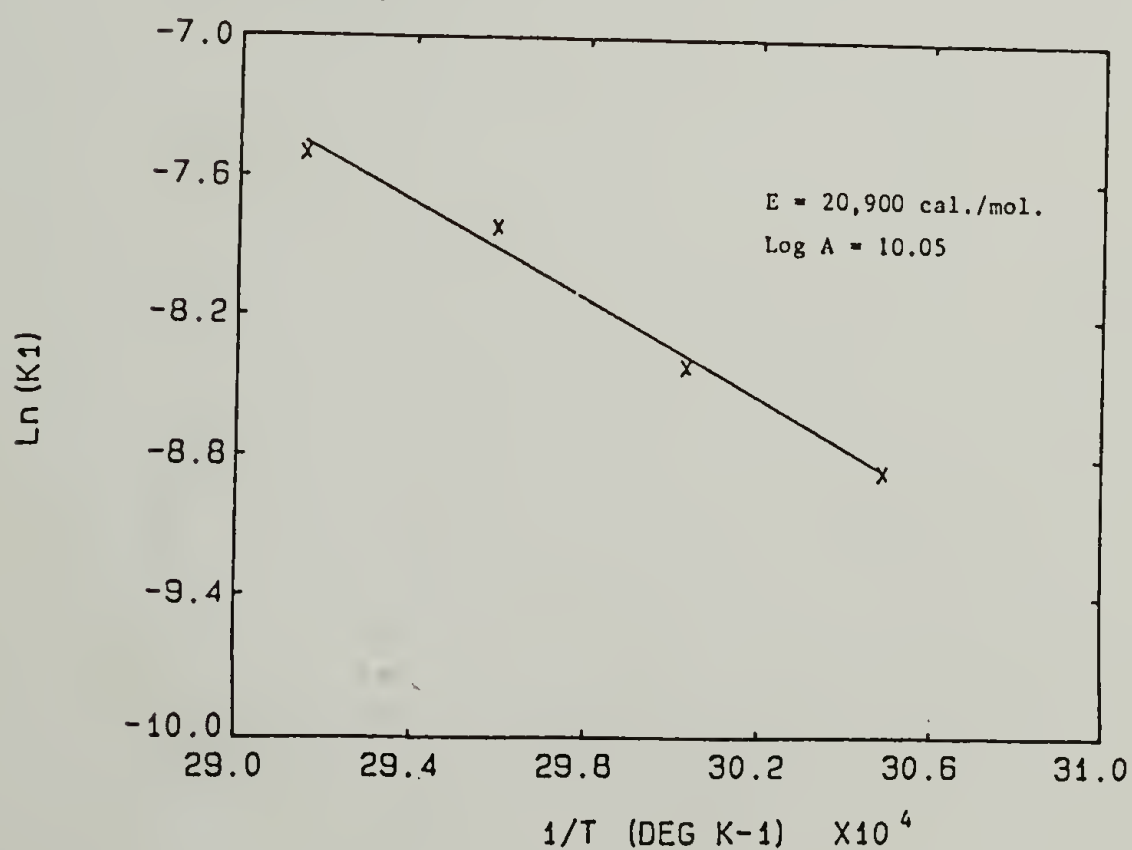


Figure 63. Arrhenius Plot for the Neutral Hydrolysis of Poly-(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) in 100% H_2O

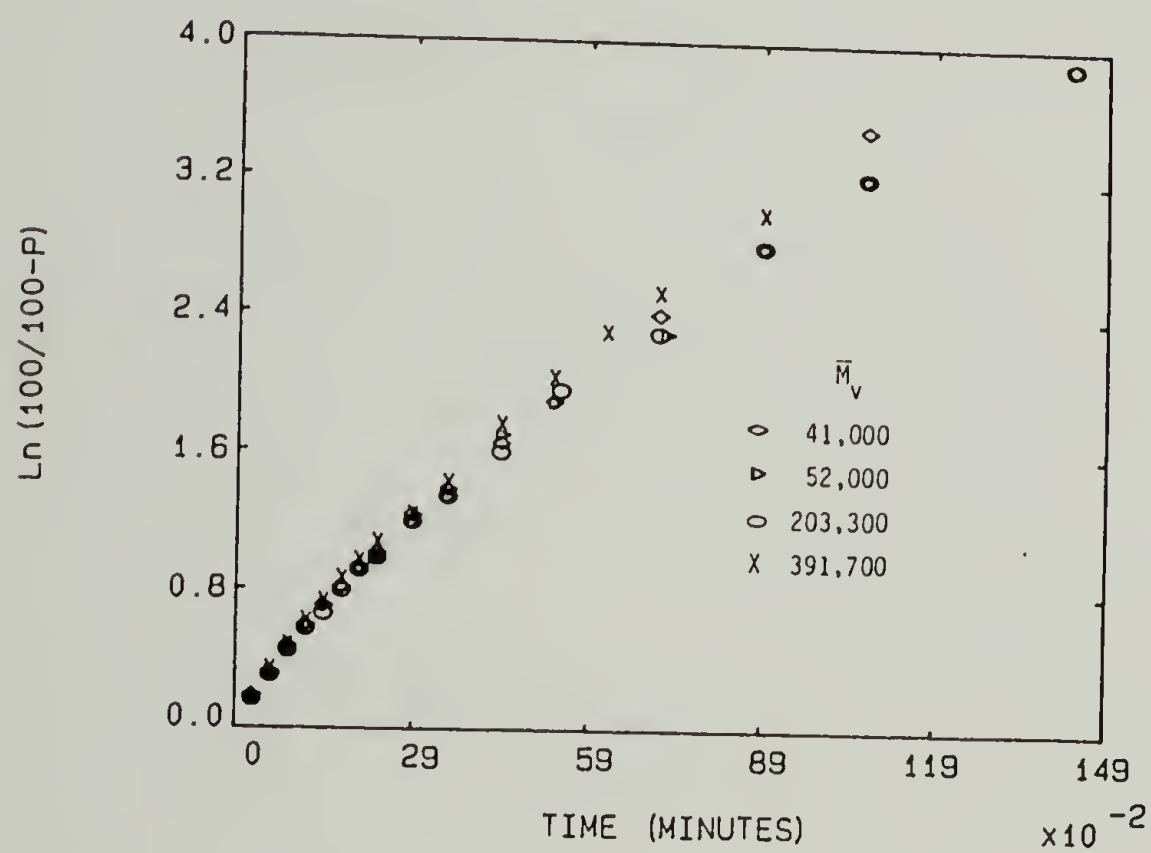


increased water content in the solvent has effectively quenched the neighboring group effects observed in 90/10 (v/v) DMSO/H₂O and the polymer behaves similarly to its low molecular weight analog methyl toluenesulfonate. A more detailed discussion of solvent effects is included in section 5.

d. Attempted Hydrolysis of poly(methyl styrenesulfonate-co-acrylic acid). Due to the weak acidity of acrylic acid comonomer, determination of equivalence points with visual indicators (e.g. bromothymol blue) in the hydrolysis of poly(methyl styrenesulfonate-co-acrylic acid) (26/74 mole% copolymer) was not possible. Construction of titration curves, as shown in Figure 26-28, confirmed this difficulty. However, the feasibility of employing conductimetric titration to circumvent this problem was demonstrated (Figure 29) for future work.

4. Molecular weight effects. Experimental results for the neutral hydrolysis of various molecular weight poly(methyl styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H₂O are summarized in Figure 23. Values of the first order rate constants, calculated according to Equation 24 (see Figure 64), are given in Table 31. Examination of the data in Table 31 indicates that molecular weight has a negligible

Figure 64. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Various Molecular Weight Poly(Methyl Styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H₂O



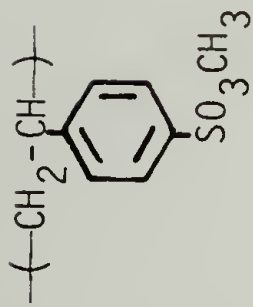


Table 31. Values of k_1 for the Neutral Hydrolysis of Various Molecular Weight Poly(methyl styrenesulfonates) at 70°C in 90/10 (v/v) DMSO/H₂O

Polymer	\bar{M}_v	1st Step $10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$	2nd Step $10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$
Poly(methyl styrenesulfonate)	391,700	5.1	3.1
"	203,300	4.7	2.5
"	52,000	4.8	2.5
"	41,000	4.8	2.9

effect on the hydrolysis kinetics, at least in the molecular weight range studied ($M_v = 41,000$ to $391,700$). Similar results have been reported for the hydrolysis of poly(vinyl acetate) (molecular weight range $23,000$ to $86,000$) (75,76).

5. Solvent effects. The effect of variation in the water content of aqueous dimethyl sulfoxide on the neutral hydrolysis of poly(methyl styrenesulfonate-co-styrene) (57/43 mole % copolymer) at 70°C in 90/10 (v/v) DMSO/ H_2O , 50/50 (v/v) DMSO/ H_2O , and 100% H_2O are summarized in Figure 21. First order rate constant (k_1) calculations, according to Equation 24, are shown in Figures 61, 65, and 66, and the results are summarized in Table 32.

The data in Figure 61 shows that in 90/10 (v/v) DMSO/ H_2O two steps are observed in the hydrolysis reaction indicative of neighboring group effects as discussed previously. However, linear plots obtained in Figures 65 and 66 indicate that neighboring group effects are not observed for hydrolysis in 50/50 (v/v) DMSO/ H_2O and 100% H_2O . Furthermore, rate constants obtained from these plots (Table 32) agree quite well with those for the low molecular weight analog methyl toluenesulfonate.

An understanding of the above-mentioned solvent effects can be achieved by consideration of the solvation properties of dimethyl sulfoxide. Two specific properties of dimethyl

Figure 65. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) at 70°C in 50/50 (v/v) DMSO/H₂O

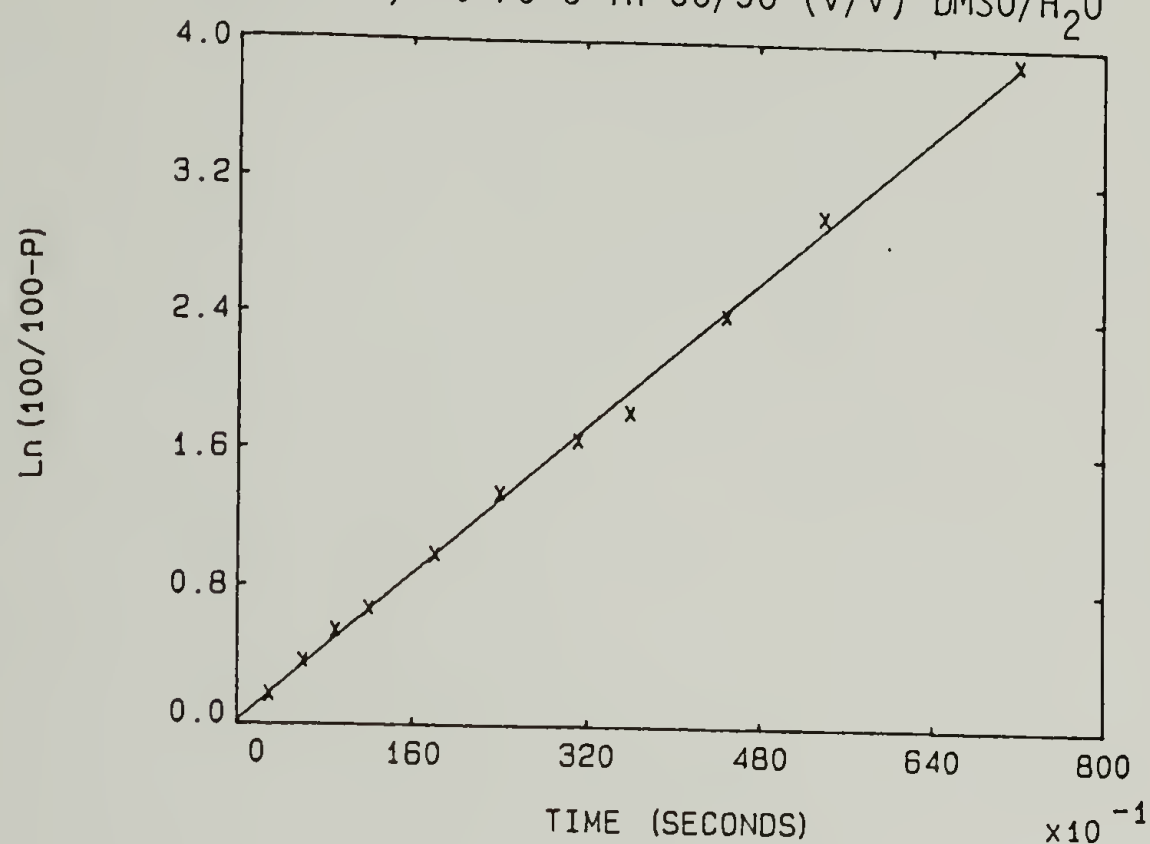
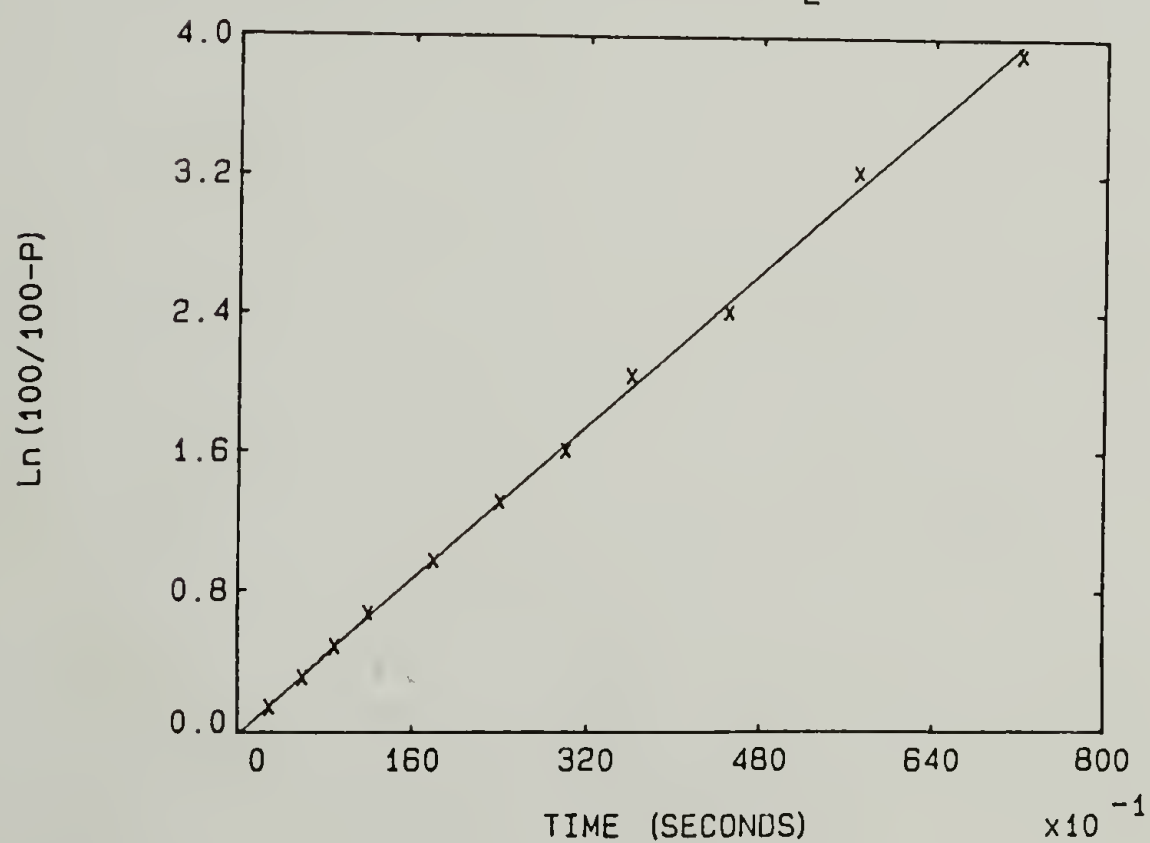


Figure 66. Plot of $\ln(100/100-p)$ vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) at 70°C in 100% H₂O



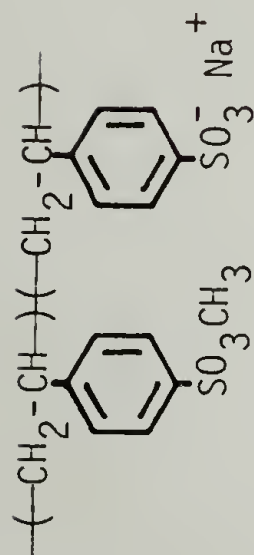
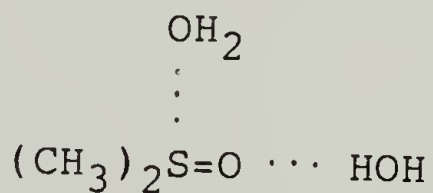


Table 32. Values of k_1 for the Neutral Hydrolysis of Poly-(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in Various Solvents

Compound *	Solvent	$10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$
Methyl Toluenesulfonate ..	90/10 (v/v) DMSO/H ₂ O	5.1
Poly(MSS-co-NaSS)		
1st step	" " "	3.7
2nd step	" " "	2.9
Poly(MSS-co-NaSS)	50/50 (v/v) DMSO/H ₂ O	5.4
Poly(MSS-co-NaSS)	100% H ₂ O	5.5

* MSS = Methyl styrenesulfonate
NaSS = Sodium styrenesulfonate

sulfoxide solutions are of importance in the current investigation. First of all, the inability of DMSO to solvate anions is well known (113, 114). Aprotic, highly polar solvents, such as DMSO, do not solvate small, "hard" anions, solvate large and polarizable anions only weakly, and solvate cations strongly. The solvation of anions is much more effective with protic solvents, such as water, due to the formation of hydrogen-bonded complexes. Of second consideration in dimethyl sulfoxide solutions is the strong association between dimethyl sulfoxide and water. One molecule of DMSO associates with two moles of water (113), the complex having the following structure (115):



Consideration of the aforementioned properties of DMSO, i.e. poor anion solvation and complex formation with water, would lead one to expect anion solvation to be poor in aqueous DMSO solvent systems containing high concentrations of DMSO. In 90/10 (v/v) DMSO/H₂O (1 mole DMSO: 0.4 moles water) one would expect much less anion solvation than in 50/50 (v/v) DMSO/H₂O (1 mole DMSO: 4 moles water) or in 100% H₂O. As a result, the poorly solvated sulfonic acid anion in 90/10 (v/v) DMSO/H₂O would be expected to exert a much stronger

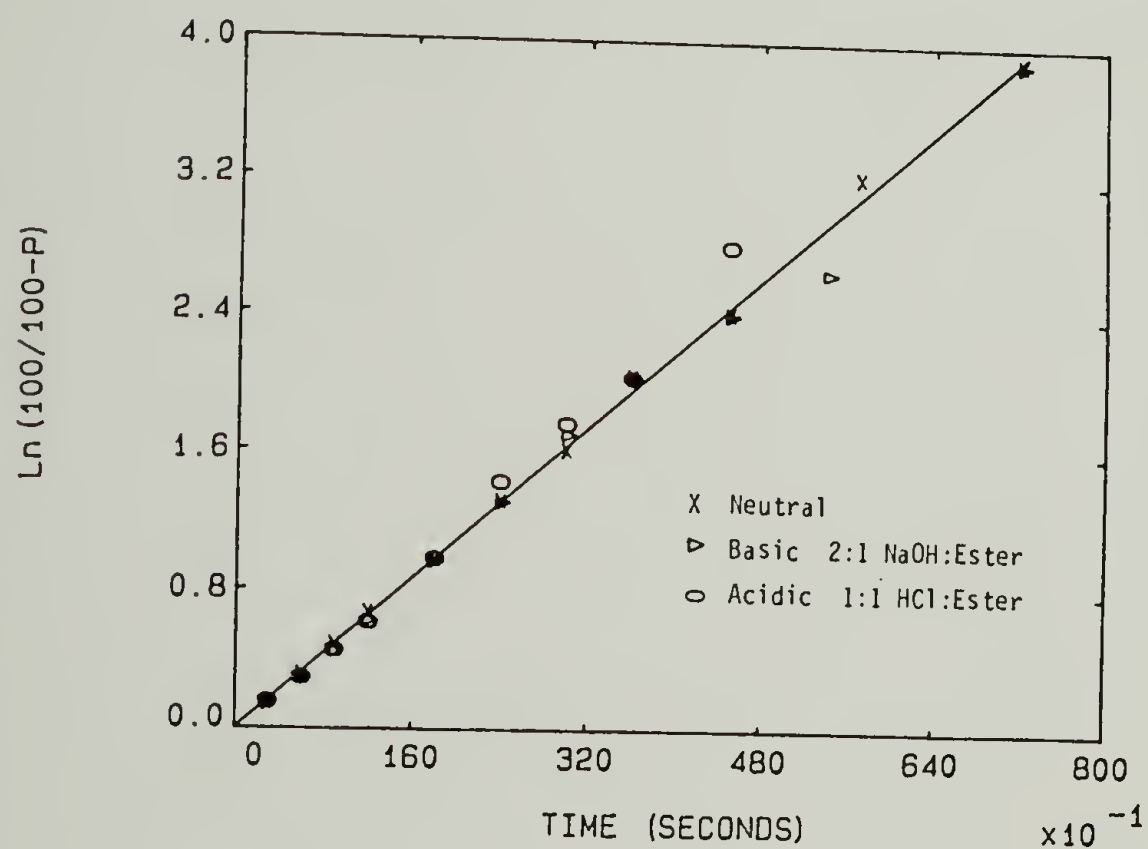
and longer-range neighboring group effect than in solvent systems containing higher concentrations of water and this indeed is what is observed. In solvents containing higher concentrations of water [e.g. 50/50 (v/v) DMSO/H₂O or 100% H₂O] the sulfonate anions are obviously solvated to such an extent so that neighboring group effects are not observed. The decreased solvation of the sulfonate anion in 90/10 (v/v) DMSO/H₂O is supported by viscosity data (Table 22). The viscosity of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 90/10 (v/v) DMSO/H₂O ($\eta_{\text{red}} = 4.93$) is over twice of that in 100% H₂O ($\eta_{\text{red}} = 1.96$), indicative of greater mutual repulsion of neighboring ionic groups.

6. Effect of acid and base on the hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate).

The availability of a water-soluble copolymer allowed for investigation of the effect of added base and acid on the hydrolysis of alkyl styrenesulfonate containing polymers. Experimental data for the hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) (57/43 mole % copolymer) in neutral, acidic (1:1 HCl:ester), and basic (2:1 NaOH:ester) conditions at 70°C in 100% H₂O are presented in Figure 22. Calculated values for the first order rate constants (Figure 67) are summarized in Table 33.

Consideration of the results in Figure 67 and Table 33

Figure 67. Plot of $\ln(100/100-p)$ vs. Time for the Neutral, Acidic, and Basic Hydrolysis of Poly(Methyl Styrenesulfonate-co-Sodium Styrenesulfonate) at 70°C in 100% H₂O



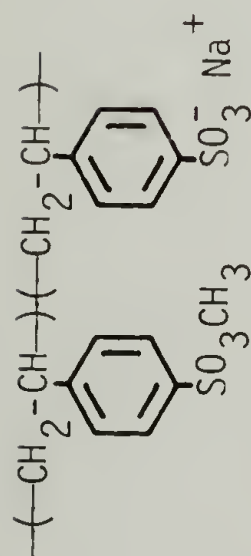


Table 33. Values of k_1 for the Neutral, Acidic, and Basic Hydrolysis of Poly(methyl styrenesulfonate-co-sodium styrenesulfonate) at 70°C in 100% H_2O

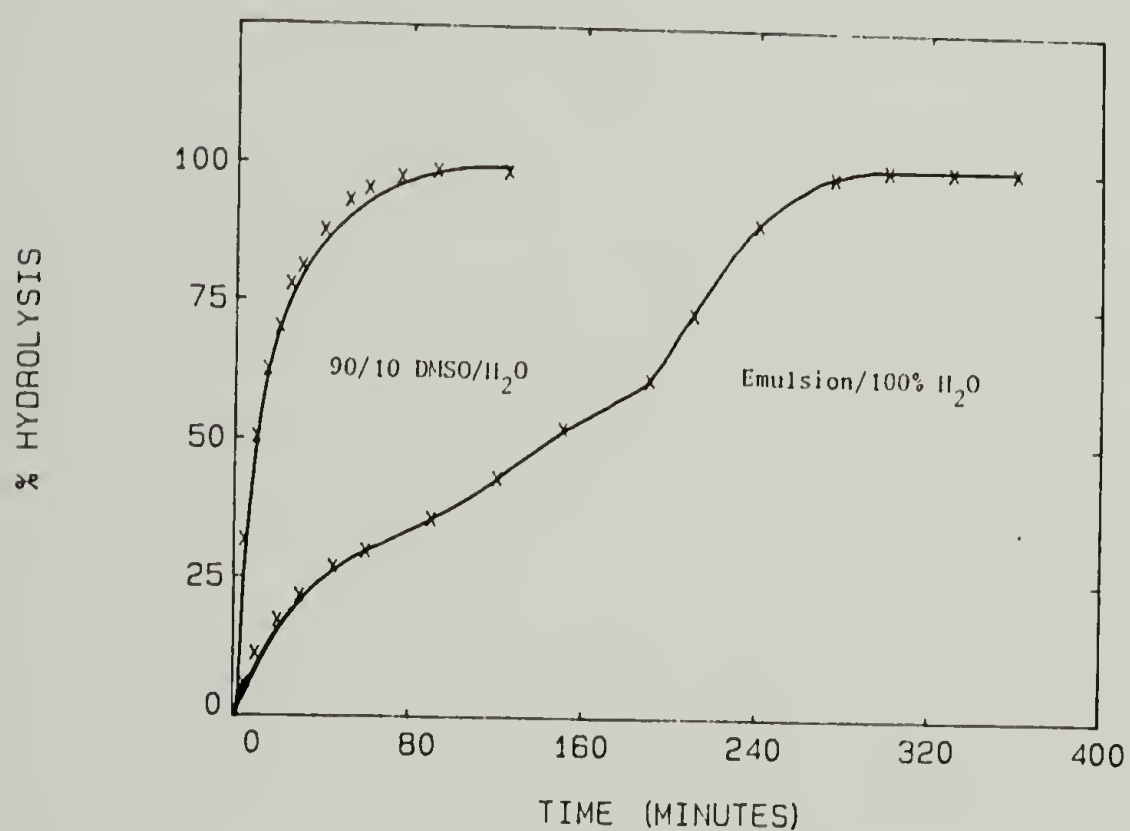
Copolymer *	Conditions	$10^4 \cdot k_1 \text{ (sec}^{-1}\text{)}$
Poly(MSS-co-NaSS)	Neutral	5.5
" " "	Acidic	5.9
" " "	Basic	5.3

* MSS = Methyl styrenesulfonate
NaSS = Sodium styrenesulfonate

indicates that hydrolysis of the sulfonate ester-containing copolymer is neither acid or base catalyzed. The hydrolysis of low molecular weight sulfonate esters is well known not to be catalyzed by acids (see Introduction) so that analogous results obtained for the copolymer are not surprising. However, the hydrolysis of low molecular weight sulfonate esters is known to be catalyzed by bases but this effect is not observed in the copolymer. This result is attributable to strong neighboring group effects. Repulsion between a negatively charged hydroxide ion and a negatively charged sulfonate ion would be expected to be large. The experimental data indicates that this repulsion is so strong so as to prevent approach of hydroxide ions to neighboring ester groups and as a result hydrolysis occurs entirely by reaction of the ester moiety with water (i.e. neutral hydrolysis). Similar strong neighboring group effects have been reported for the alkaline hydrolysis of poly(methacrylamide), poly(N-methacrylamide) and poly(N,N-diethylacrylamide) where maximum degrees of hydrolysis of 72, 55, and 35% respectively are observed (79).

7. Poly(methyl styrenesulfonate) emulsion. Experimental results for the neutral hydrolysis of a poly(methyl styrenesulfonate) emulsion, prepared by emulsion polymerization as described previously, at 80°C in 100% H₂O are summarized in Figure 68. Also included in Figure 68 are

Figure 68. Plot of % Hydrolysis vs. Time for the Neutral Hydrolysis of Poly(Methyl Styrenesulfonate) at 75°C in 90/10 (v/v) DMSO/H₂O and Poly(Methyl Styrenesulfonate) Emulsion at 80°C in 100% H₂O



the results obtained for the neutral hydrolysis of poly(methyl styrenesulfonate) in homogeneous solution [90/10 (v/v) DMSO/H₂O]. Comparison of the data indicates that the hydrolysis of the emulsion occurs much more slowly due to the heterogeneous nature of the reaction. Also noteworthy is the observed upturn in the hydrolysis curve at approximately 50% conversion. Copolymer water solubility studies (Section D-12) indicate that it is at about 40-50% hydrolysis (i.e. 40-50% sulfonic acid content) that the homopolymer would be expected to become water soluble. Thus, the increase in reaction rate, at approximately 50% hydrolysis, in the hydrolysis of the emulsion is accounted for as this corresponds to the point where the system becomes homogeneous.

F. Thermal Analysis of Homopolymers.

Glass transition temperatures (T_g), determined by differential scanning calorimetry (DSC), for the methyl, ethyl, n-propyl, and isopropyl esters of poly(styrene-sulfonic acid) are summarized in Table 34. As observed, the glass transition temperature decreases monotonically with increasing side chain length. Similar results have been reported for poly(alkyl acrylates) (116,117), poly(alkyl methacrylates) (118), and poly(alkyl styrenes) (119) as illustrated in Tables 35 and 36. These effects can be

Table 34. Glass Transition Temperatures of Poly(alkyl styrenesulfonates).

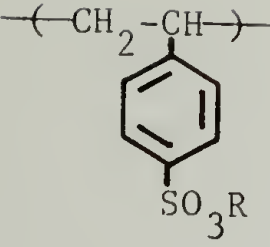
	R	T _g (°C)
	Methyl	177
	Ethyl	147
	n-Propyl	123
	Isopropyl	167

Table 35. Glass Transition Temperatures of Poly(alkyl acrylates) and Poly(alkyl methacrylates) (116-118).

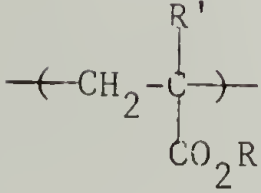
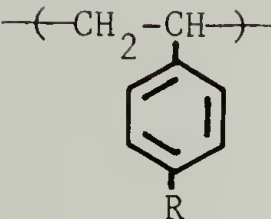
	R	Poly(acrylates) T _g (°C)	Poly-(methacrylates) T _g (°C)
	Methyl	8	105
	Ethyl	-24	65
	n-Propyl	-44	35
	Isopropyl	-6	81

Table 36. Glass Transition Temperatures of Poly(alkyl styrenes) (119).

	R	T _g (°C)
	Methyl	93
	Ethyl	27
	Isopropyl	87

explained on the basis of "internal" plasticization (120). As the length of the ester side chain increases, neighboring chains are pushed further apart, increasing the free volume at a given temperature and decreasing the hindrance to chain backbone motions. Insofar as the glass transition temperature can be considered to be at least approximately correlated with an isofree-volume state (121), this concept qualitatively explains the lowering of the glass transition temperature. In the case of the isopropyl ester the increase in glass transition temperature is most probably due to chain backbone stiffening resulting in increased hindrance to chain backbone motions.

Thermal stability results for the various homopolymers, as determined by thermogravimetric analysis (TGA), are summarized in Table 21. As the data indicates, thermal stability decreases as the length of the alkyl chain increases. Residual (%) at 500°C results indicate that degradation most probably occurs through desulfonation, which would account for weight losses of approximately 55%. However, the limited data is inconclusive and more detailed degradation studies are necessary to definitively determine the mechanism of thermal degradation. Data for the isopropyl ester indicates that it is more thermally stable than either the ethyl or n-propyl esters and again a more complete understanding of the degradation mechanism is

necessary in order to account for this behavior.

G. Conclusions and Further Work

This dissertation describes the synthesis, characterization, and hydrolysis behavior studies of homopolymers and copolymers containing alkyl esters of styrenesulfonic acid.

Methyl, ethyl, n-propyl, and isopropyl styrenesulfonates were successfully synthesized from sodium styrenesulfonate and homopolymerized by free radical initiation. Monomer synthesis procedures involving the sulfochlorination of (2-bromoethyl)benzene were found to be inferior due to sulfone formation which led to insoluble, crosslinked polymers. Alkyl styrenesulfonates were found to readily copolymerize with a variety of comonomers. Reactivity ratio studies indicated that this facile copolymerization stems from the highly reactive double bond generated by the electron-withdrawing character of the sulfonate moiety.

Hydrolysis studies of the various homopolymers and copolymers indicated that the polymers behave similarly to their low molecular weight analogs and exhibited the following order or reactivity: methyl > isopropyl > ethyl > n-propyl. In solvent systems containing high

concentrations of dimethyl sulfoxide, neighboring group effects were observed (due to inadequate anion solvation) resulting in a decrease in the hydrolysis rate as the reaction proceeded. This effect was not observed in solutions containing higher concentrations of water where the sulfonic acid groups are fully solvated. Strong neighboring group effects were also observed in alkyl styrenesulfonate-sodium styrenesulfonate copolymers in that hydrolysis was found to be uncatalyzed by bases. Finally, hydrolysis behavior was found to be independent of molecular weight, at least in the molecular weight range studied ($\bar{M}_v = 41,000$ to $391,700$).

For the future, numerous avenues are open for development. The synthesis of monomers from other alcohols, in order to extend the range of hydrolytic behavior, would be worthwhile. Also, extension of this work into other sulfonated monomers, e.g. those based on vinyl sulfonic acid, would be interesting.

Further investigation into the hydrolysis behavior of polymer emulsions might also be explored. The hydrolysis of ethyl, n-propyl, and isopropyl ester-containing polymer emulsions as well as the effect of variables such as alkalinity and particle size on hydrolysis kinetics might be of interest in this area.

Whatever the direction this research takes in the future, it is clear that alkyl styrenesulfonate containing homopolymers and copolymers are of potential consideration for use as controlled release polyelectrolytes, as the feasibility of their synthesis has been demonstrated.

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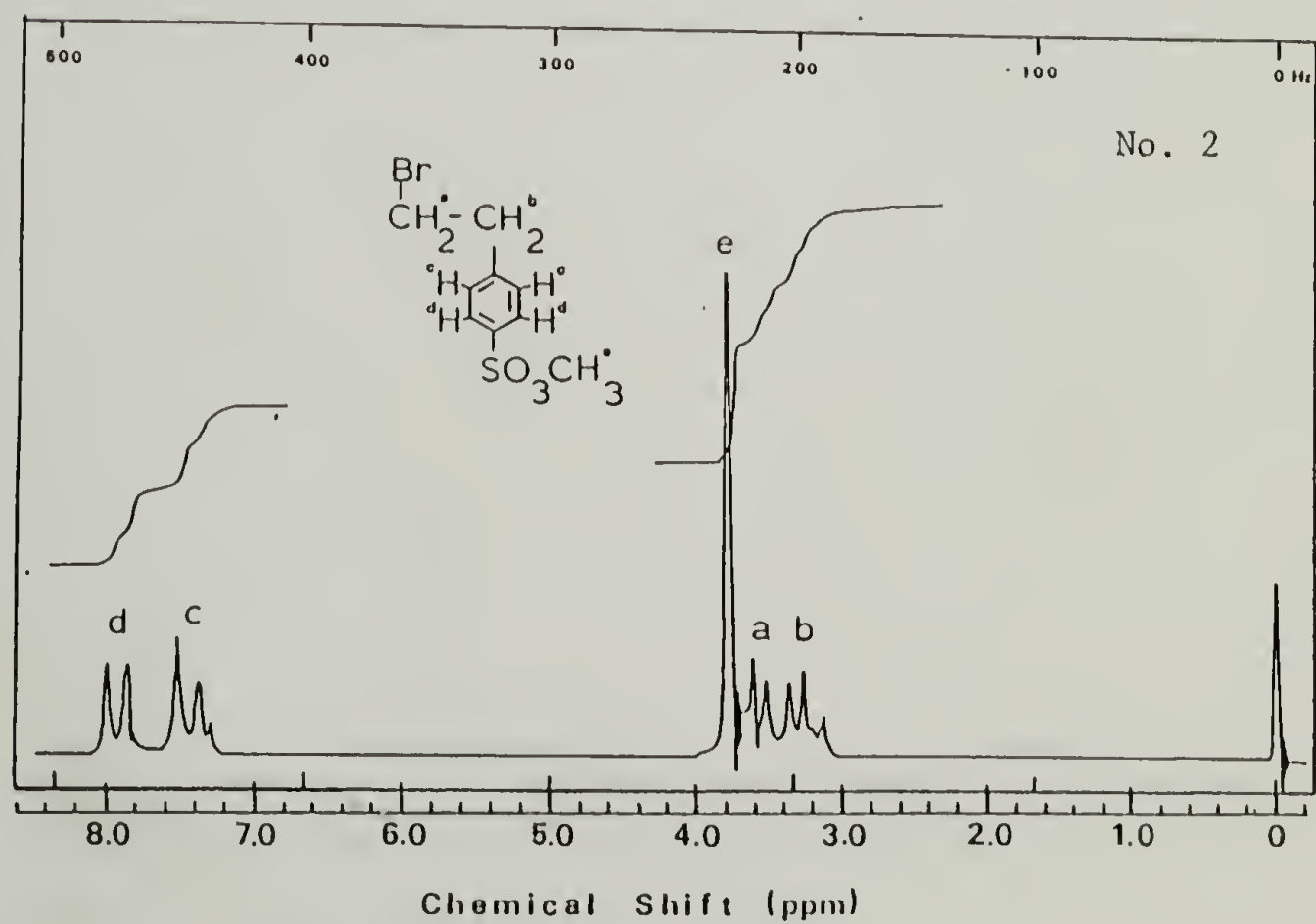
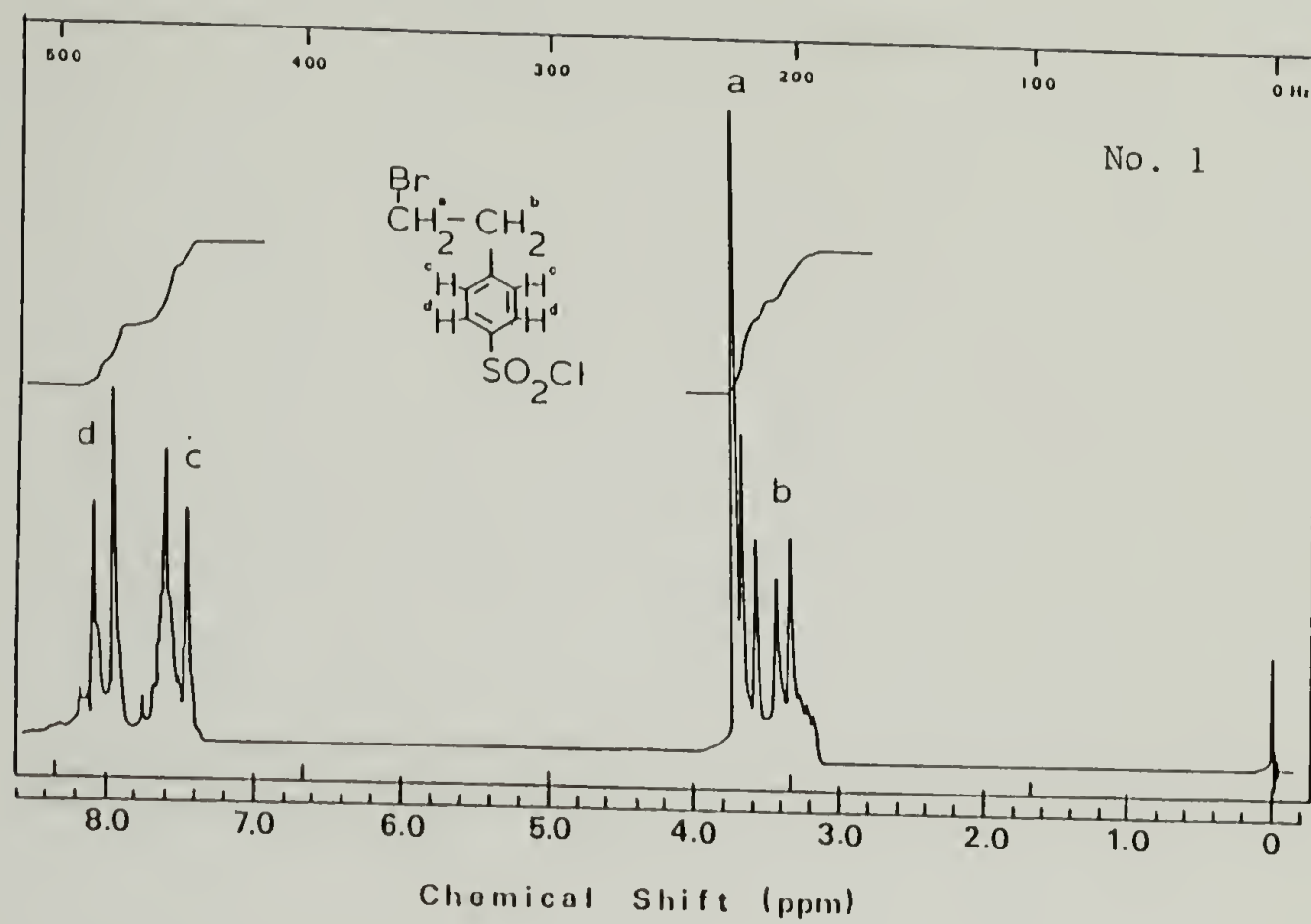
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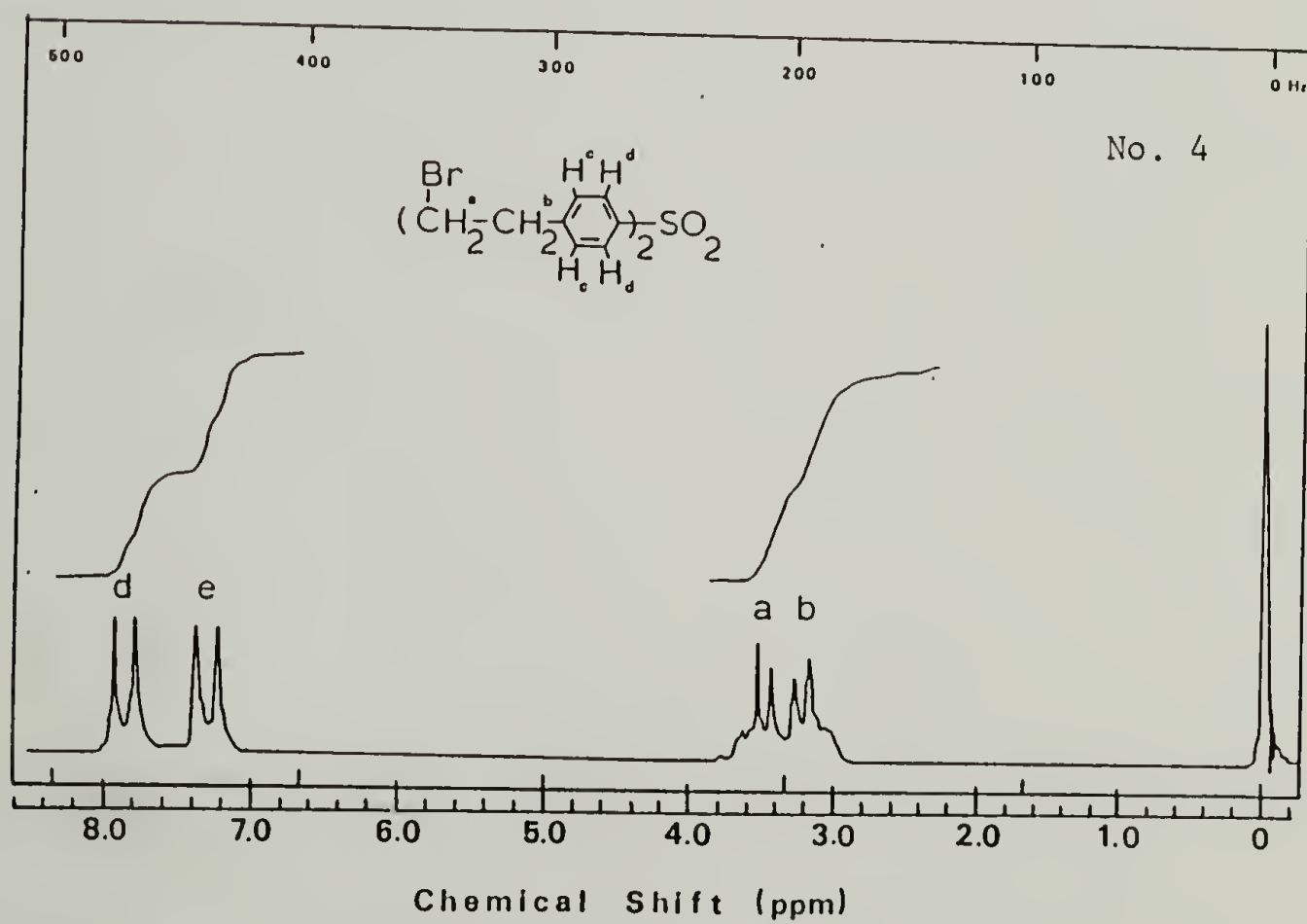
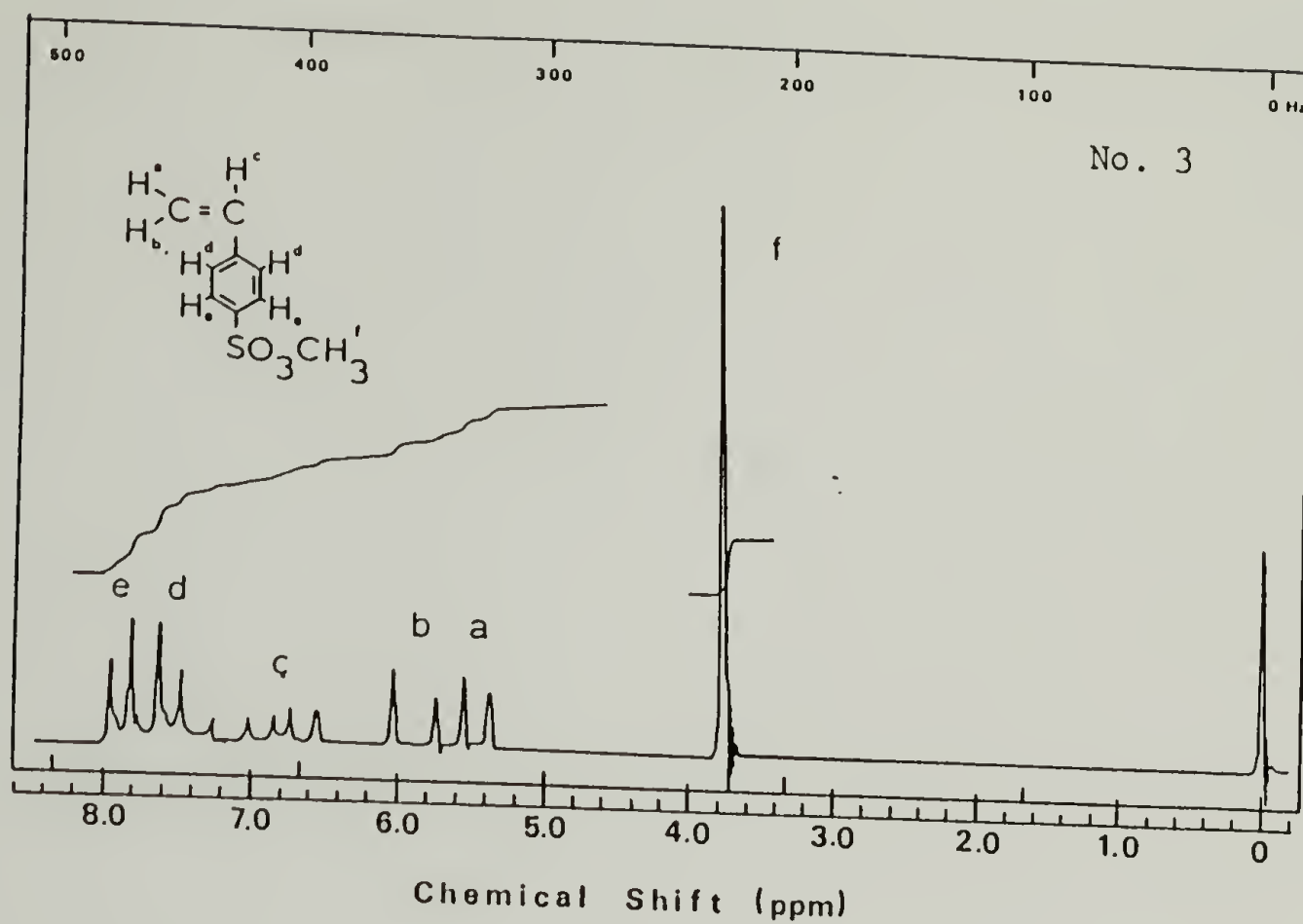
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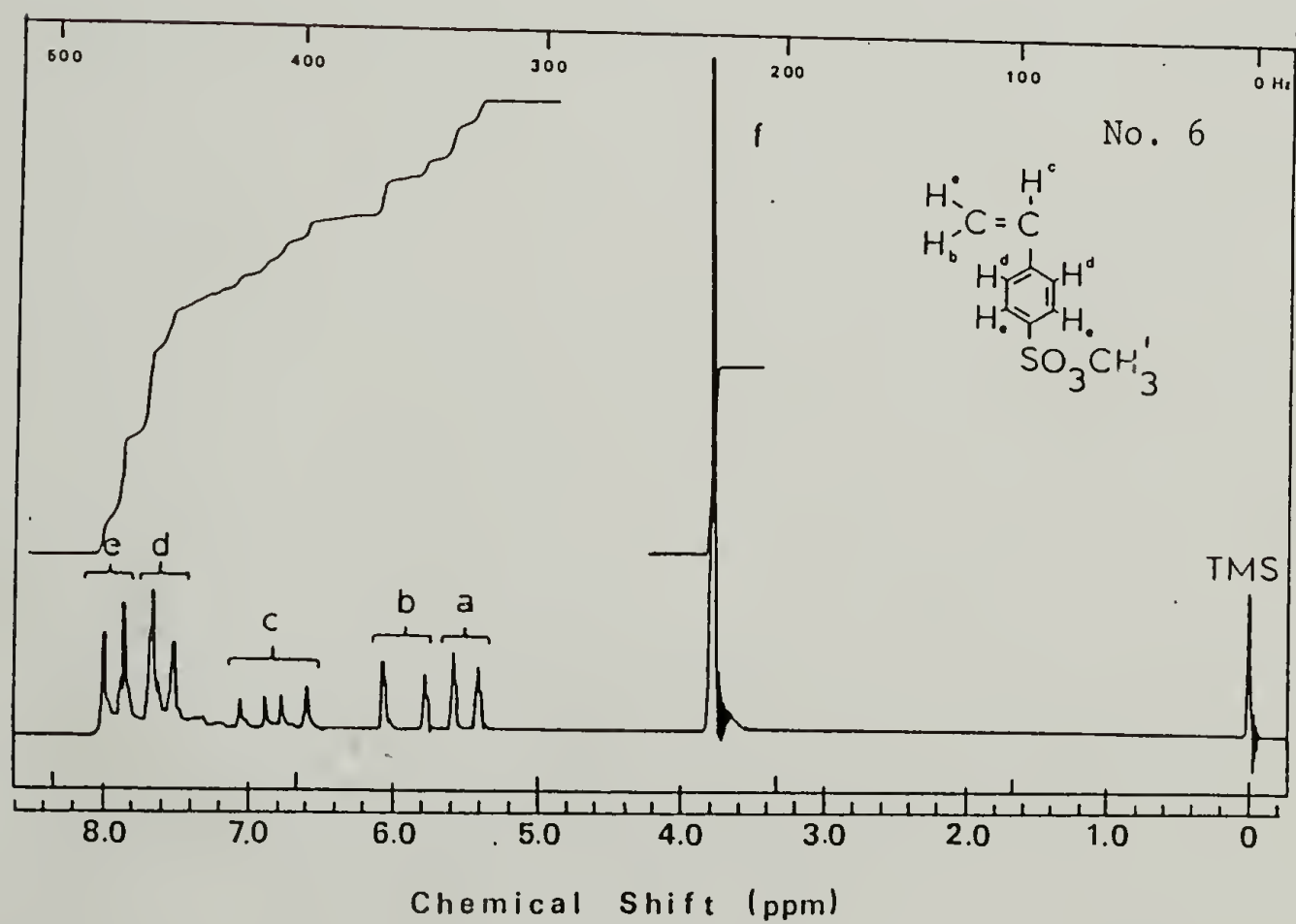
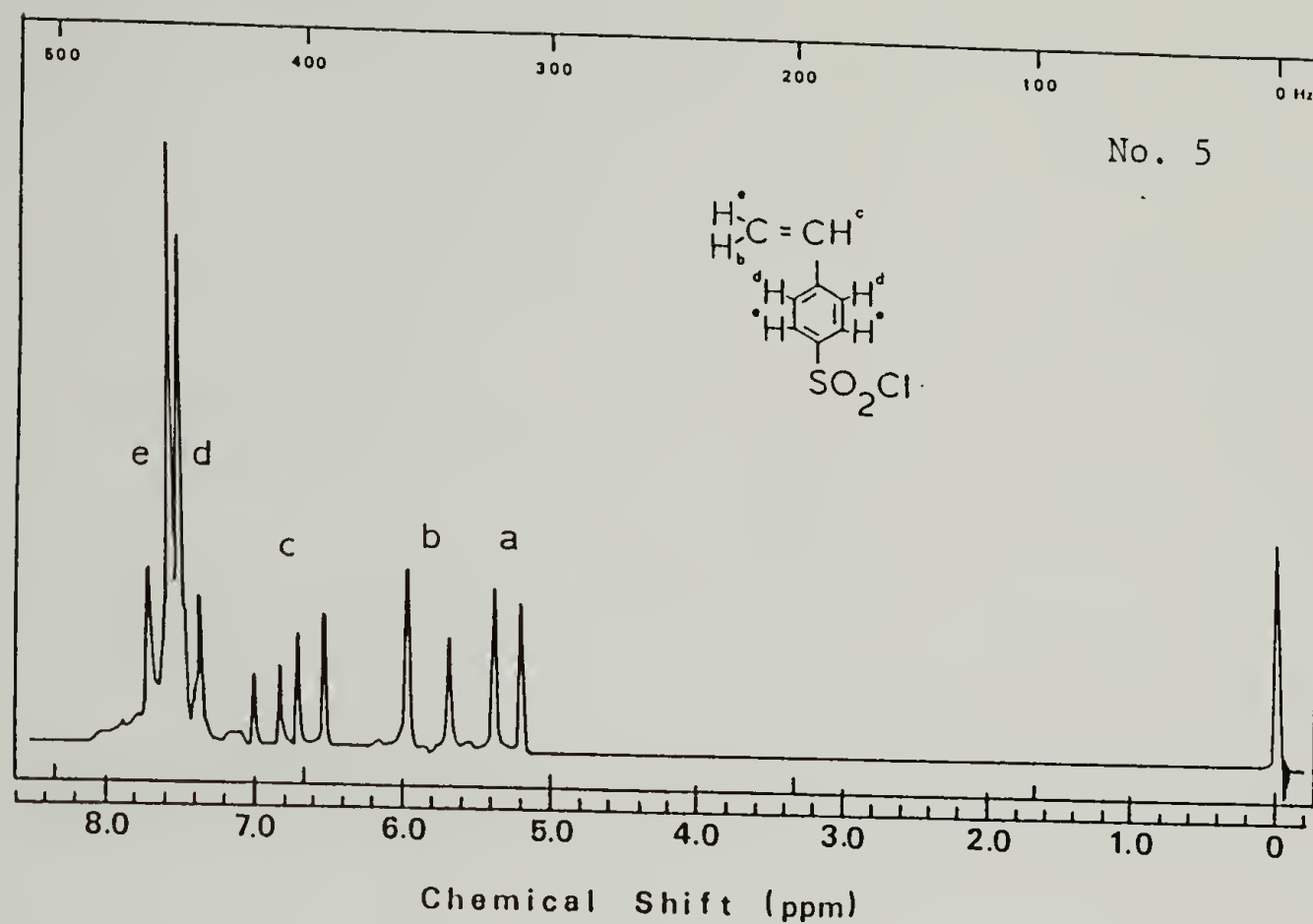
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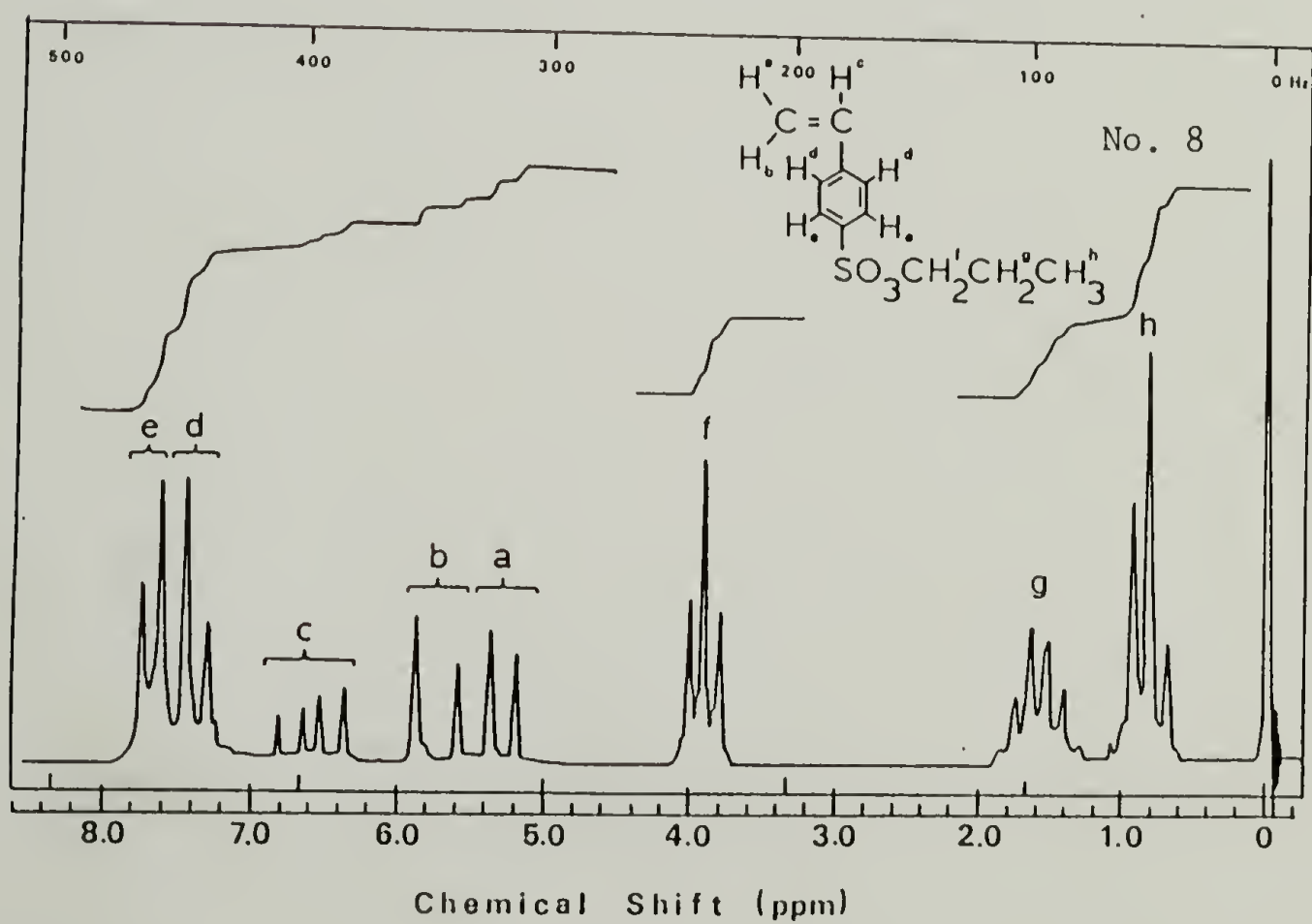
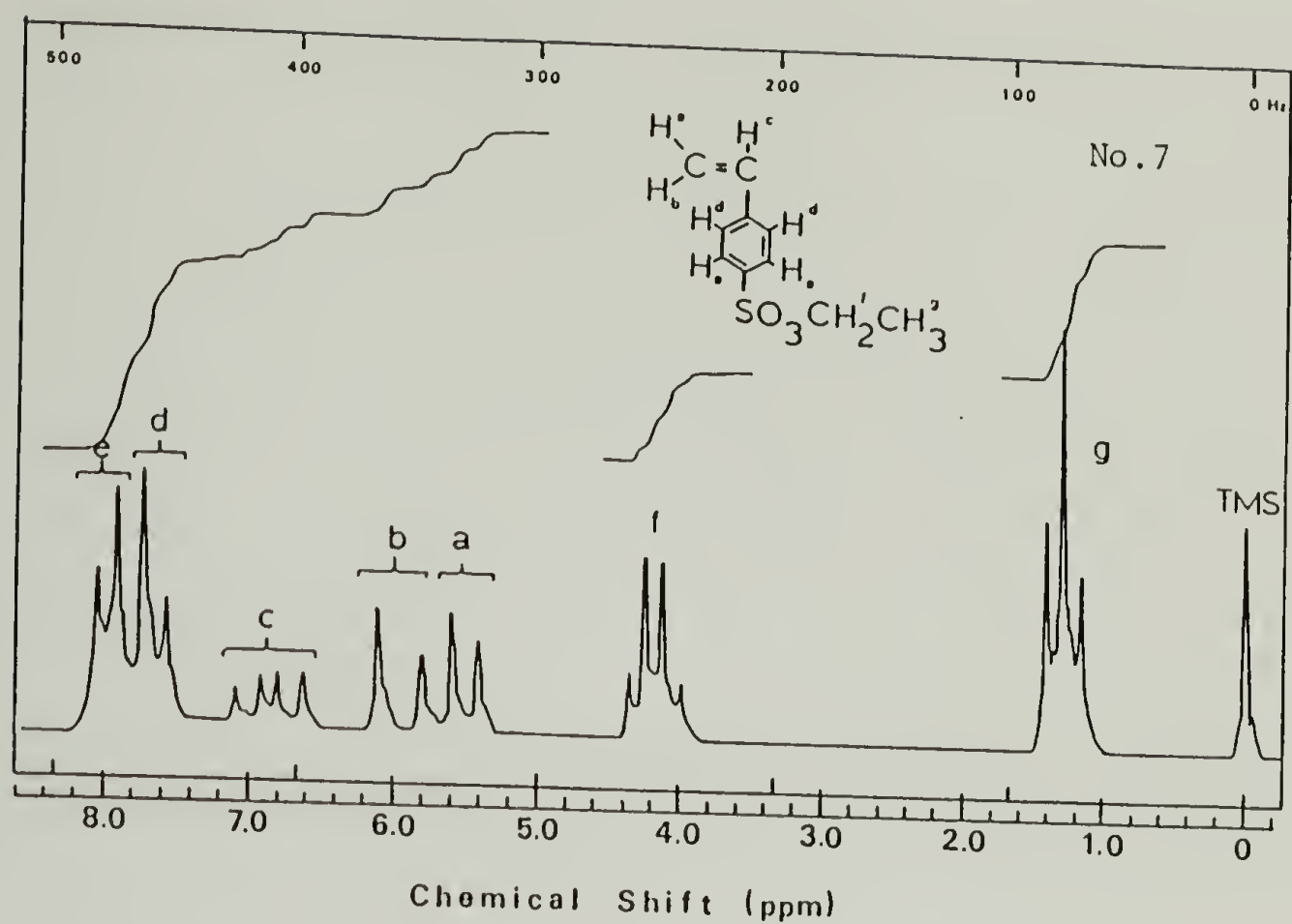
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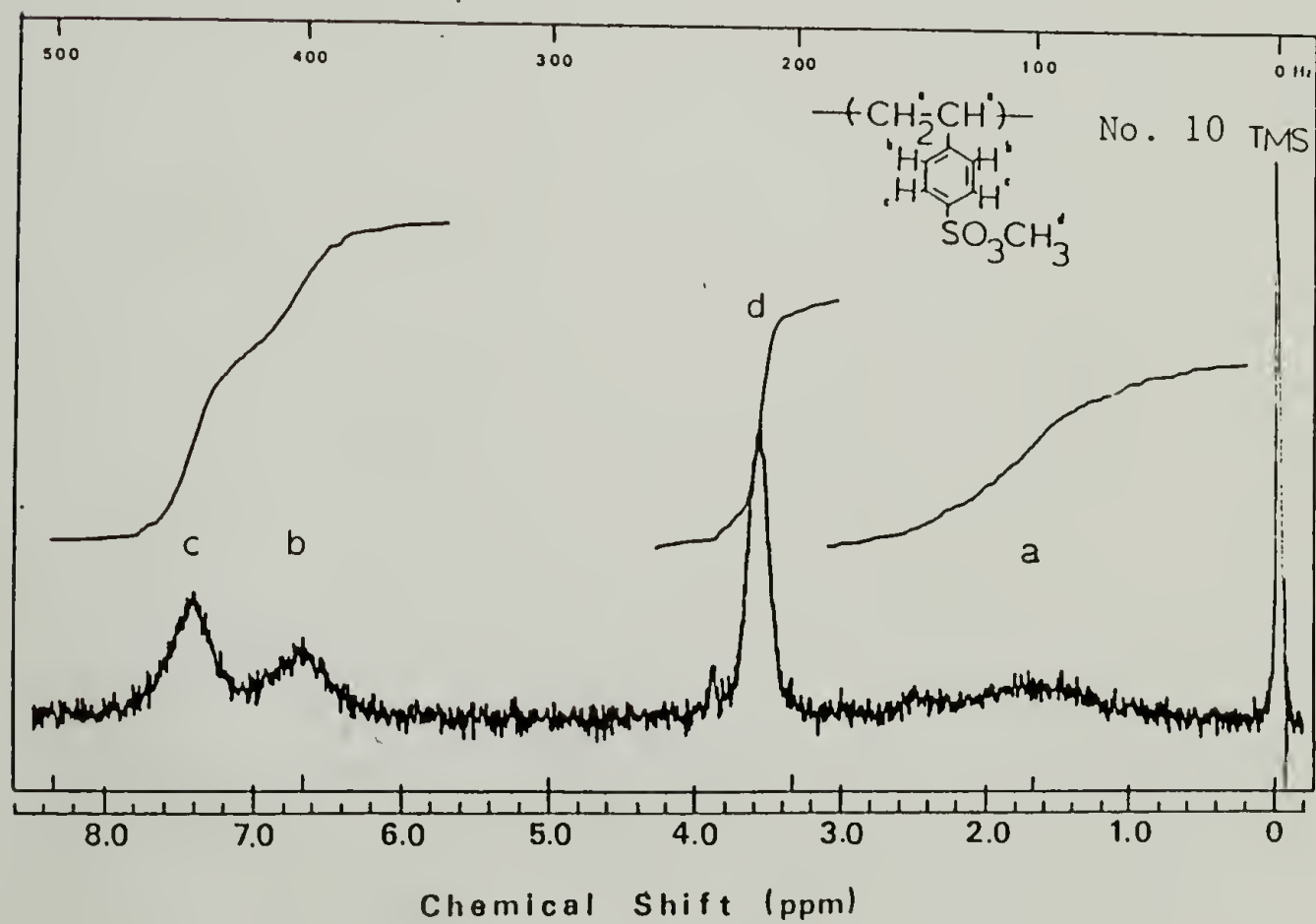
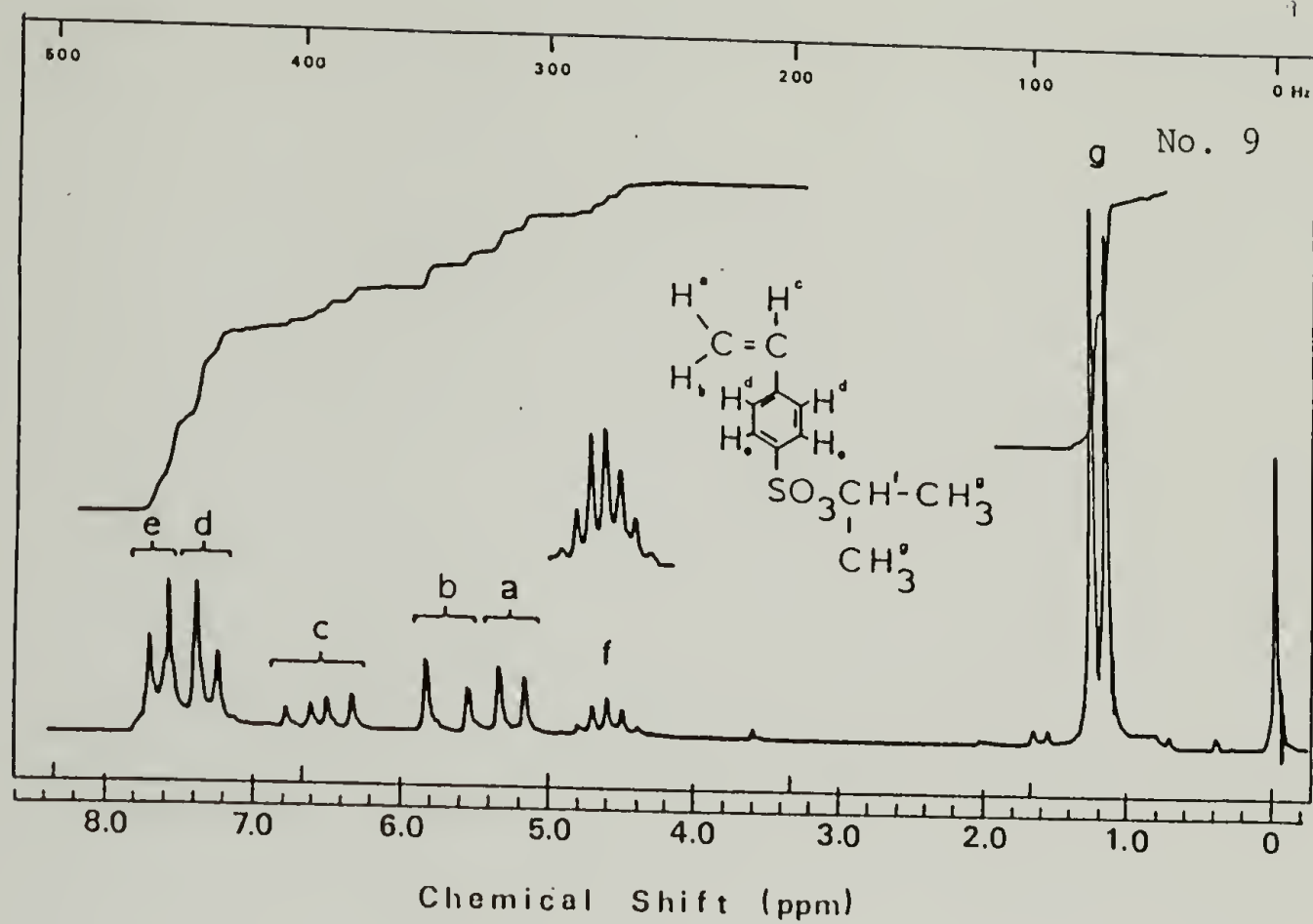
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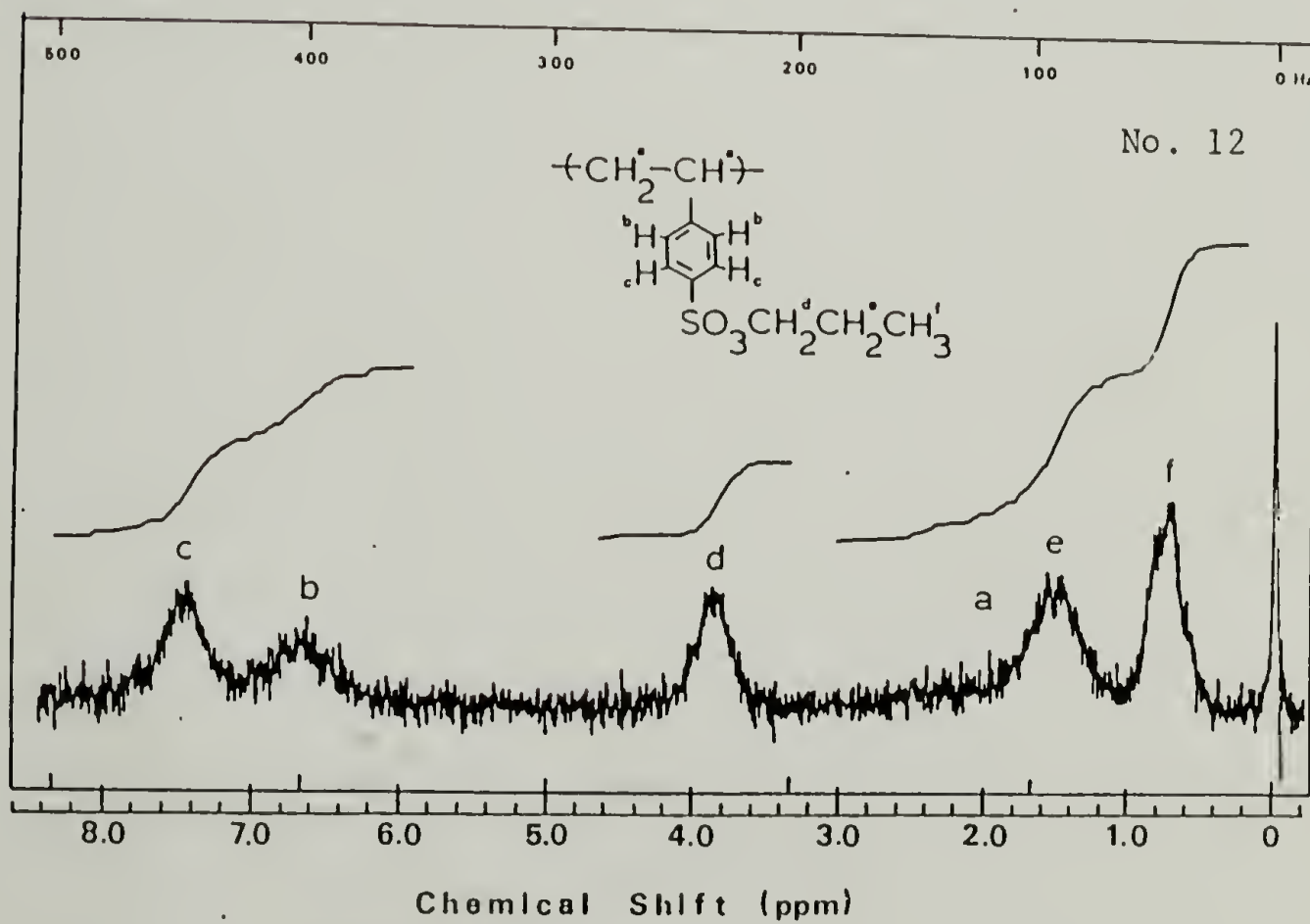
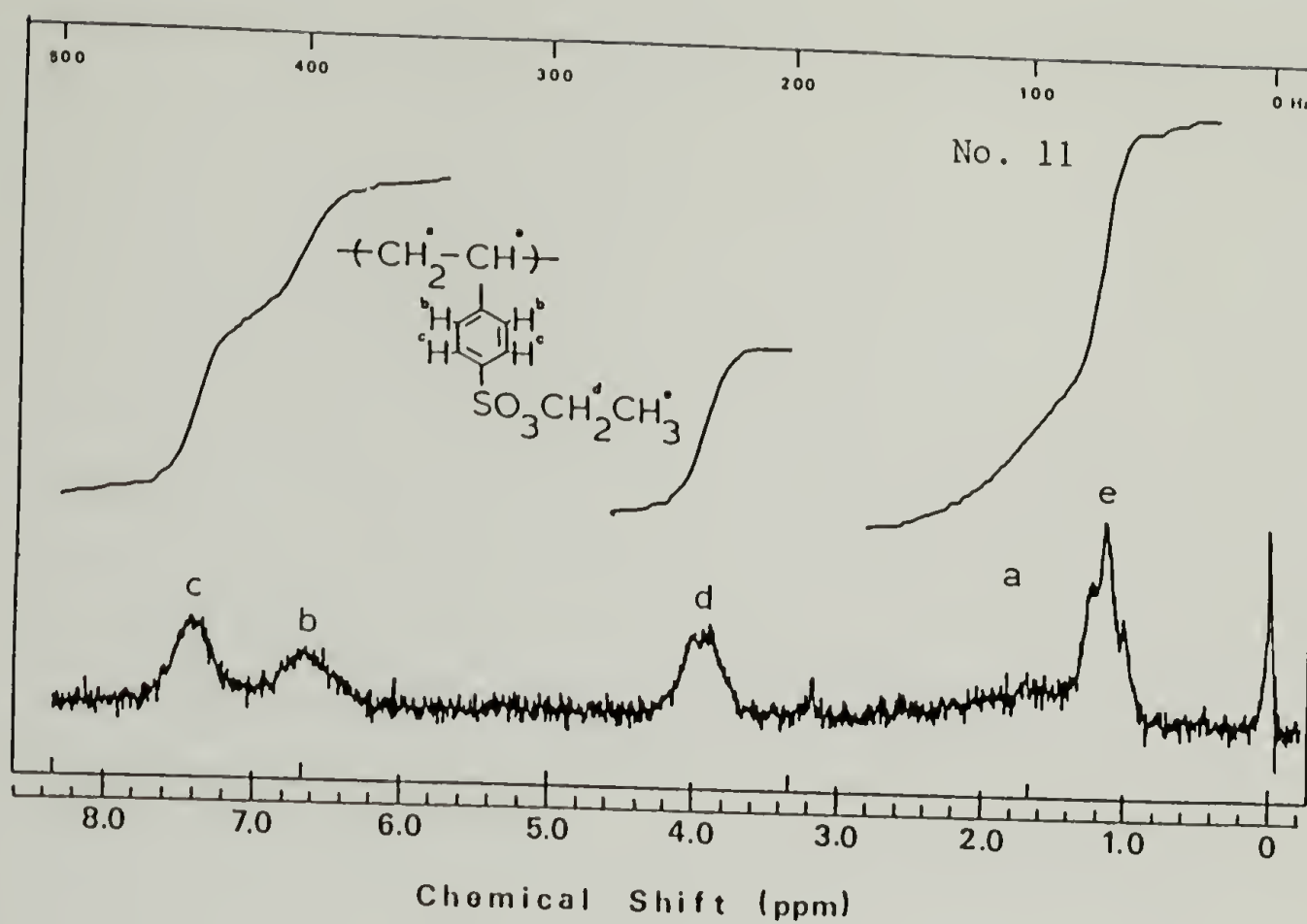


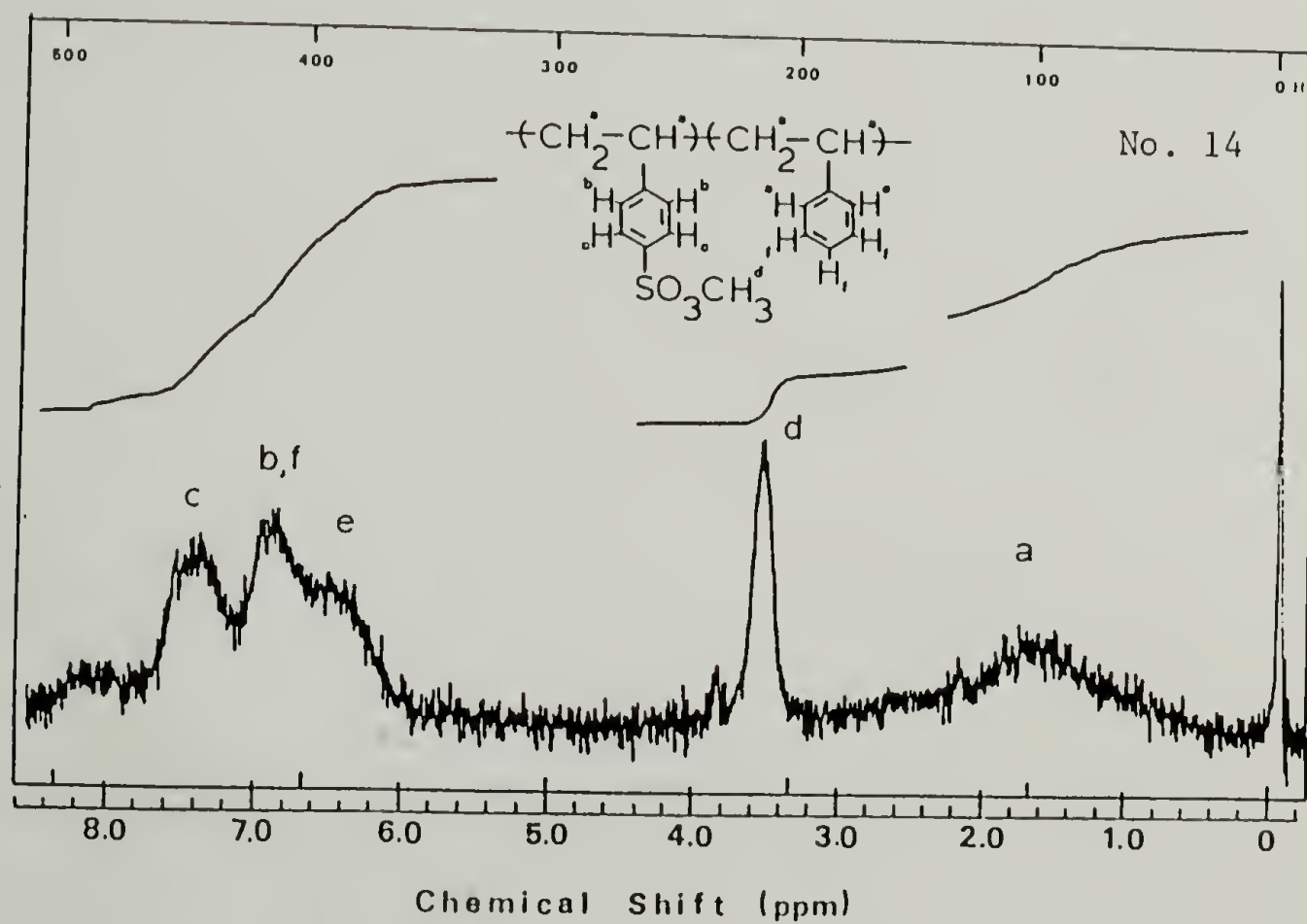
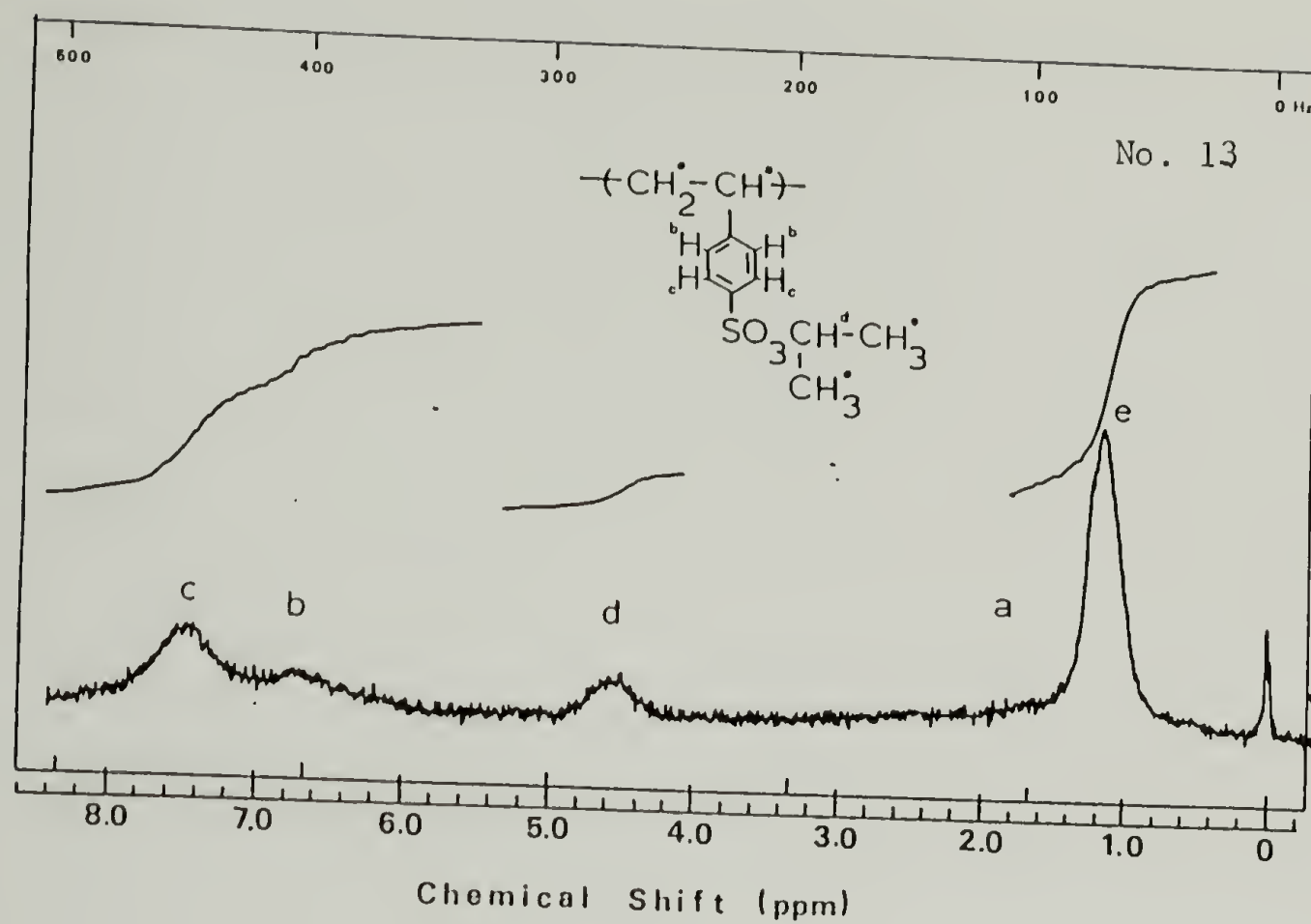


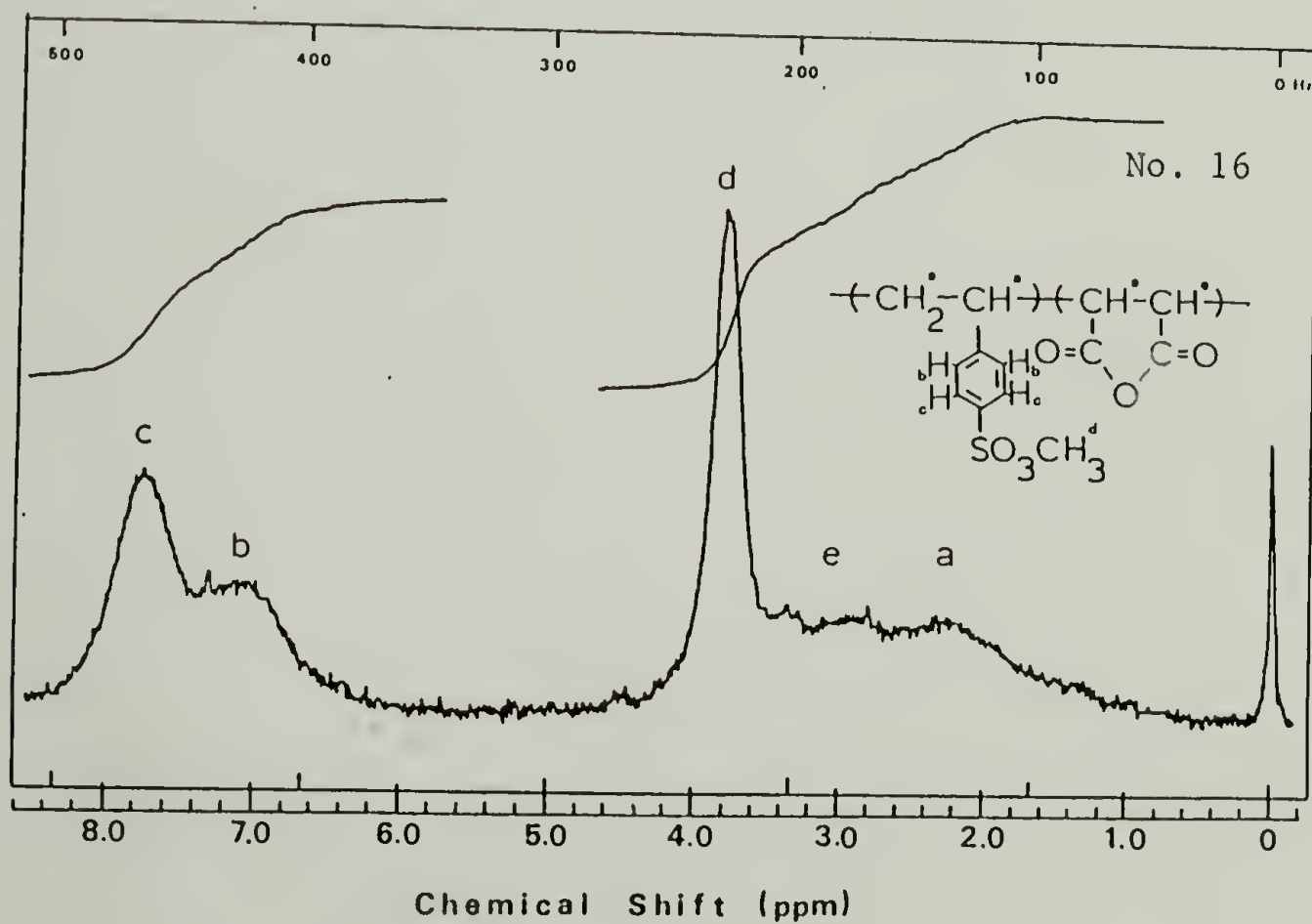
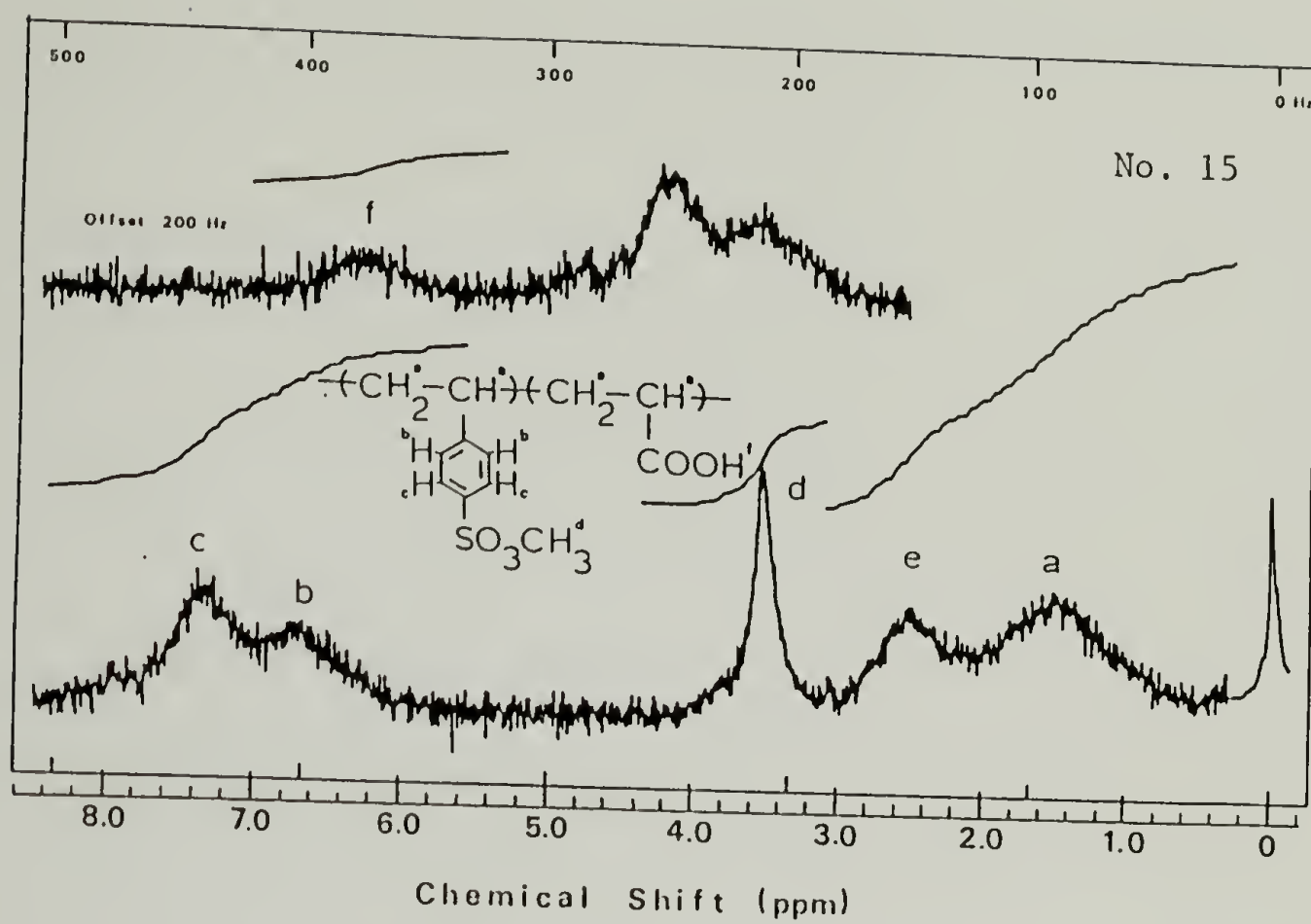








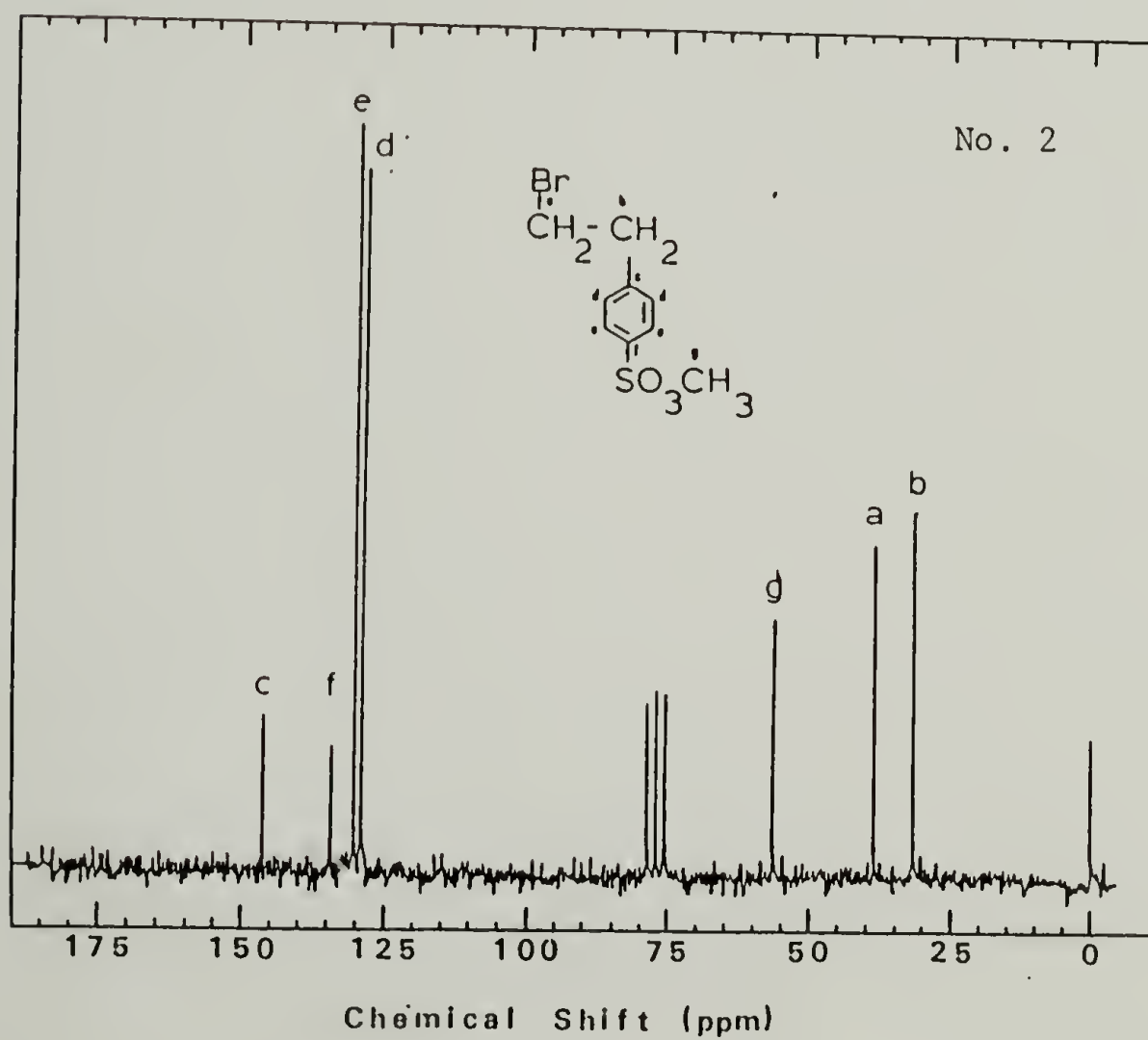
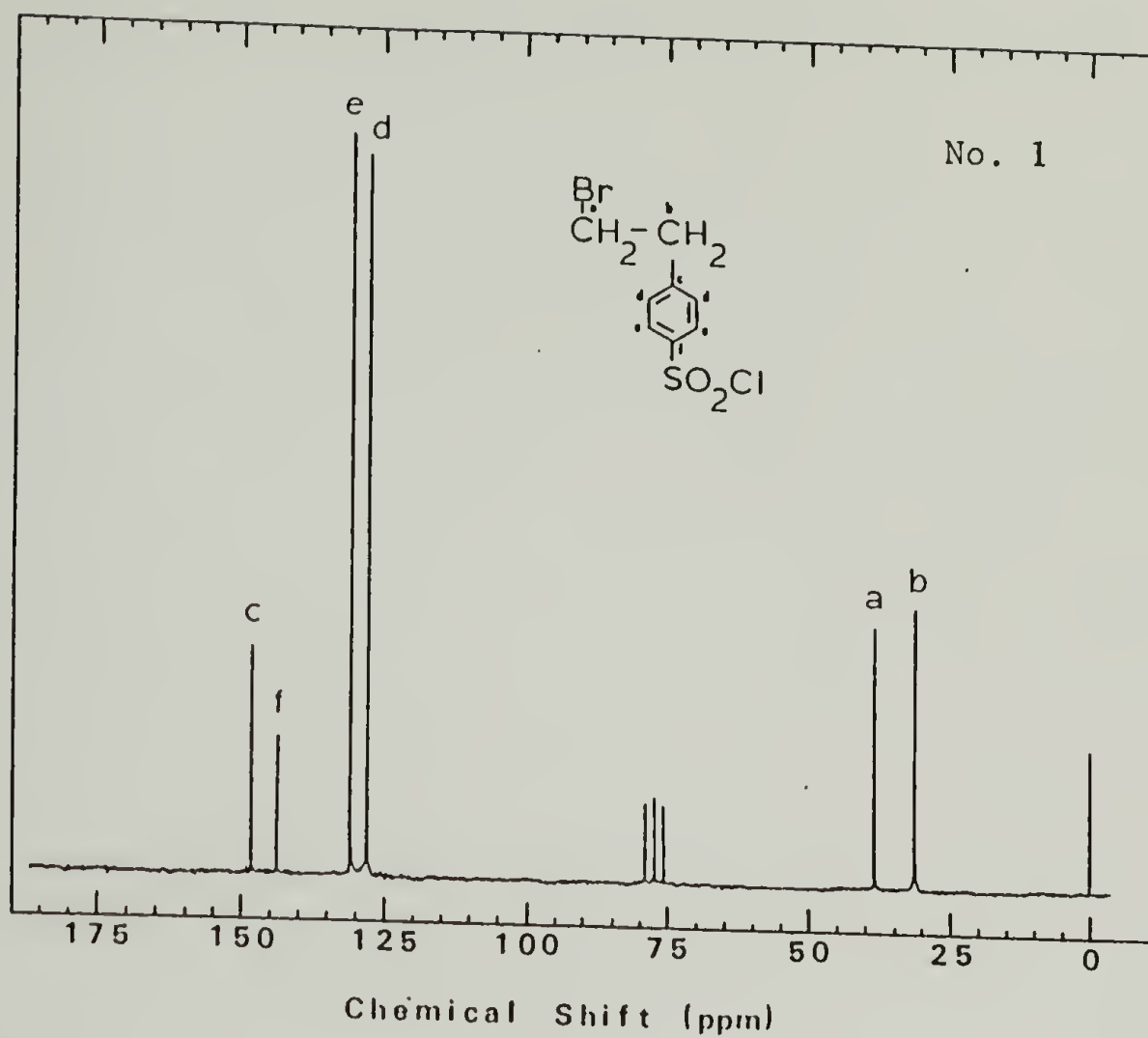


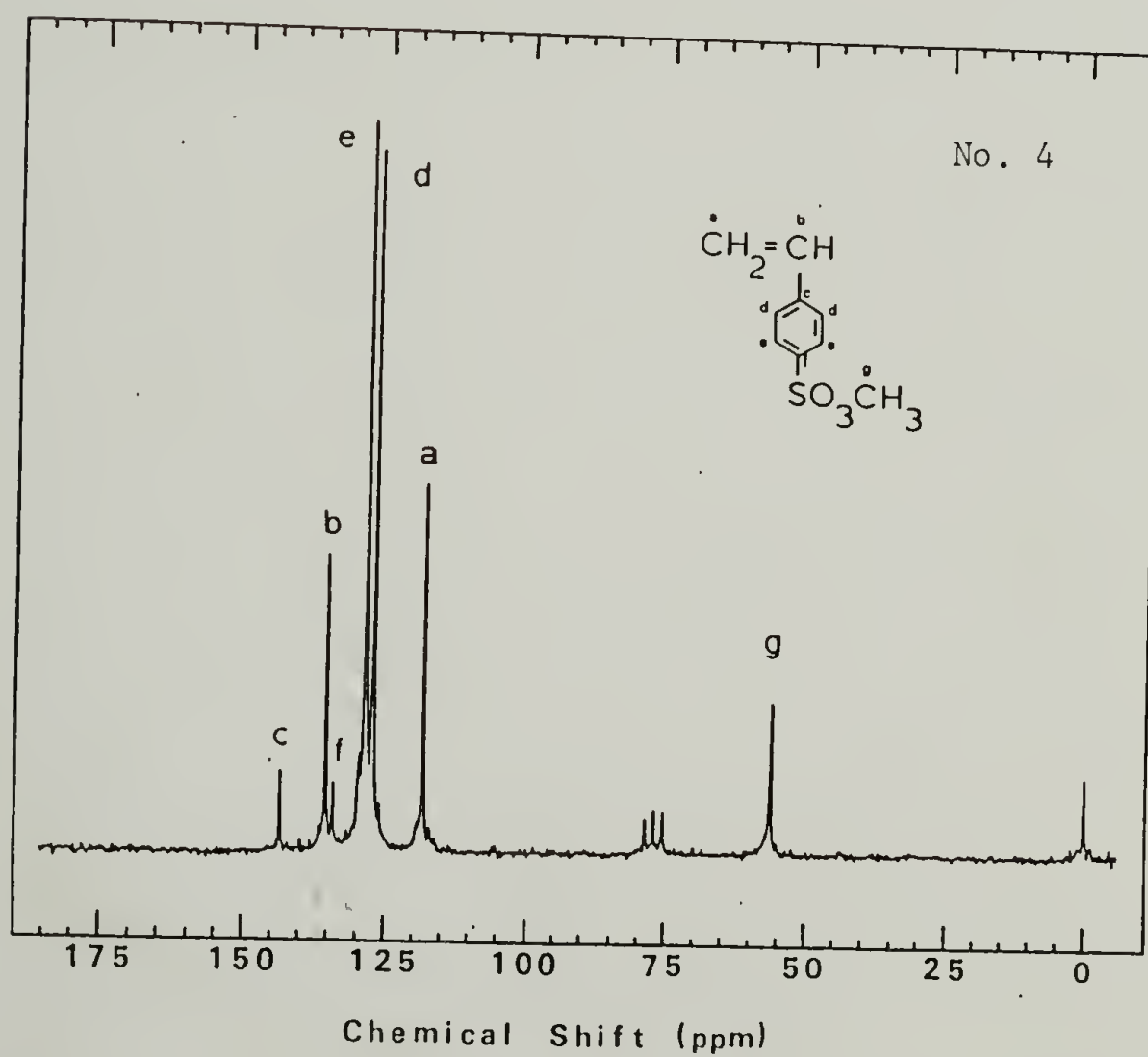
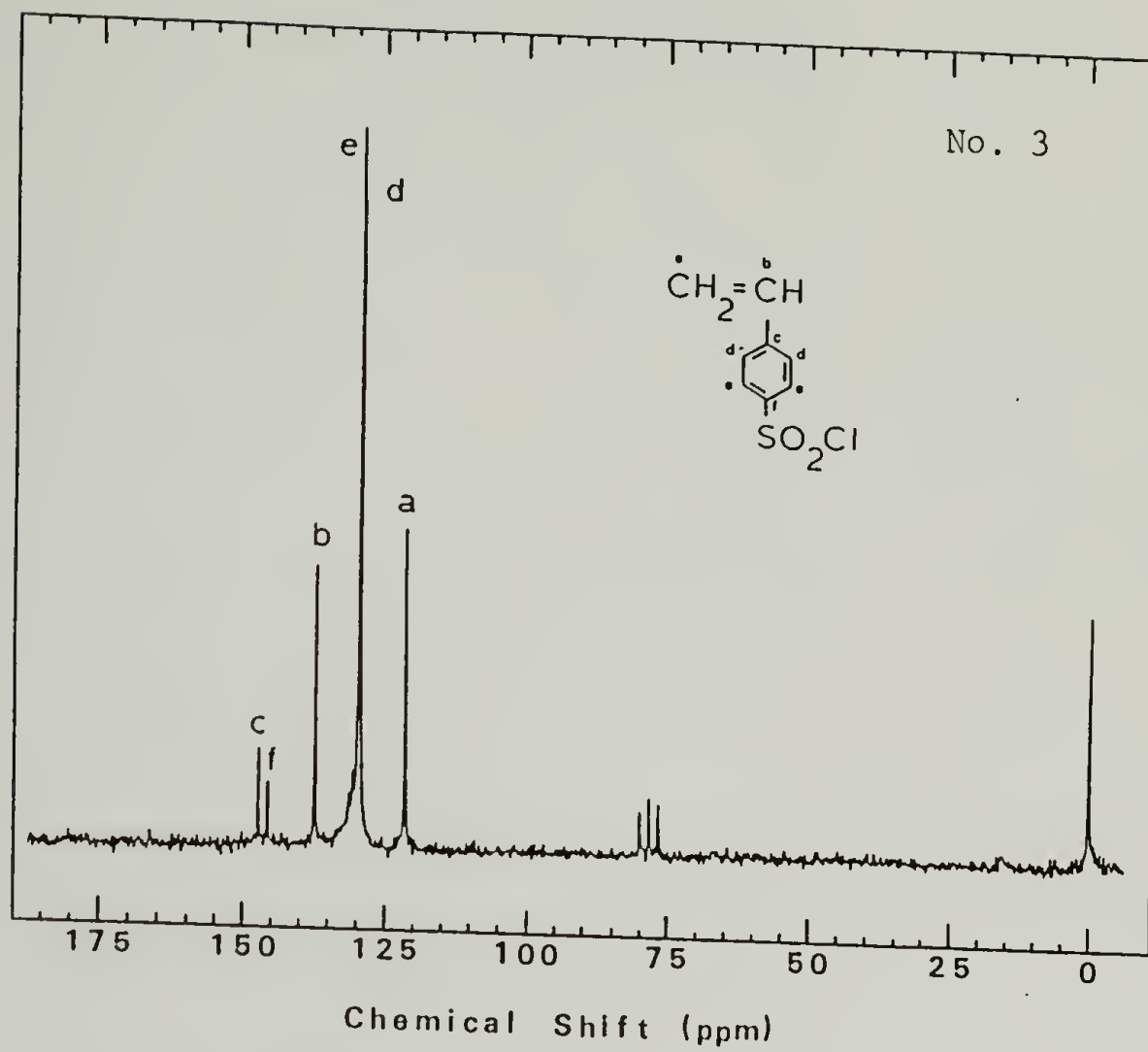


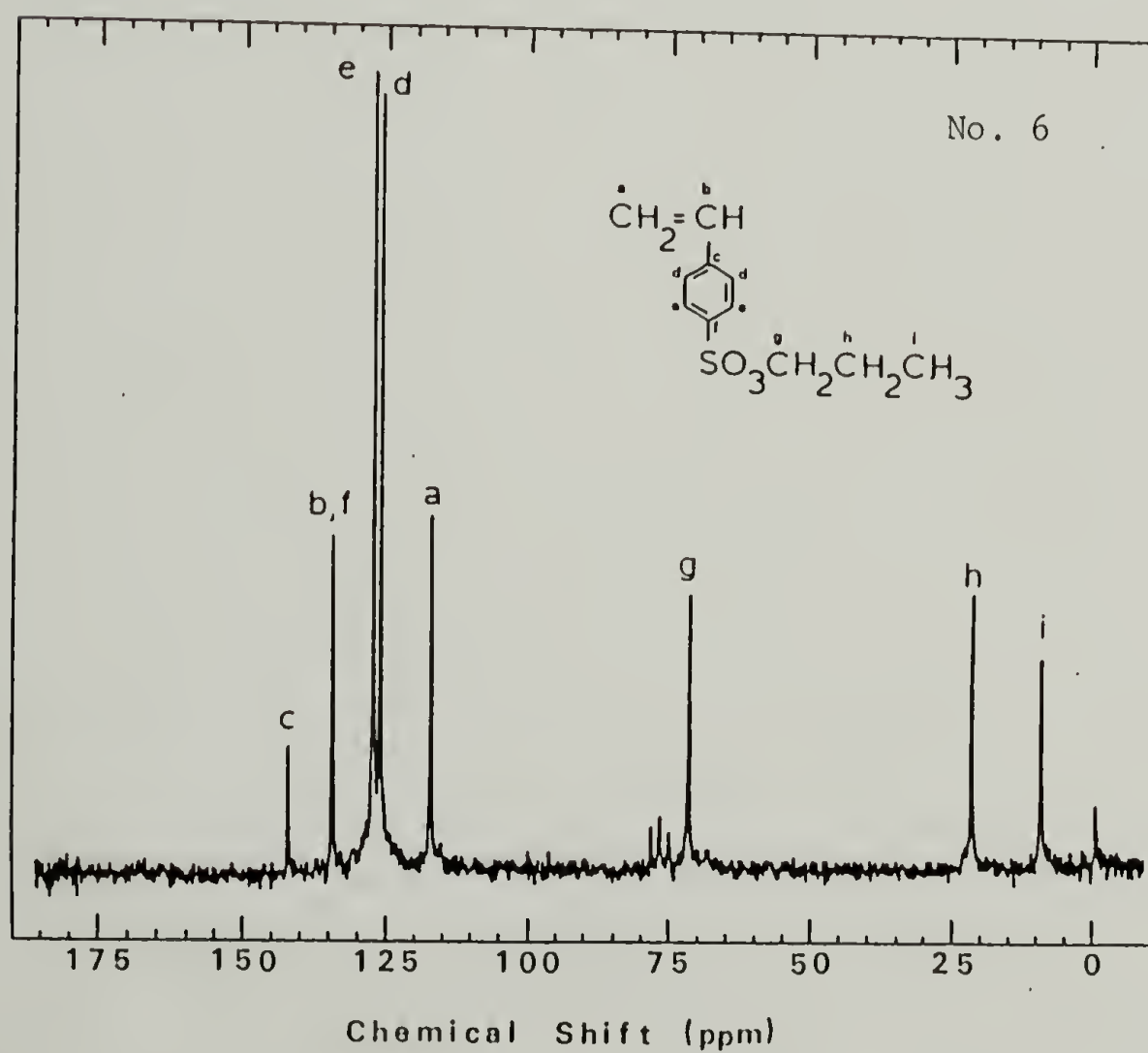
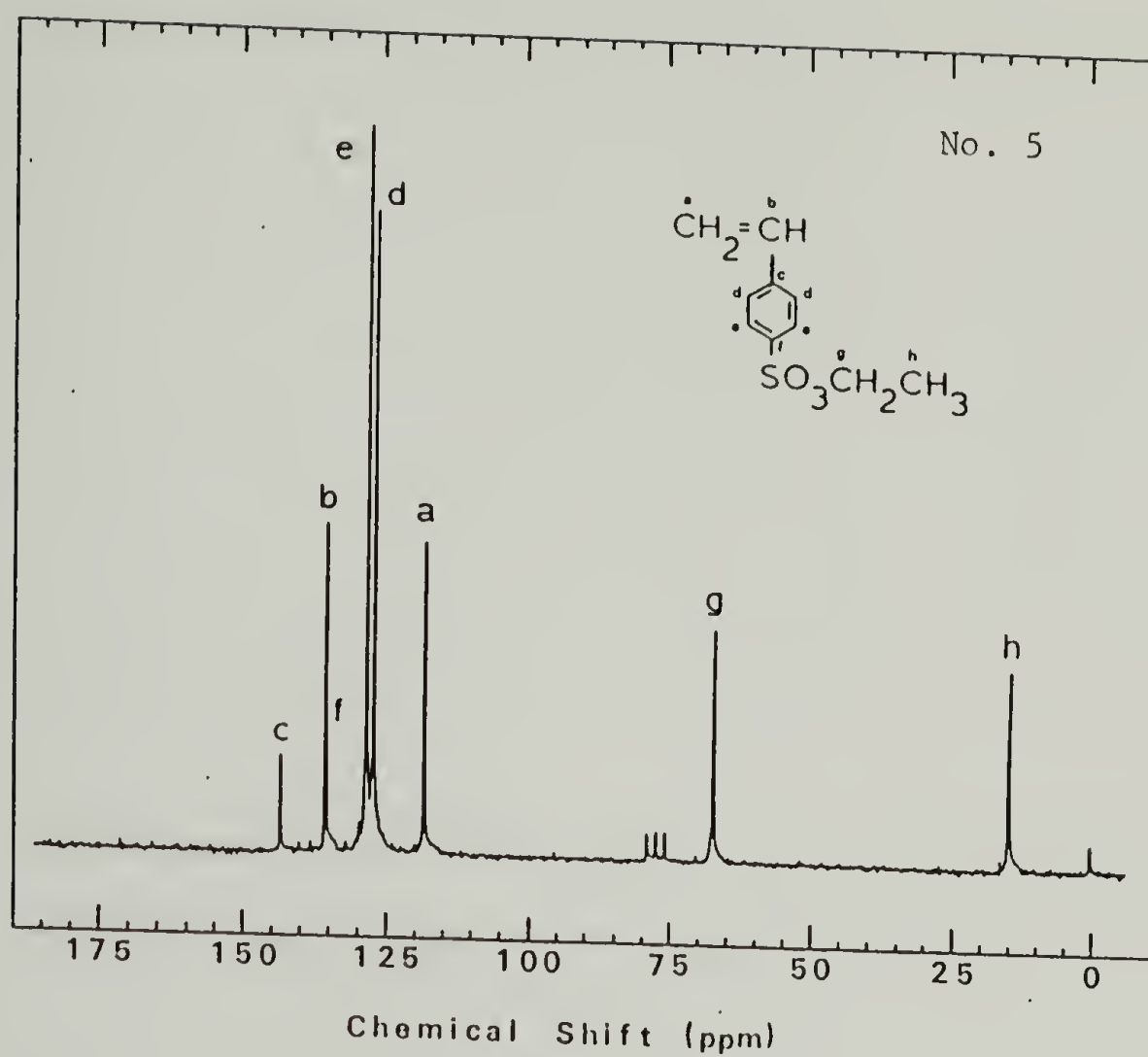
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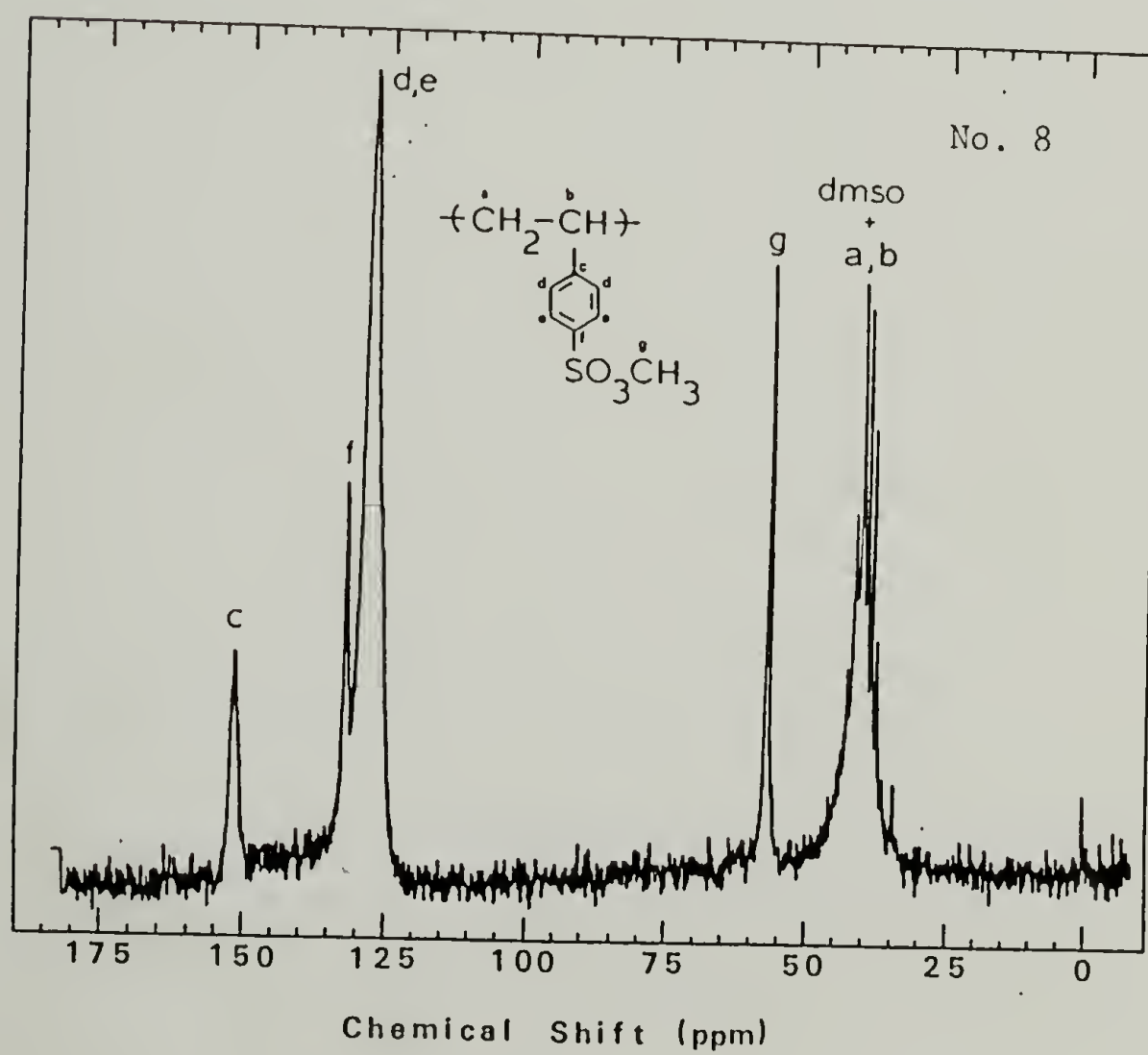
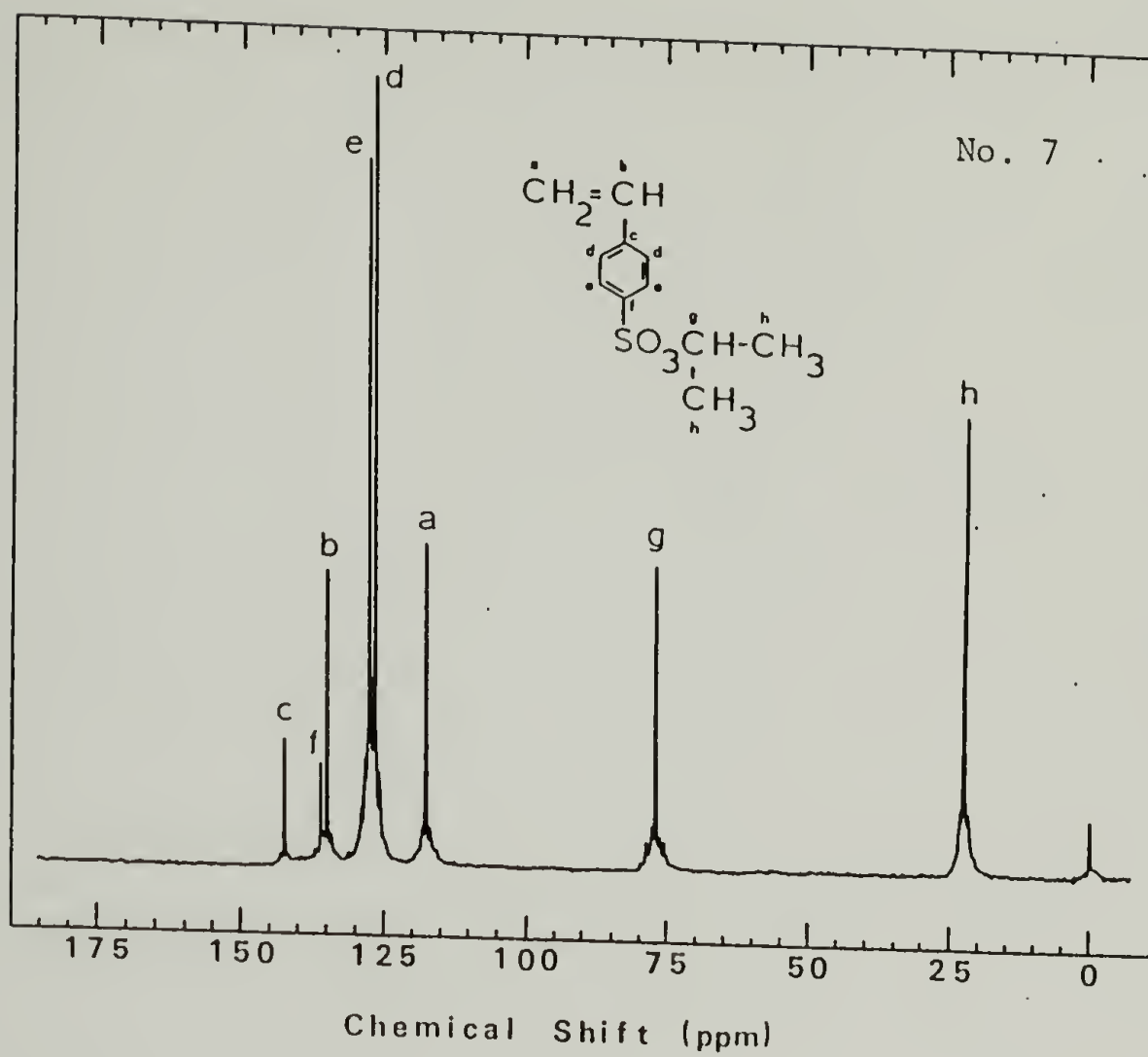
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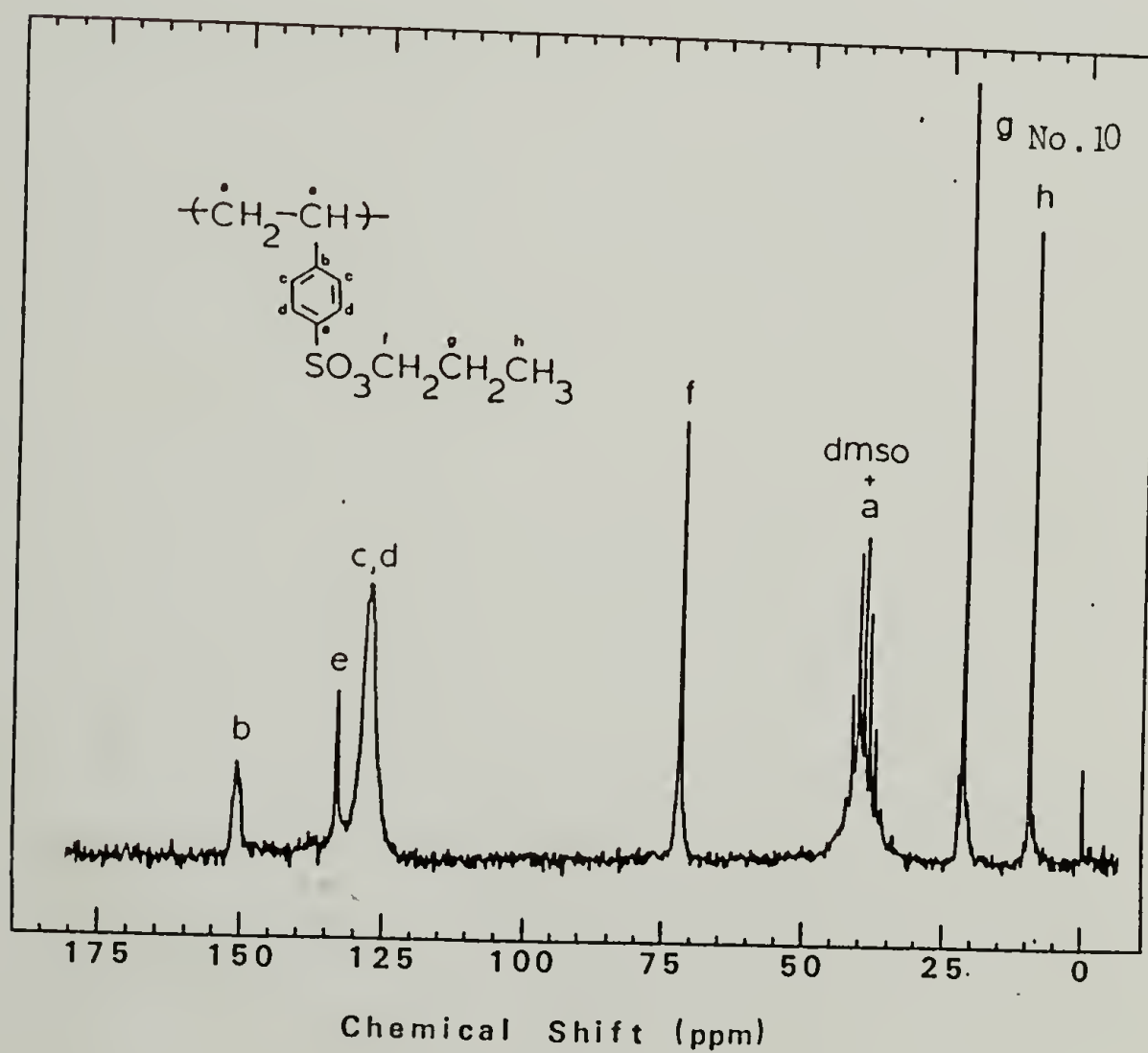
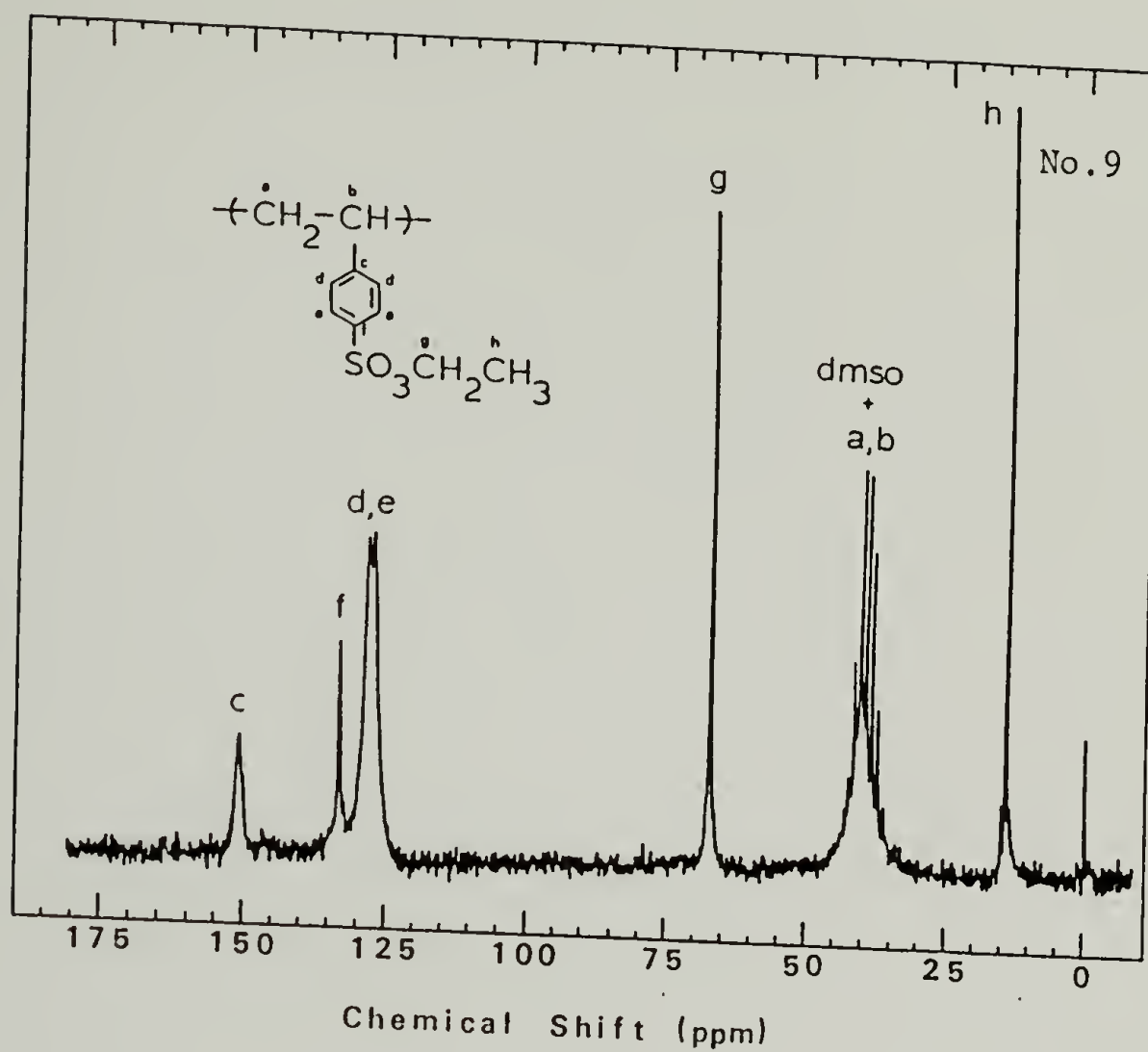
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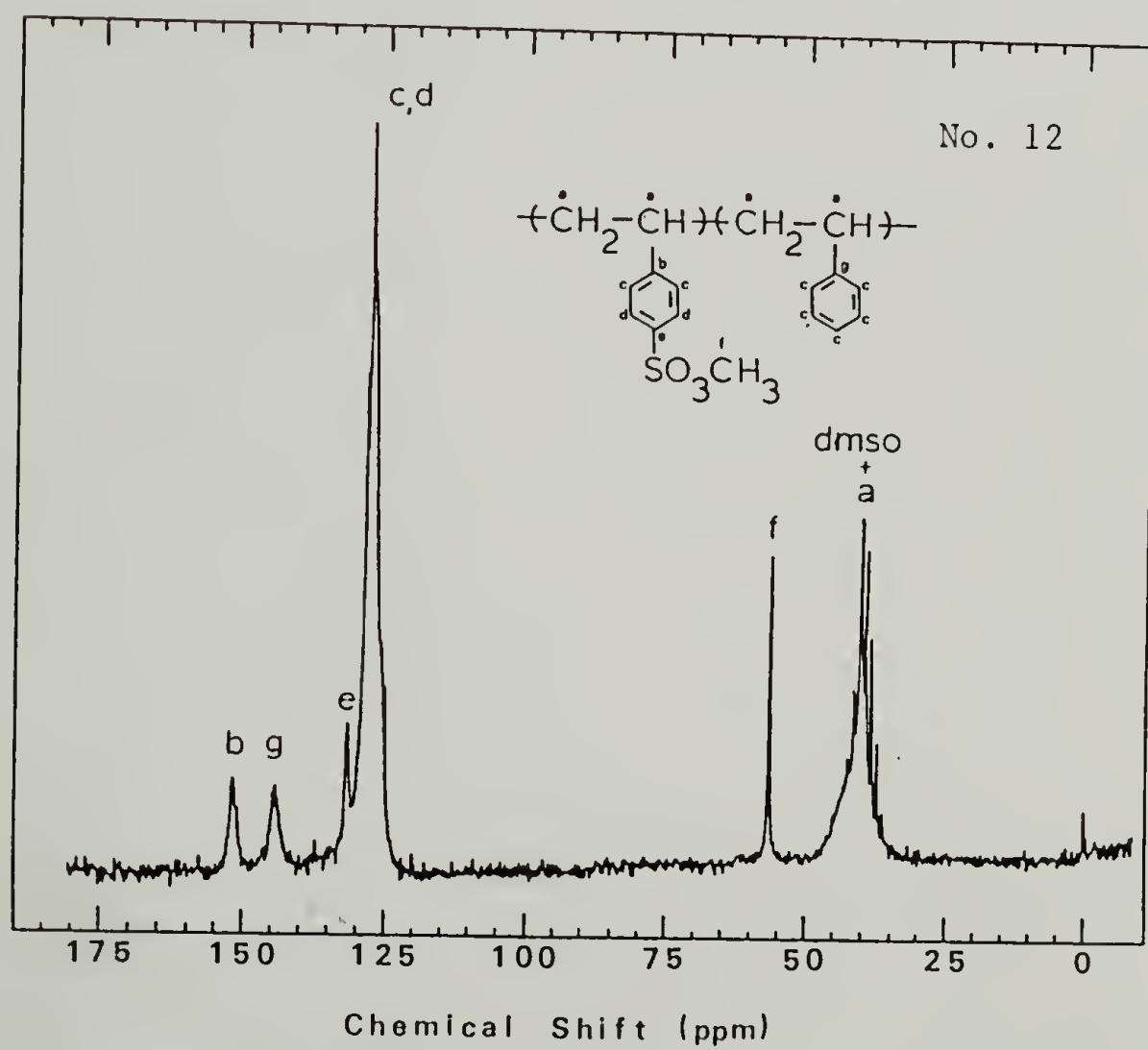
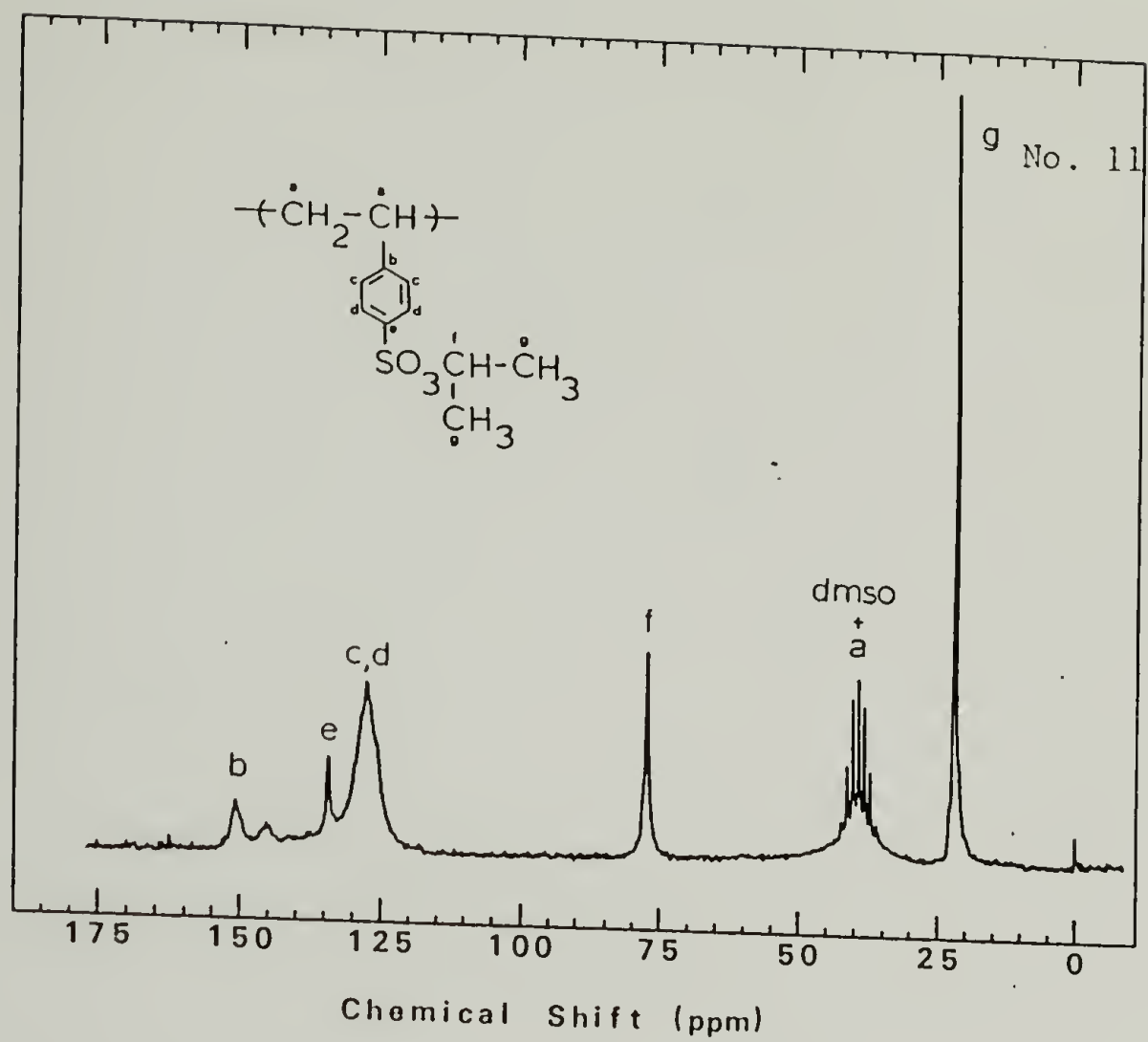


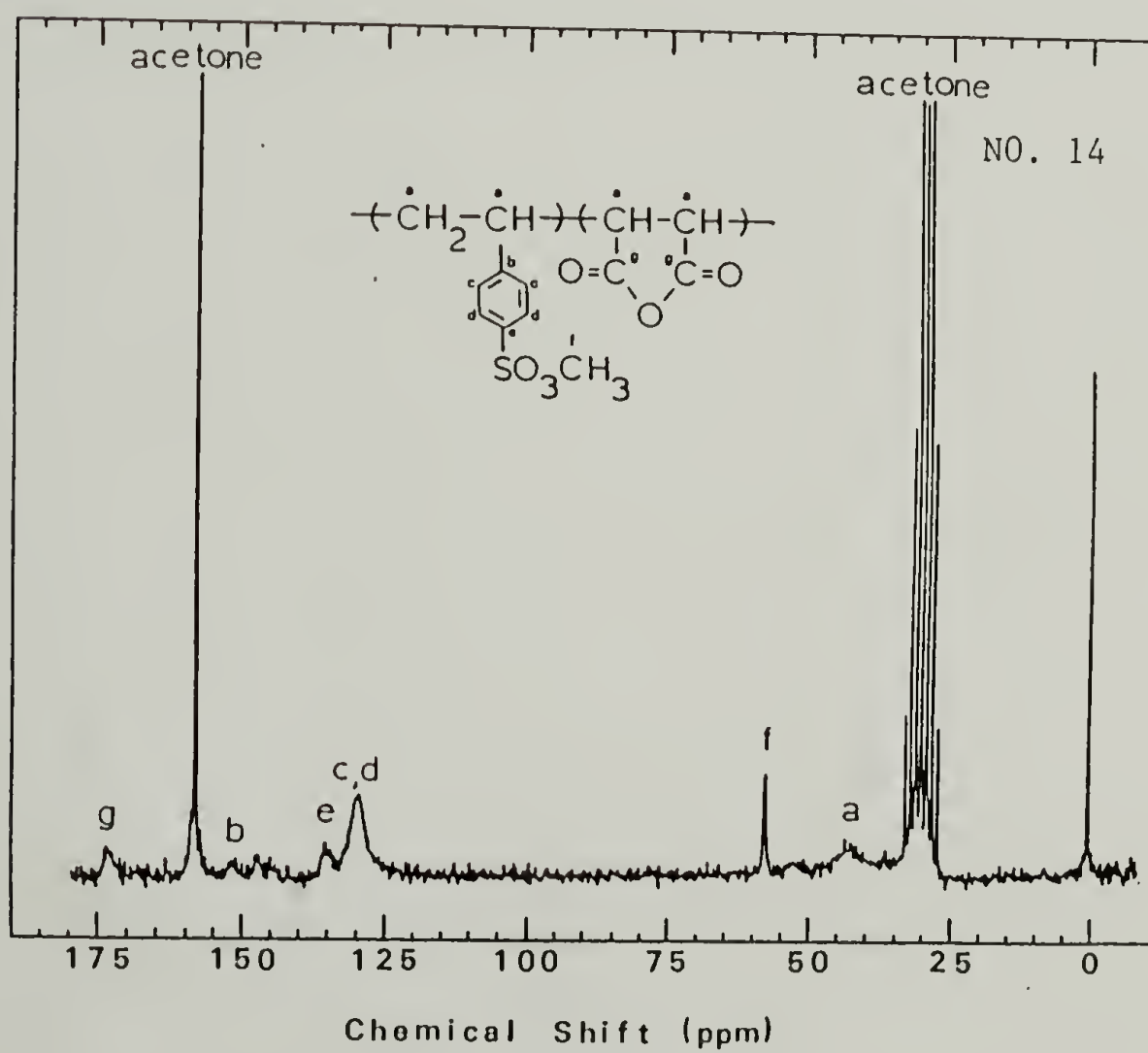
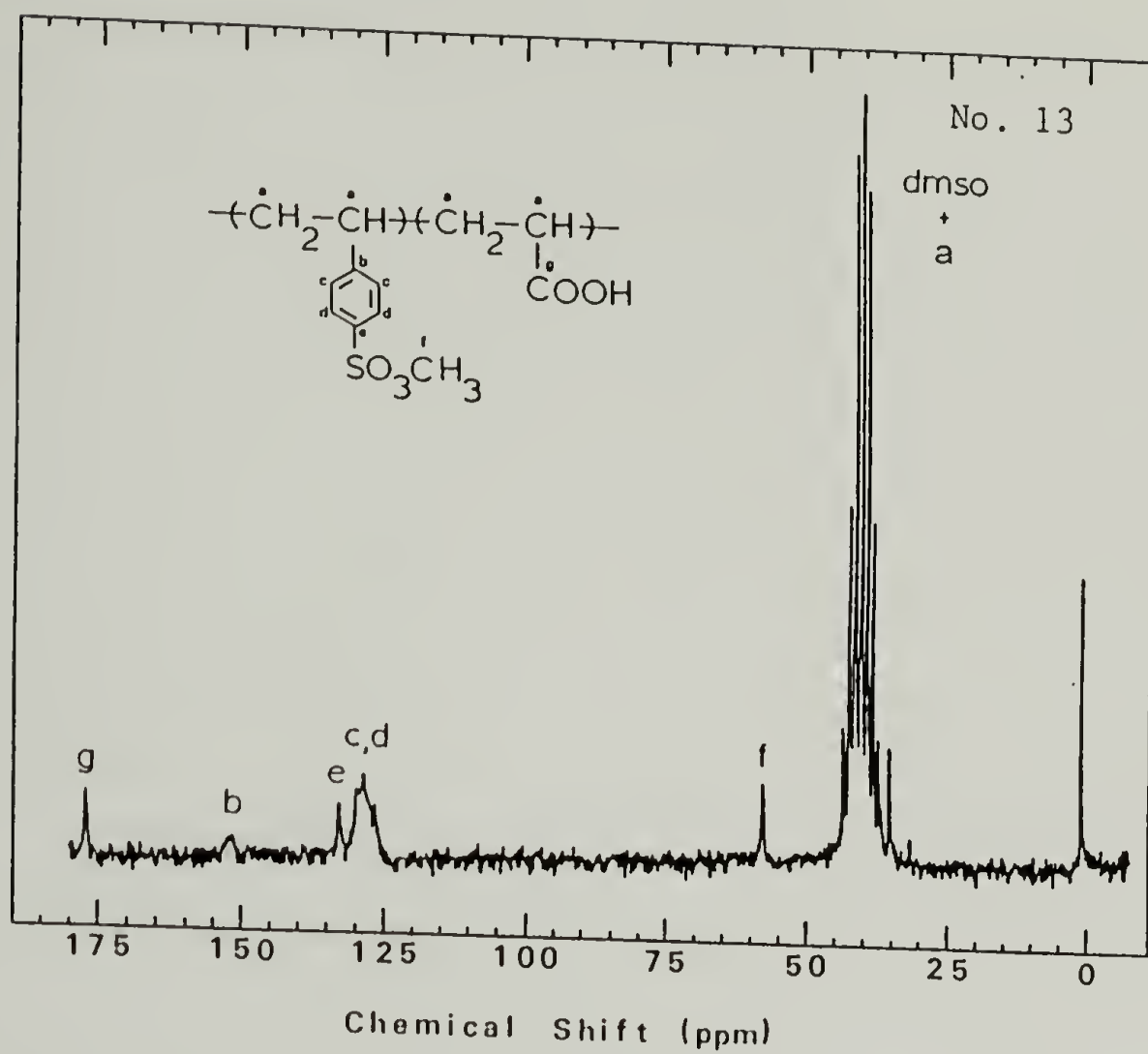






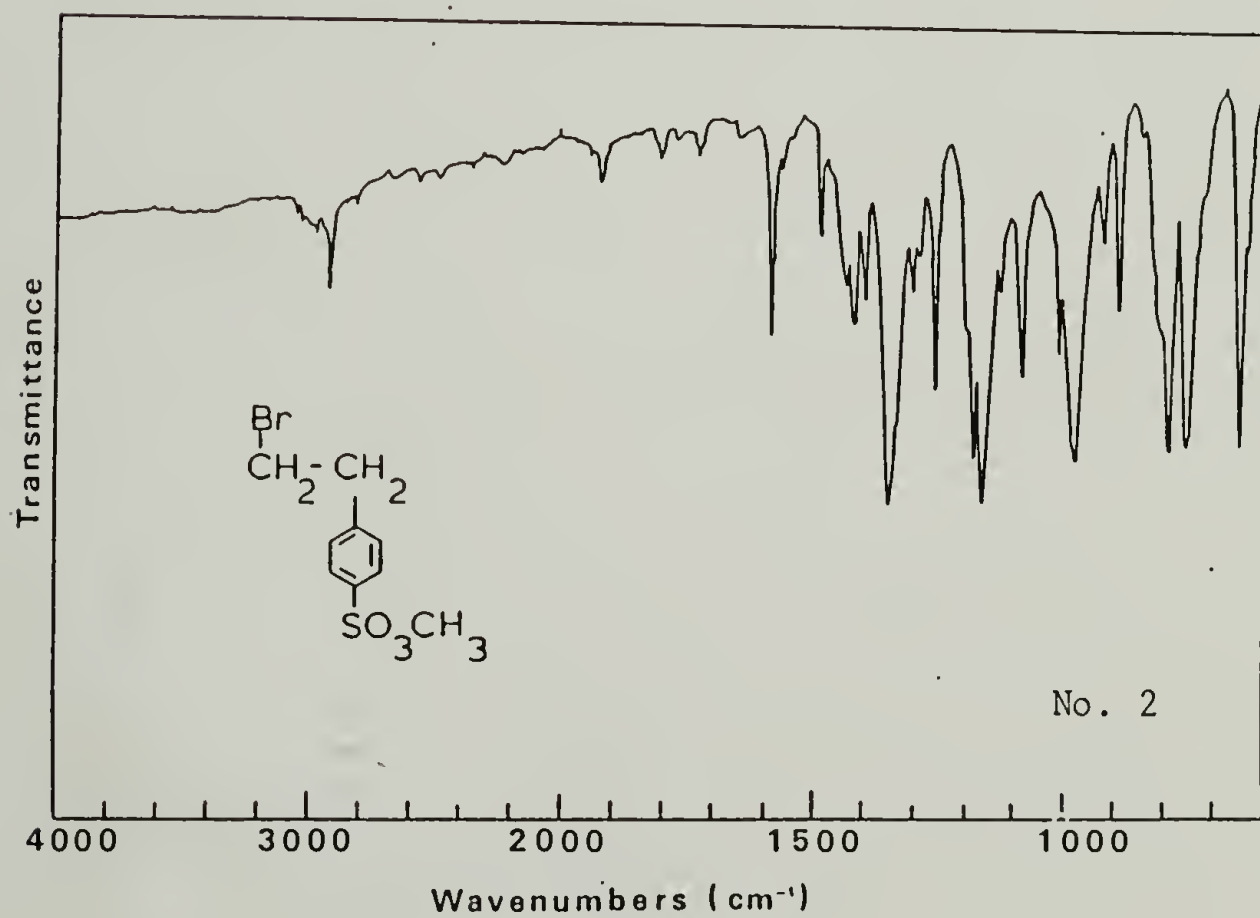
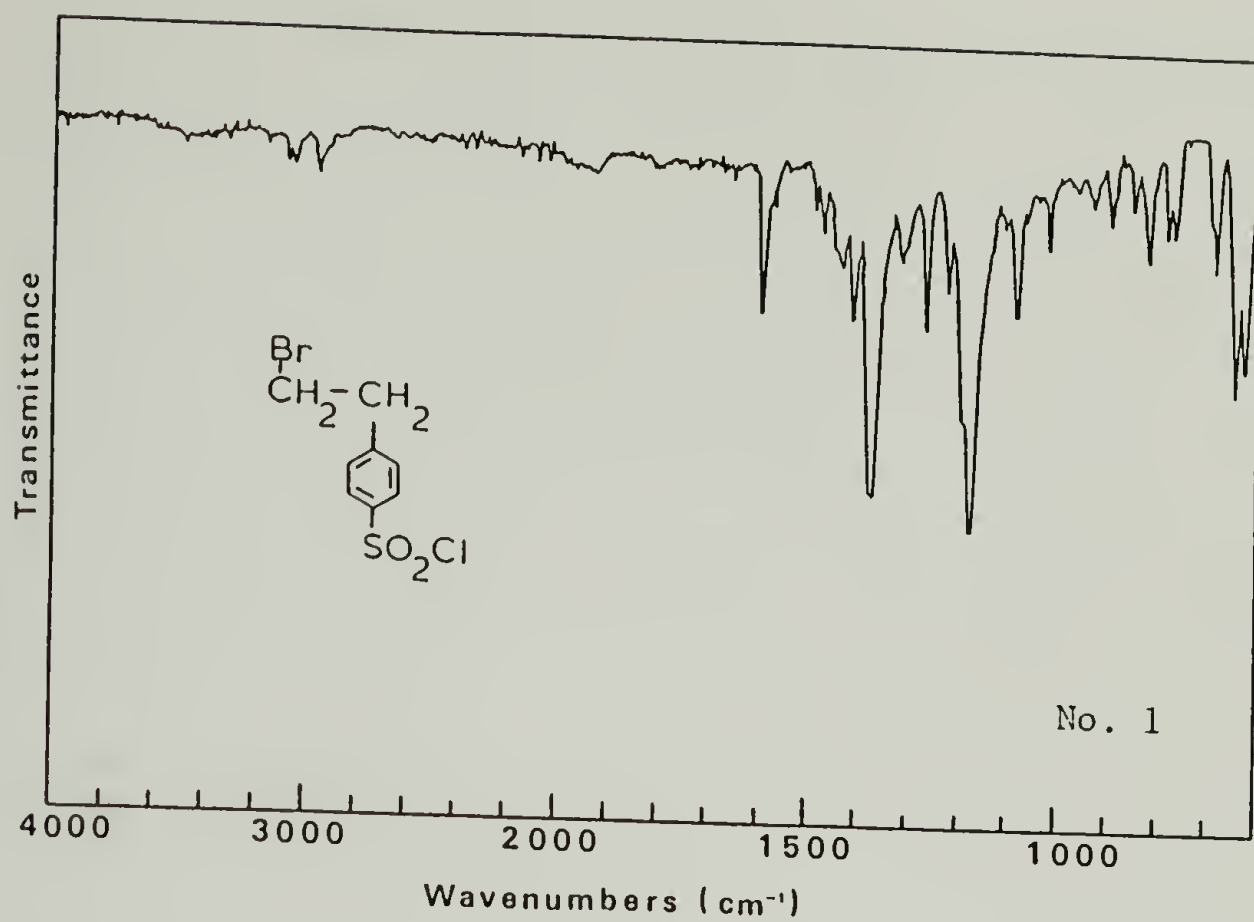


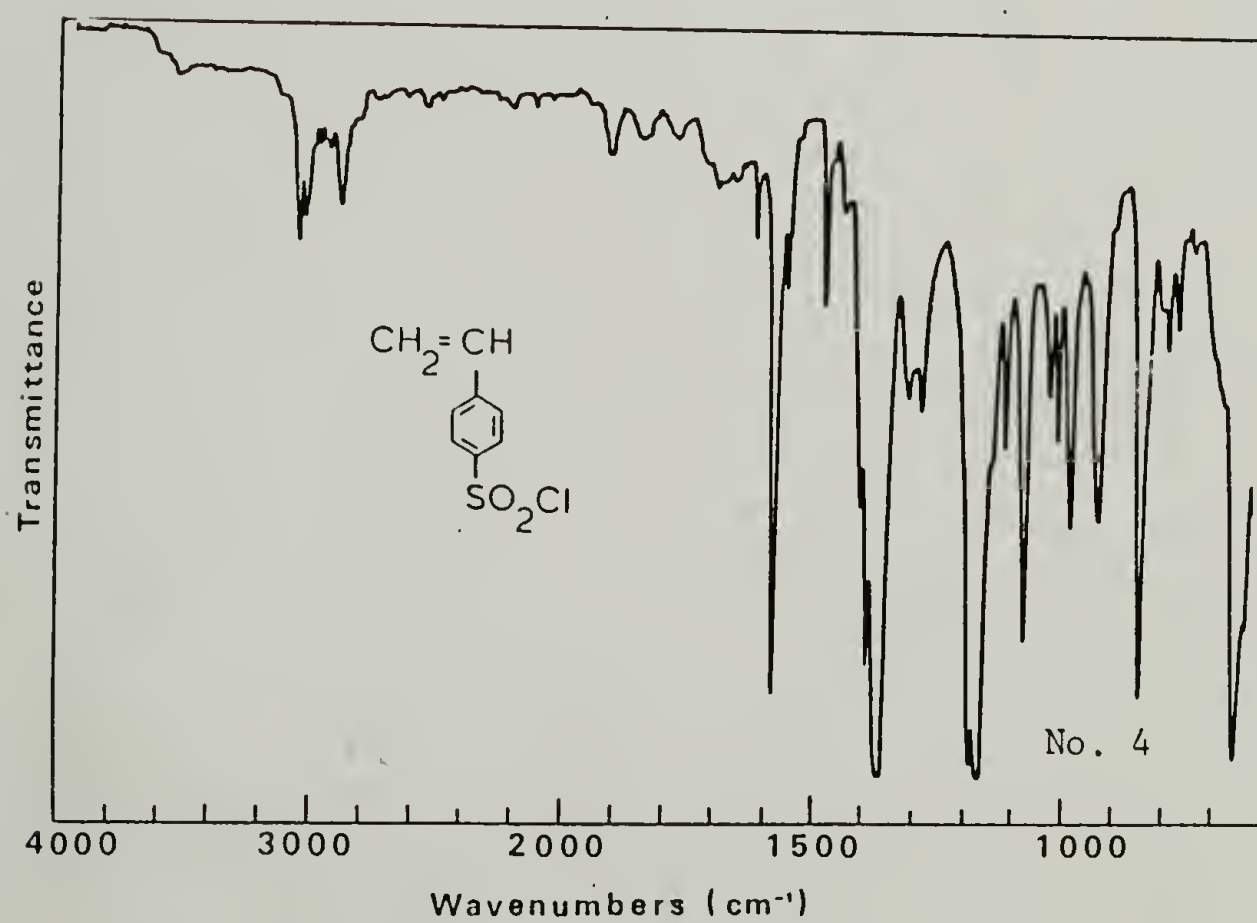
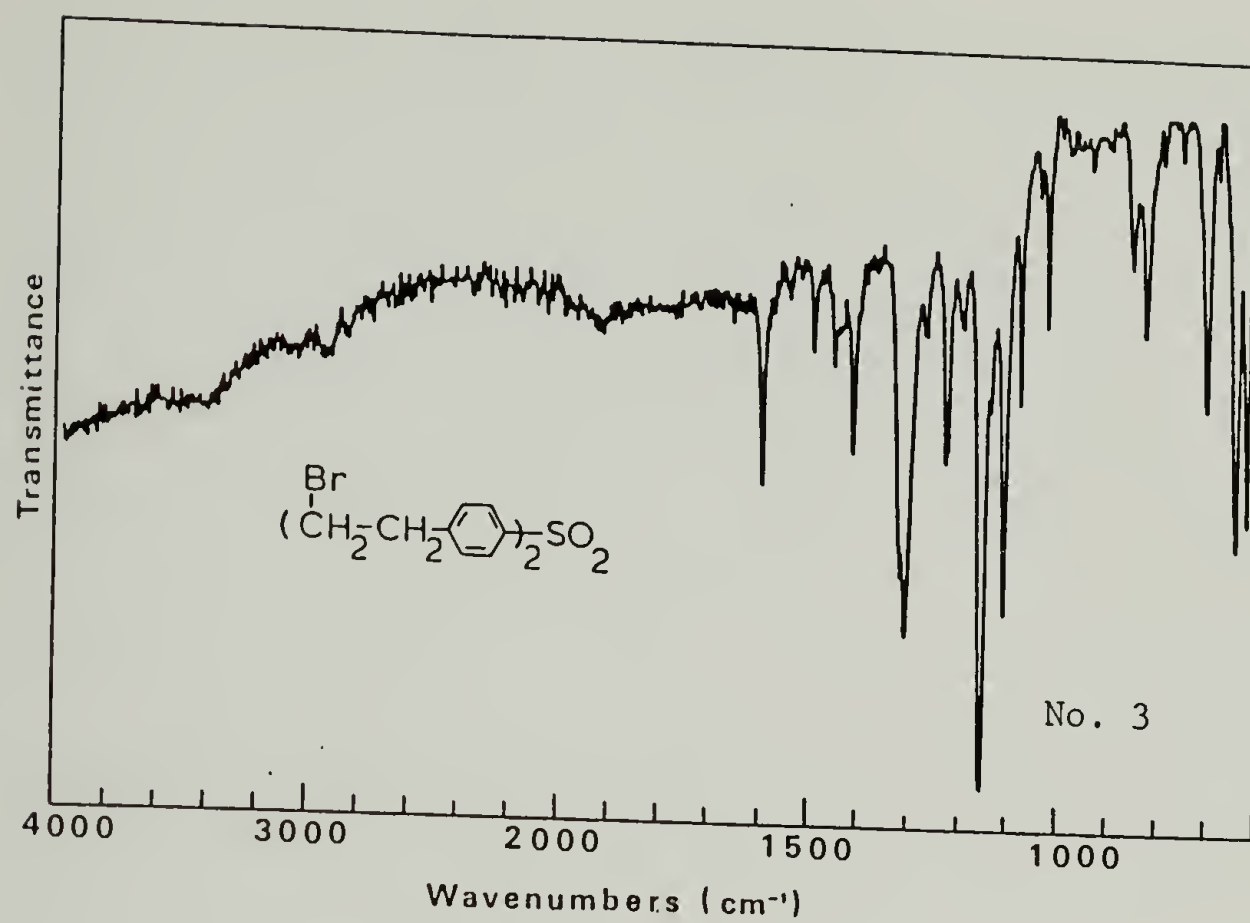


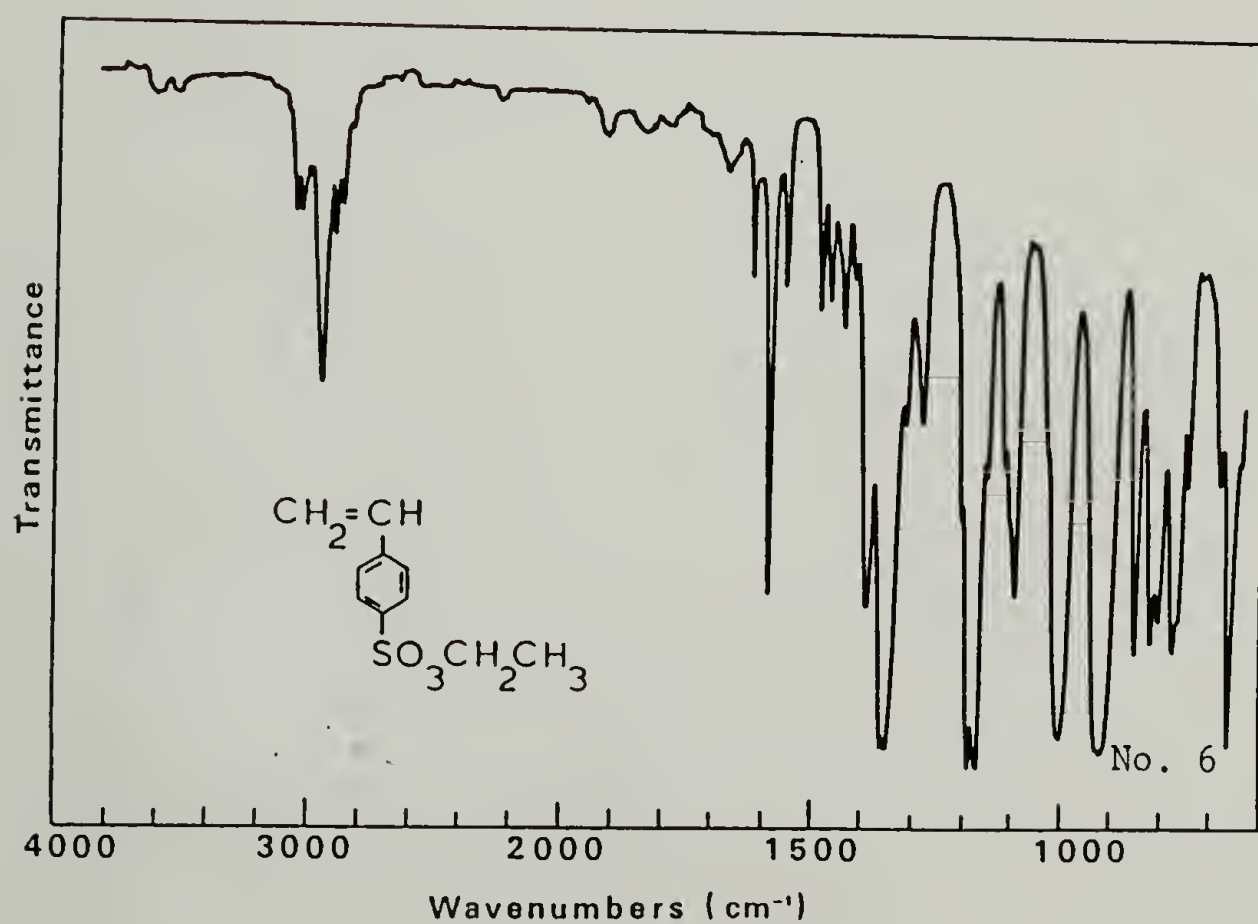
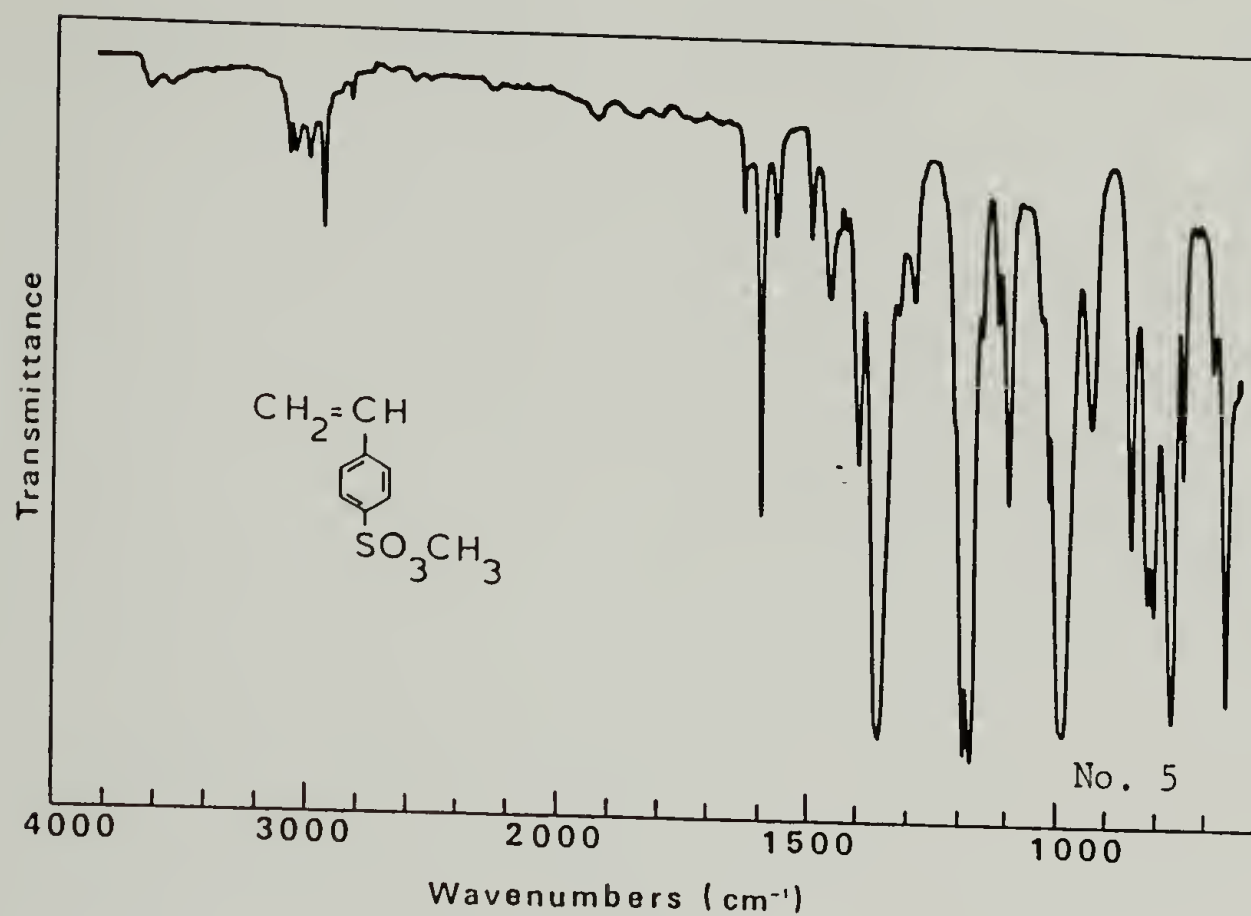


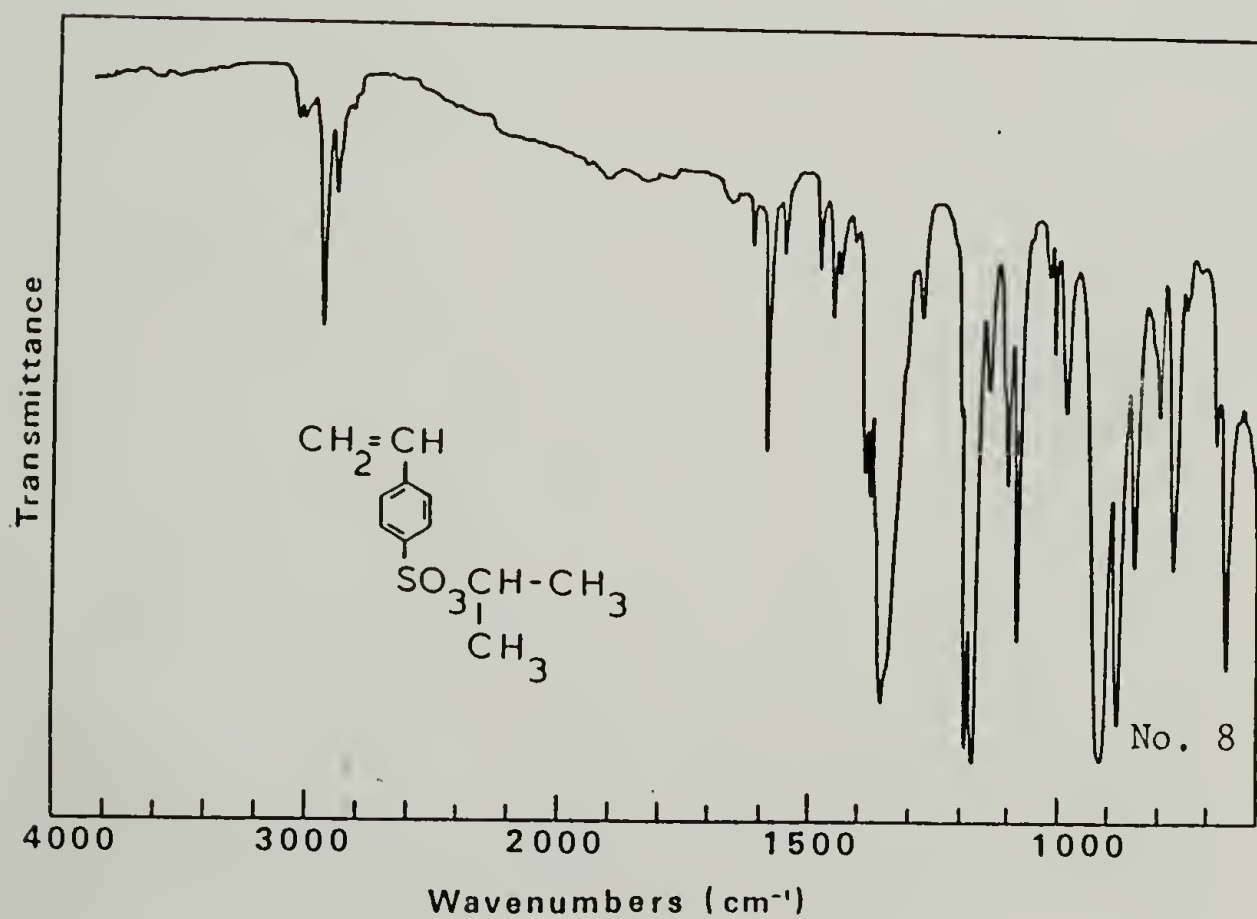
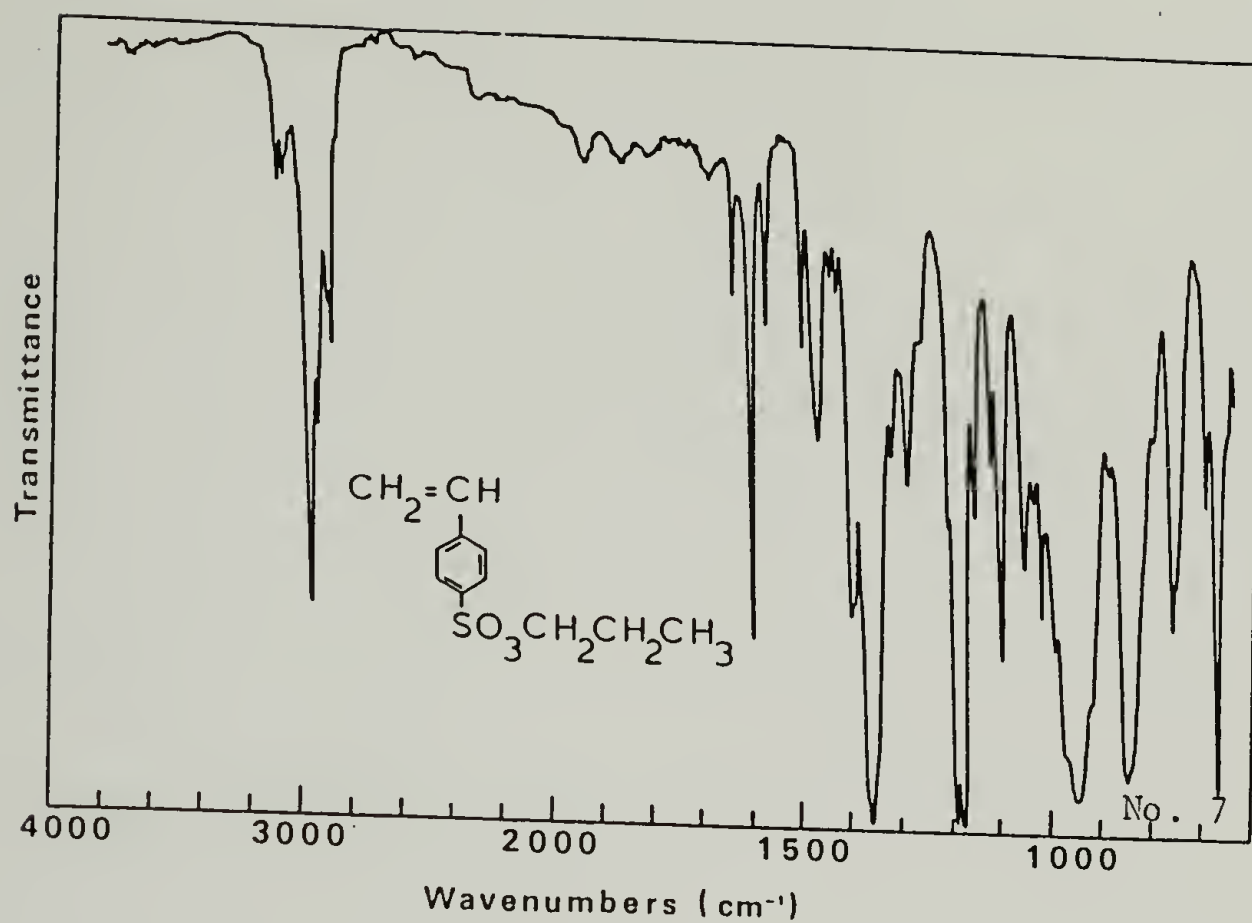
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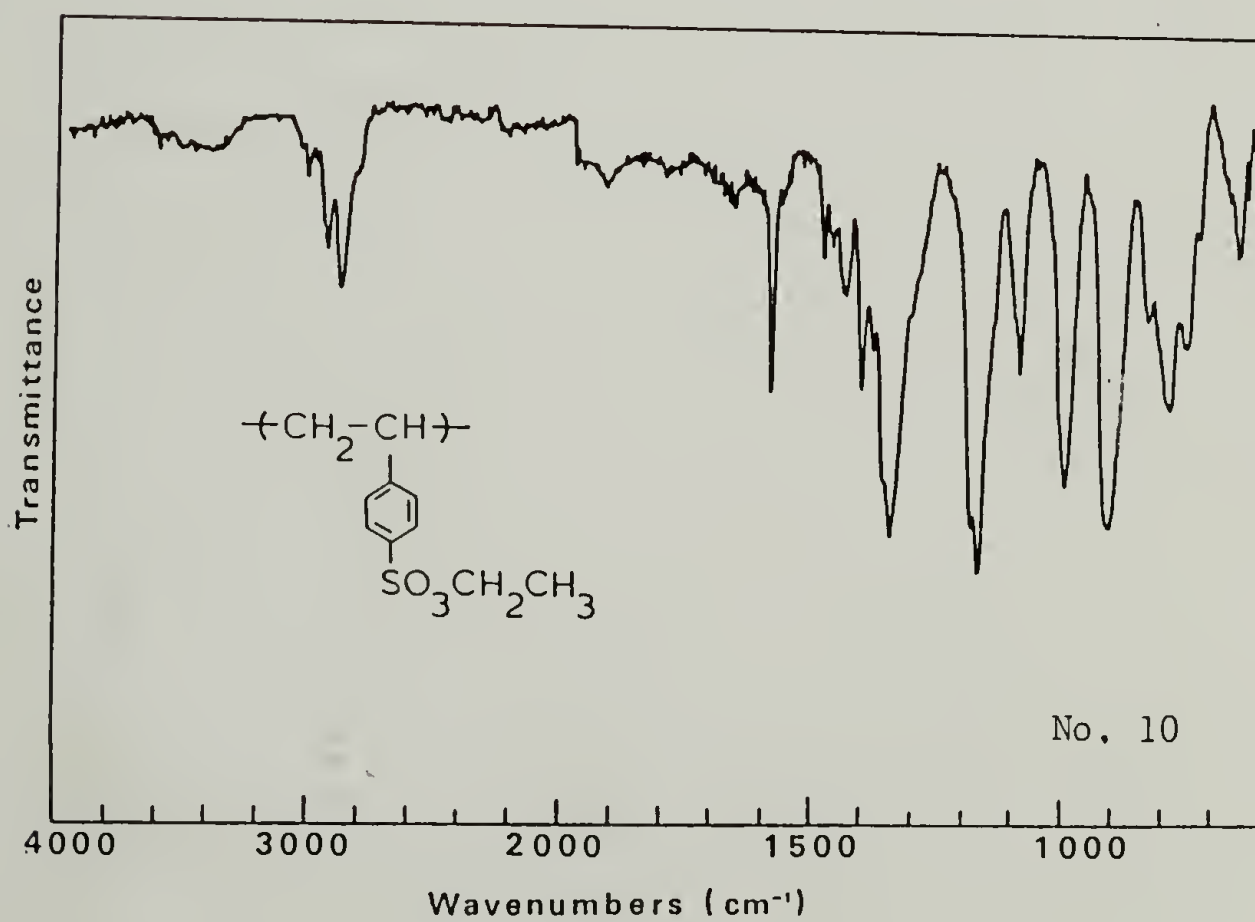
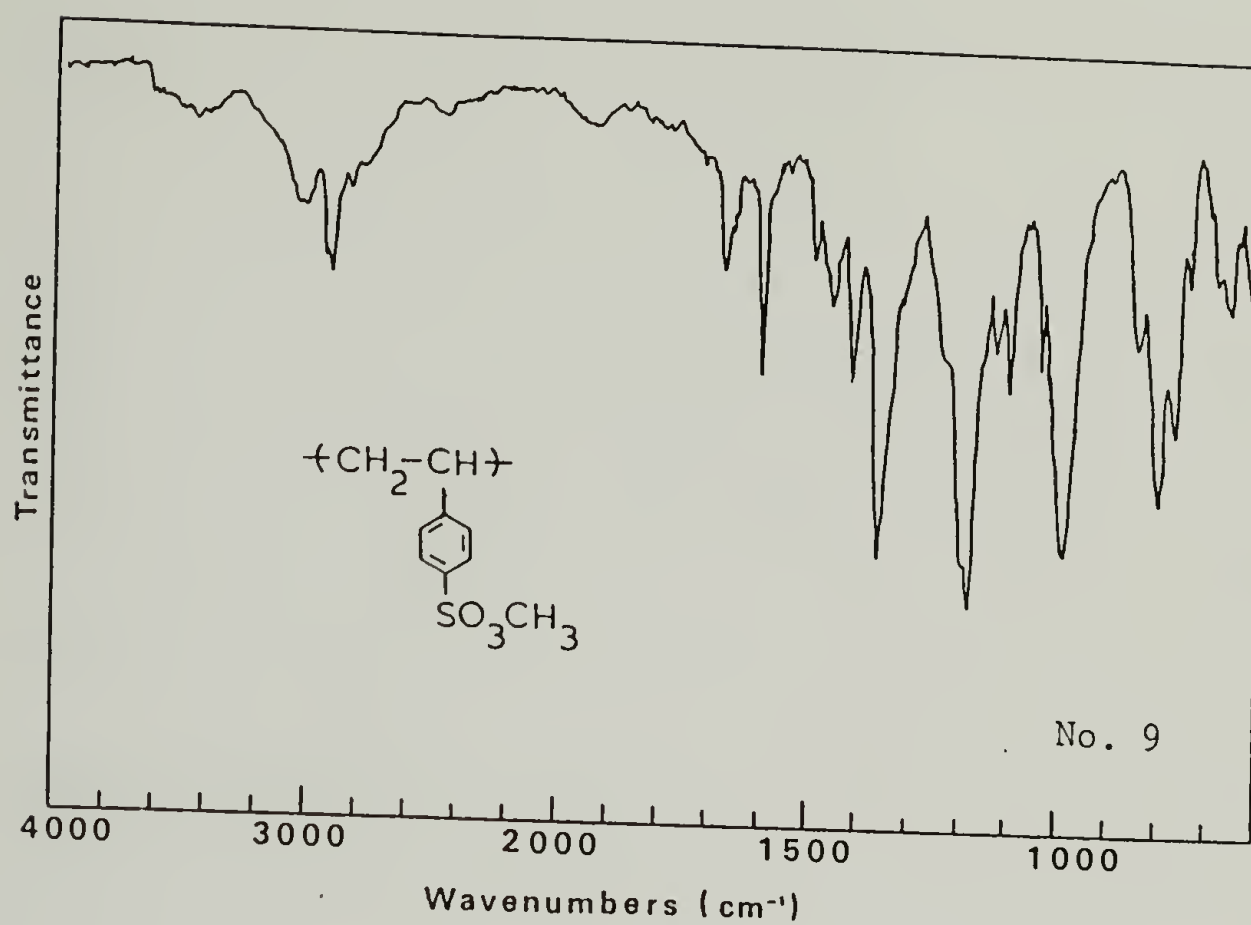
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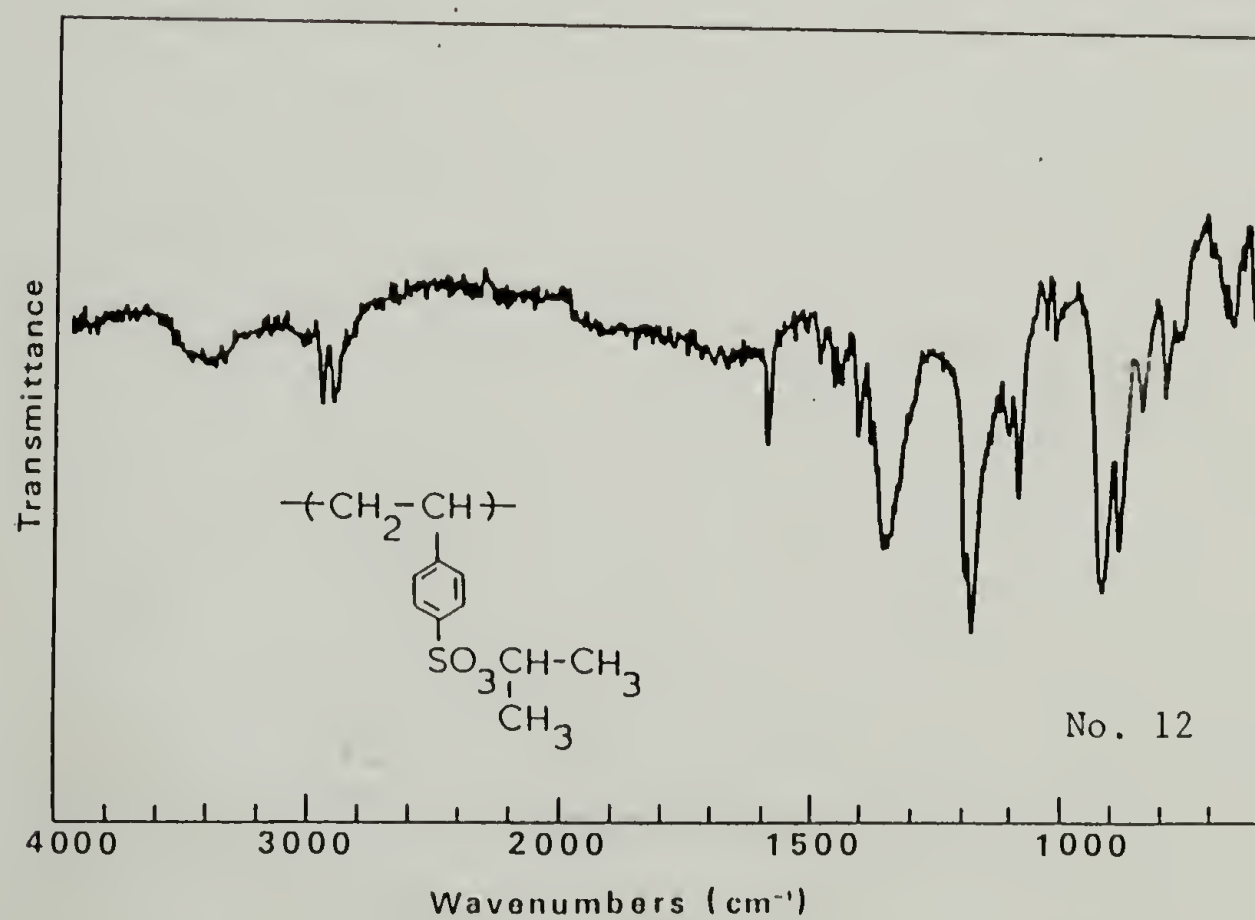
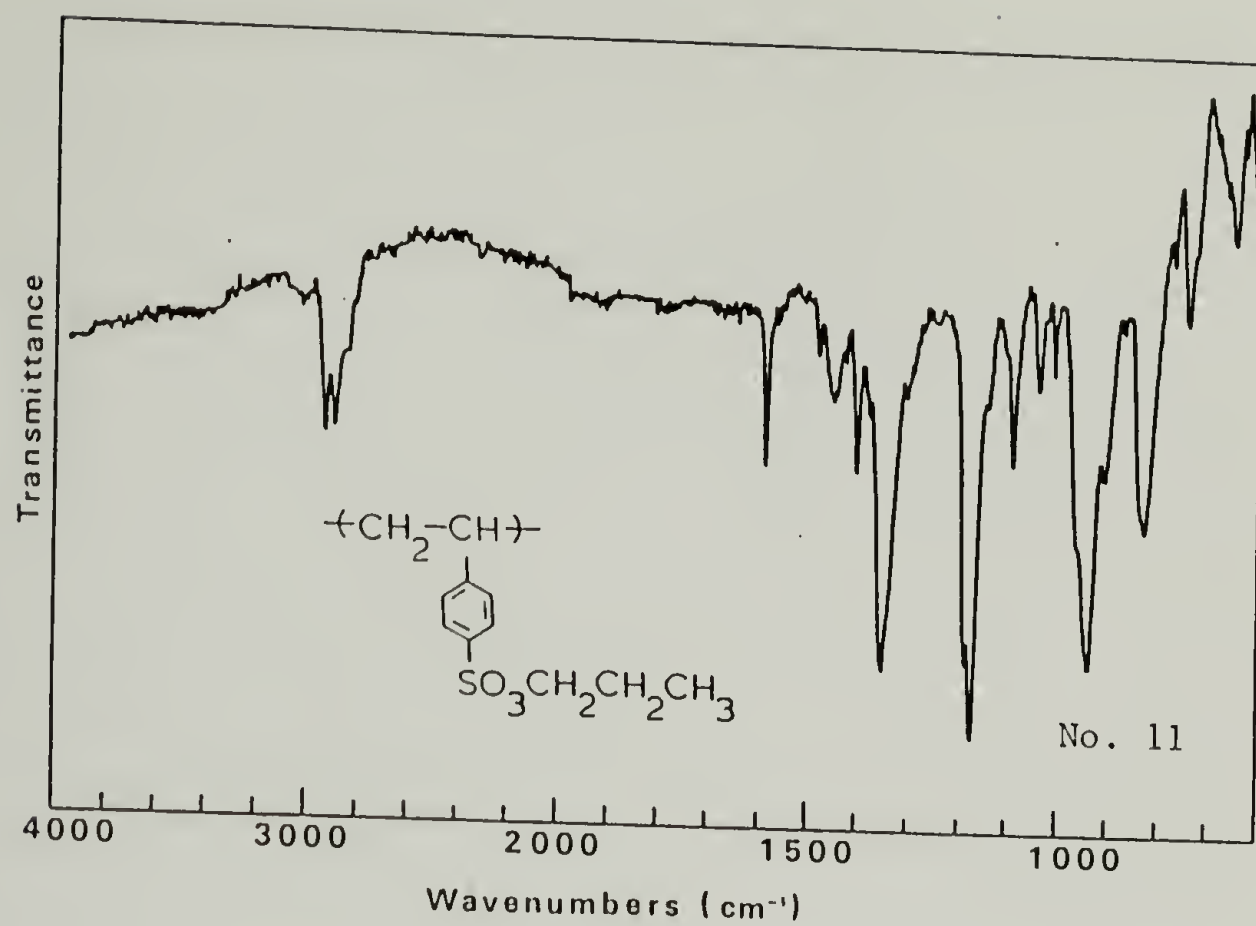


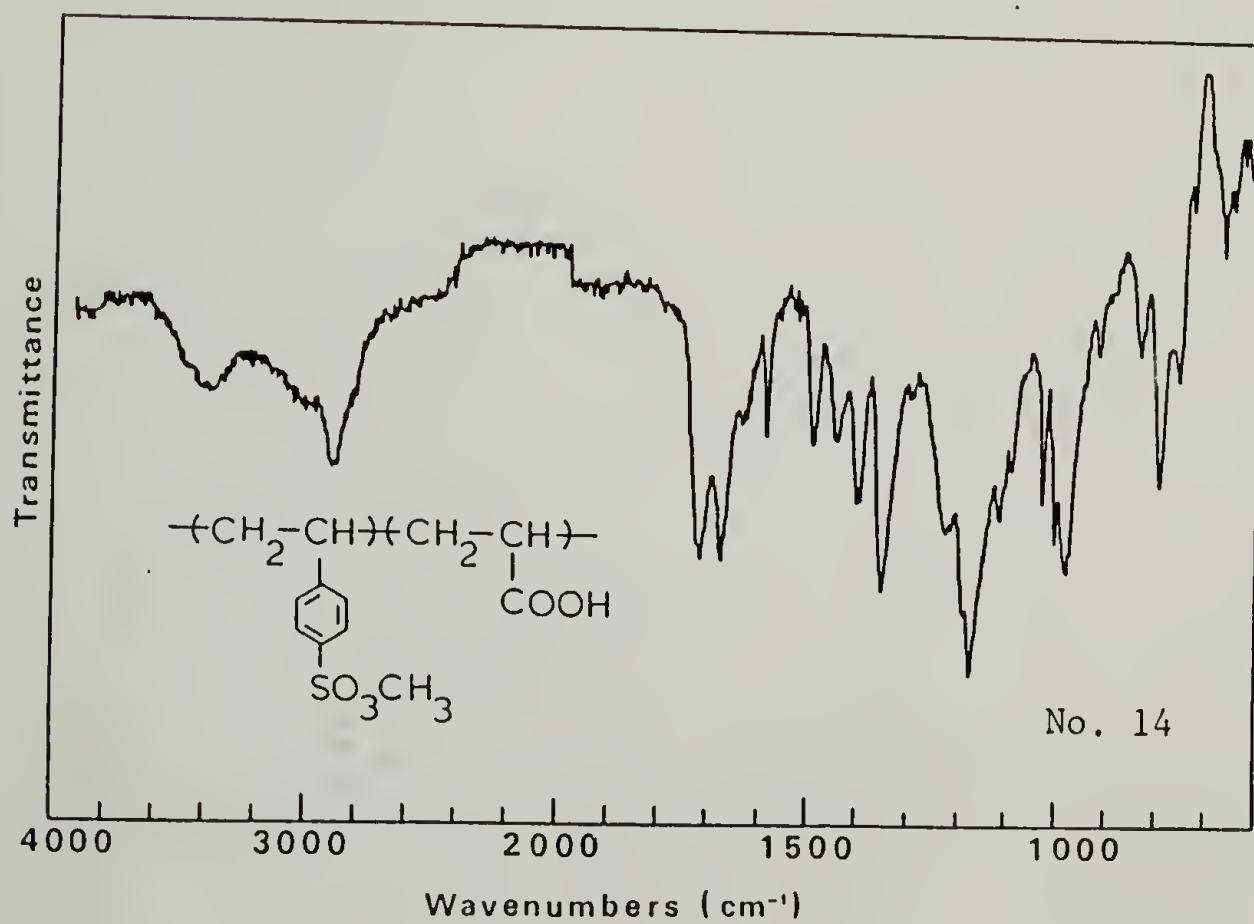
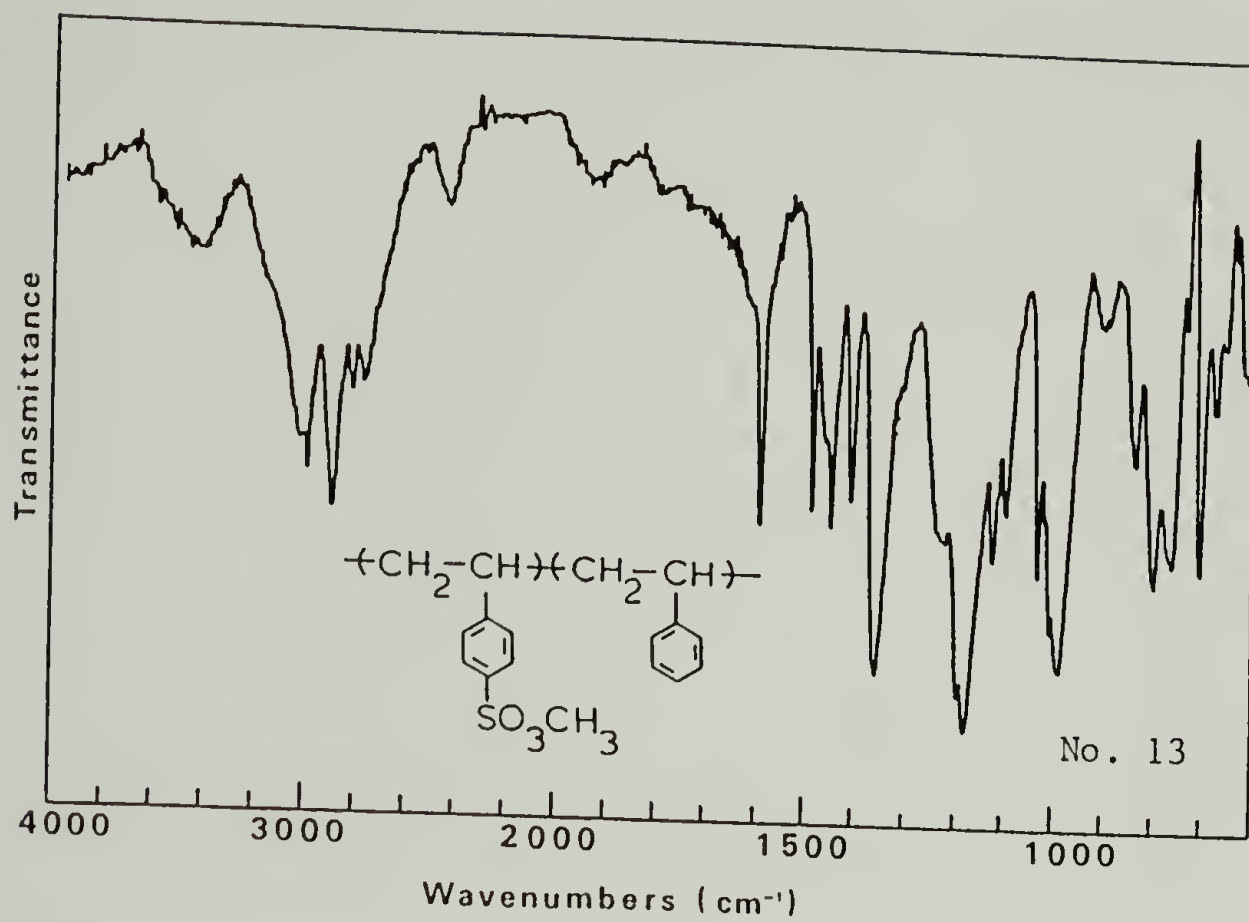


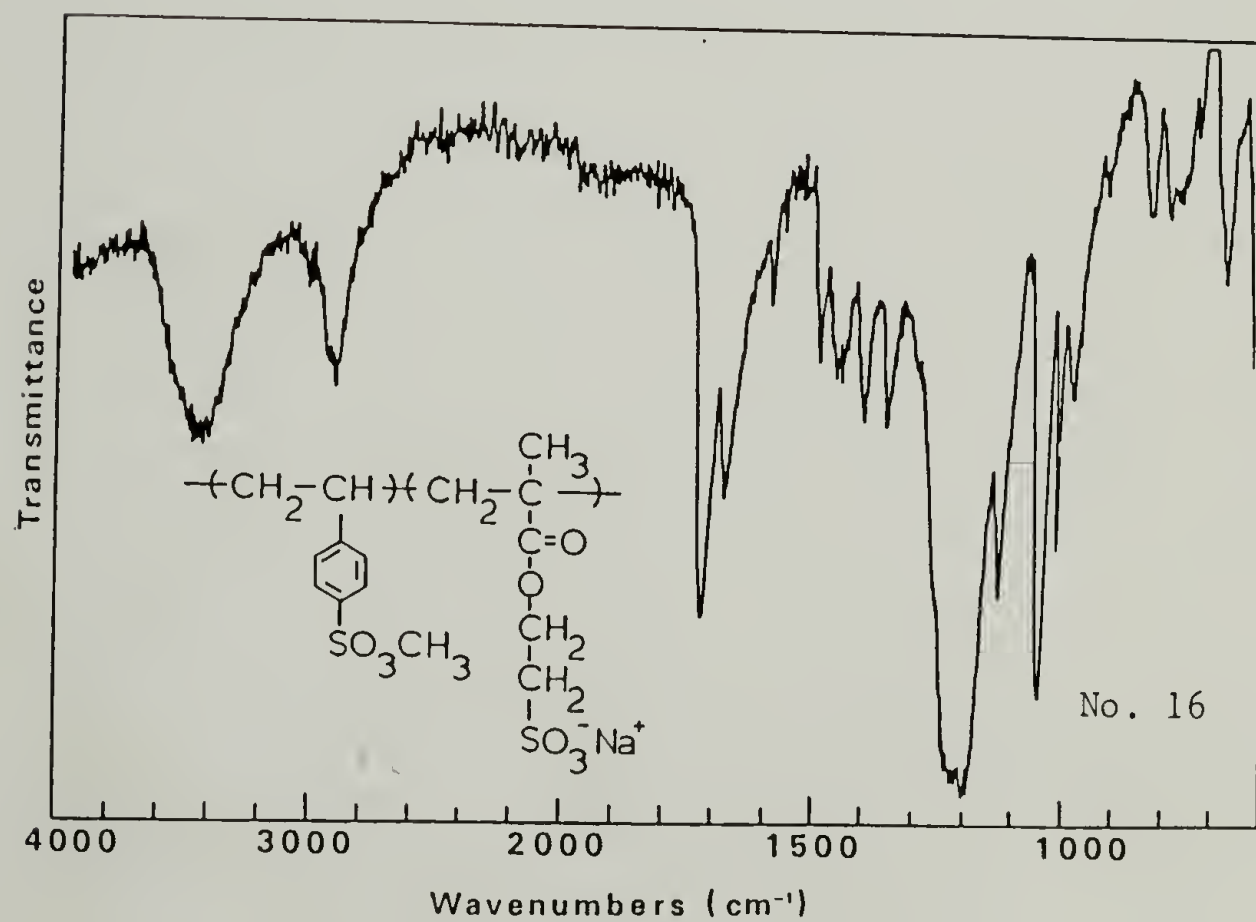
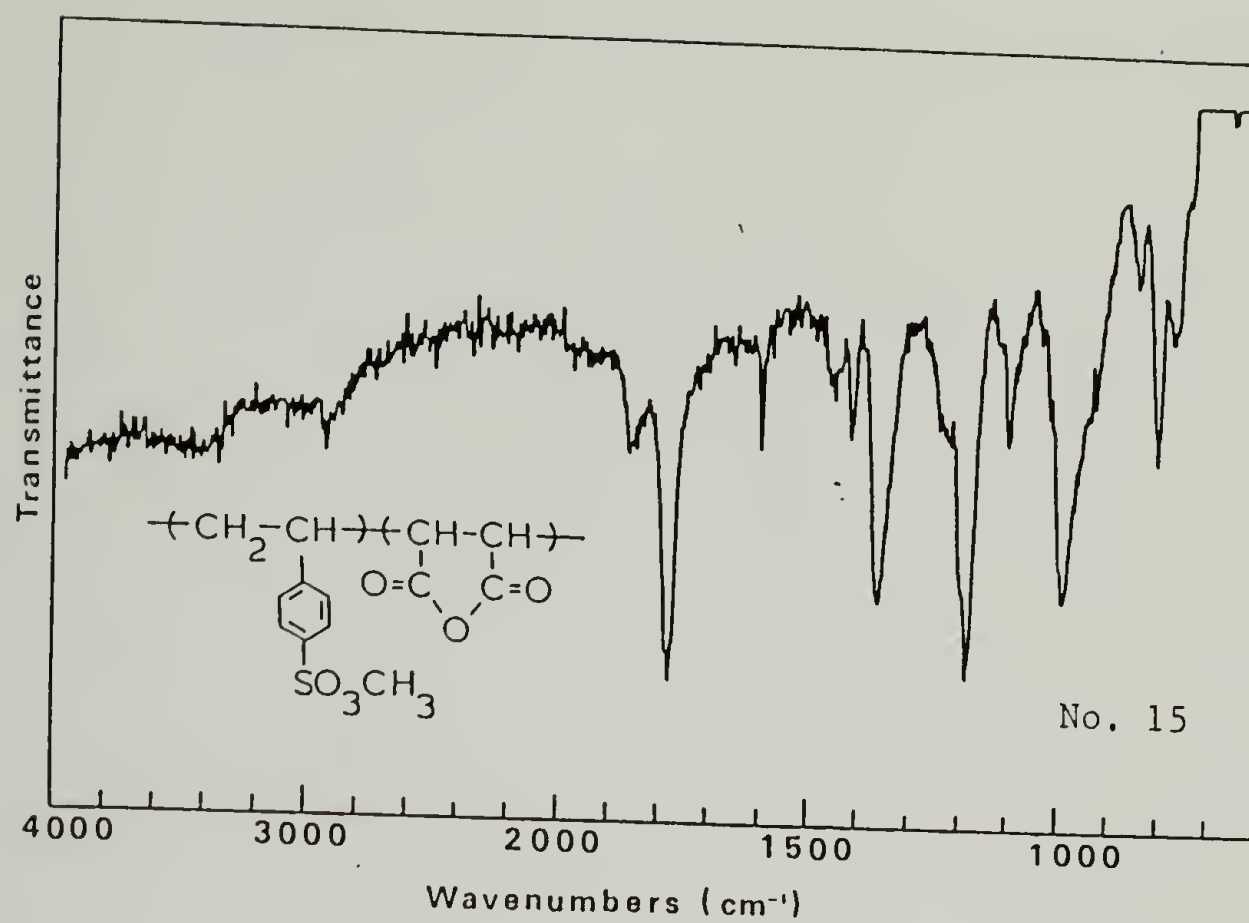


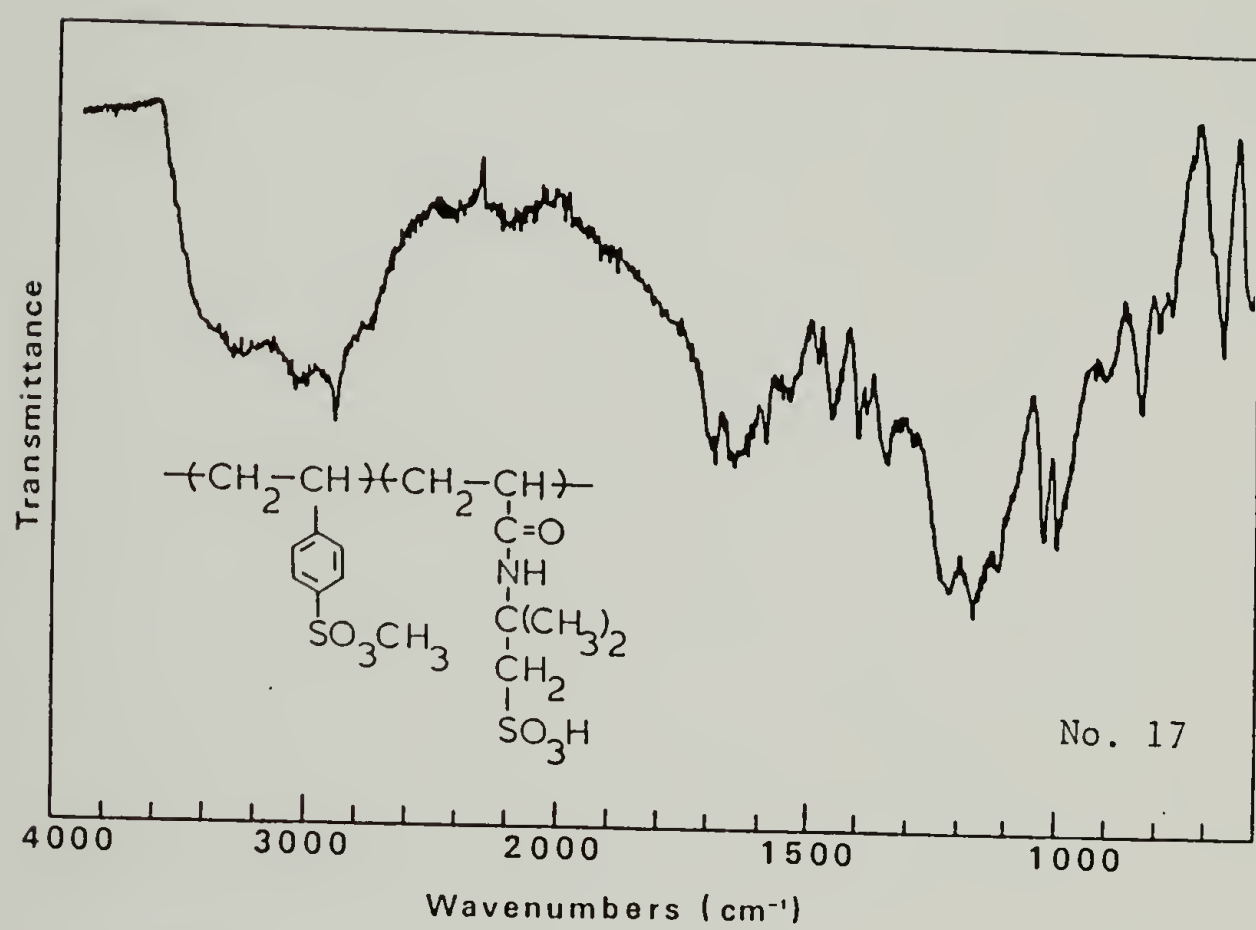












A P P E N D I X D

HYDROLYSIS DATA

1. Neutral hydrolysis of methyl toluenesulfonate in 90/10 (v/v)
DMSO/H₂O.

Temperature 50°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	5	0.05
1200	10	0.11
1800	14	0.15
2700	21	0.24
3600	26	0.30
5400	37	0.46
7200	46	0.62
9000	54	0.78
10800	60	0.92
14400	70	1.20
18000	78	1.51
21600	84	1.83

Temperature 55°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	8	0.08
1200	15	0.16
1800	21	0.24
2700	30	0.36
3600	38	0.48
6000	56	0.82
7200	63	0.99
9000	70	1.20
10800	77	1.47
12600	82	1.71
18000	92	2.53

1. Neutral hydrolysis of methyl toluenesulfonate, cont'd.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	12	0.13
1200	23	0.26
1800	32	0.39
2400	41	0.53
3000	48	0.65
3600	54	0.78
4500	62	0.97
5400	69	1.17
7200	79	1.56
10800	90	2.30
14400	95	3.00

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	10	0.11
600	18	0.20
1200	34	0.42
1800	46	0.62
2400	56	0.82
3000	64	1.02
3600	71	1.24
4500	79	1.56
5400	84	1.83
7200	92	2.53
10800	98	3.91

1. Neutral hydrolysis of methyl toluenesulfonate, cont'd.

Temperature 70°C :

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	14	0.15
600	26	0.30
900	37	0.46
1200	46	0.62
1500	54	0.78
1800	60	0.92
2400	71	1.24
3000	78	1.51
3600	84	1.83
4500	90	2.30
5400	93	2.66

2. Neutral hydrolysis of ethyl toluenesulfonate in 90/10 (v/v)
DMSO/H₂O.

Temperature 50°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
3600	12	0.13
7200	21	0.24
14400	38	0.48
21600	51	0.71

-continued-

2. Neutral hydrolysis of ethyl toluenesulfonate, cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
28800	62	0.97
36000	70	1.20
64800	89	2.21
79200	93	2.66
86400	95	3.00

Temperature 55°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
1800	10	0.11
3600	18	0.20
5400	25	0.29
7200	32	0.39
10800	46	0.63
14400	55	0.80
18000	63	0.99
32400	85	1.90

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	5	0.05
900	8	0.08
1800	14	0.15
2700	19	0.21

-continued-

2. Neutral hydrolysis of ethyl toluenesulfonate, cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
3600	27	0.31
5400	37	0.46
7200	46	0.62
10800	62	0.97
14400	72	1.27
18000	80	1.61
21600	87	2.04
25200	90	2.30

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	9	0.09
900	13	0.14
1800	23	0.26
3000	36	0.45
3600	40	0.51
5400	54	0.78
7200	65	1.05
9000	74	1.35
10800	80	1.61
12600	86	1.97
14400	89	2.21

2. Neutral hydrolysis of ethyl toluenesulfonate, cont'd.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	13	0.14
1200	24	0.27
1800	35	0.43
2400	41	0.53
3000	49	0.67
3600	56	0.82
4500	64	1.02
5400	71	1.24
7200	81	1.66
10800	91	2.41

3. Neutral Hydrolysis of n-propyl toluenesulfonate in 90/10 (v/v)
DMSO/H₂O.

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	5	0.05
1200	10	0.11
1800	14	0.15
2700	21	0.24
3600	27	0.31
5400	37	0.46

-continued-

3. Neutral hydrolysis of n-propyl toluenesulfonate, cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
7200	47	0.63
10800	61	0.94
14400	72	1.27
18000	79	1.56
21600	85	1.90

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	8	0.08
1200	15	0.16
1800	22	0.25
2700	32	0.39
3600	40	0.51
4500	48	0.65
5400	54	0.78
7200	65	1.05
10800	79	1.56
14400	88	2.12

3. Neutral hydrolysis of n-propyl toluenesulfonate, cont'd.

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	12	0.13
1200	22	0.25
1800	33	0.40
2400	42	0.54
3000	48	0.65
3600	54	0.78
4500	63	0.99
5400	70	1.20
7200	80	1.61
9000	86	1.97
10800	90	2.30

Temperature 80°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	10	0.11
600	18	0.20
900	26	0.30
1200	33	0.40
1800	46	0.62
2400	56	0.82
3000	64	1.02
3600	71	1.24
4500	78	1.51
5400	84	1.83
7200	91	2.41

3. Neutral hydrolysis of n-propyl toluenesulfonate, cont'd.

Temperature 85°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	14	0.15
600	27	0.31
900	37	0.46
1200	46	0.62
1500	54	0.78
1800	60	0.92
2400	71	1.24
3600	85	1.90
4500	90	2.30
5400	94	2.81
7200	98	3.91

4. Neutral hydrolysis of isopropyl toluenesulfonate in 90/10 (v/v)
DMSO/H₂O.

Temperature 50°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
600	5	0.05
1200	10	0.11
1800	15	0.16
2700	22	0.25
3600	28	0.33

-continued-

4. Neutral hydrolysis of isopropyl toluenesulfonate, cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
5400	40	0.51
7200	49	0.67
9000	56	0.82
10800	63	0.99
14400	73	1.31
18000	81	1.66

Temperature 55°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	5	0.05
600	9	0.09
1200	18	0.20
1800	25	0.29
2700	35	0.43
3600	44	0.58
4500	52	0.73
5400	58	0.87
7200	69	1.17
12600	87	2.04
14400	90	2.30

4. Neutral hydrolysis of isopropyl toluenesulfonate, cont'd.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	14	0.15
1200	26	0.30
1800	37	0.46
2400	46	0.62
3000	54	0.78
3600	61	0.94
4500	68	1.14
5400	75	1.39
7200	84	1.83
9000	90	2.30

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	13	0.14
600	23	0.26
900	33	0.40
1200	41	0.53
1500	49	0.67
1800	55	0.80
2400	66	1.08
3000	74	1.35
3600	80	1.61
4500	86	1.97
5400	91	2.41
7200	96	3.22

4. Neutral hydrolysis of isopropyl toluenesulfonate, cont'd.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	19	0.21
600	35	0.43
900	48	0.65
1200	57	0.84
1500	65	1.05
1800	72	1.27
2400	81	1.66
3000	88	2.12
3600	92	2.53

5. Neutral hydrolysis of poly(methyl styrenesulfonate) in 90/10
(v/v) DMSO/H₂O.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	13	0.14
900	19	0.21
1200	24	0.27
1800	33	0.40
2400	40	0.51
3000	47	0.63
3600	51	0.71

-continued-

5. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
4500	58	0.87
5400	63	0.99
7200	71	1.24
9000	77	1.47
10800	82	1.71
14400	88	2.12
18000	91	2.41
25800	96	3.22

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	10	0.11
600	21	0.24
900	28	0.33
1200	35	0.43
1500	40	0.51
1800	46	0.62
2400	53	0.76
3000	60	0.92
3660	66	1.08
4500	71	1.24
5400	76	1.43
7200	82	1.71
10800	91	2.41
14400	96	3.22
18000	98	3.91

5. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	15	0.16
600	29	0.34
900	38	0.48
1200	46	0.62
1500	52	0.73
1800	58	0.87
2100	62	0.97
2400	66	1.08
3000	71	1.24
3600	76	1.43
4500	83	1.77
5400	87	2.04
6300	90	2.30
7200	92	2.53
9000	95	3.00
10800	98	3.91

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	22	0.25
600	39	0.49
900	49	0.67
1200	57	0.84
1500	64	1.02
1800	68	1.14
2400	76	1.43
3000	82	1.71

-continued-

5. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
3600	86	1.97
4800	92	2.53
5400	94	2.81
7200	98	3.91

6. Neutral hydrolysis of poly(ethyl styrenesulfonate) in 90/10 (v/v) DMSO/H₂O.

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	4	0.04
600	8	0.08
900	11	0.12
1200	14	0.15
1860	21	0.24
2400	25	0.29
3000	29	0.34
3600	34	0.42
4500	40	0.51
5400	44	0.58
7200	53	0.76
9300	61	0.94
10800	65	1.05
14700	75	1.39
18000	80	1.61
21720	85	1.90
28800	91	2.41
36000	95	3.00

6. Neutral hydrolysis of poly(ethyl styrenesulfonate), cont'd.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	6	0.06
600	12	0.13
900	17	0.19
1200	21	0.24
1500	26	0.30
1800	30	0.36
2400	36	0.45
3120	44	0.58
3600	48	0.65
4500	55	0.80
5400	60	0.92
7200	68	1.14
9000	75	1.39
11100	82	1.71
12600	85	1.90
14400	88	2.12
18000	93	2.66

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	9	0.09
600	17	0.19
900	23	0.26
1200	30	0.36
1500	35	0.43
1800	40	0.51
2100	45	0.60

-continued-

6. Neutral hydrolysis of poly(ethyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
2400	48	0.65
3000	55	0.80
3600	61	0.94
4500	68	1.14
5400	73	1.31
7500	83	1.77
9000	88	2.12
11100	93	2.66

Temperature 80°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	12	0.13
600	25	0.29
900	33	0.40
1200	40	0.51
1500	45	0.60
1800	51	0.71
2400	60	0.92
3000	68	1.14
3600	74	1.35
4500	78	1.51
5400	85	1.90
7200	91	2.41
9000	95	3.00
10800	97	3.51

7. Neutral hydrolysis of poly(n-propyl styrenesulfonate) in 90/10 (v/v) DMSO/H₂O.

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	13	0.14
1200	21	0.24
1800	28	0.33
2400	35	0.43
3000	41	0.53
3600	46	0.62
4500	52	0.73
5400	57	0.84
7200	67	1.11
9180	73	1.31
10800	78	1.51
14400	84	1.83
18000	90	2.30
21600	93	2.66
28800	97	3.51

Temperature 80°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	10	0.11
600	19	0.21
900	24	0.27
1200	29	0.34
1800	39	0.49
2400	48	0.65
3000	53	0.76
3600	60	0.92

-continued-

7. Neutral hydrolysis of poly(n-propyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
4500	66	1.08
5400	72	1.27
7200	80	1.61
9000	86	1.97
10800	91	2.41
12600	94	2.81

Temperature 85°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
360	15	0.16
600	26	0.30
900	35	0.43
1200	41	0.53
1500	48	0.65
1800	53	0.76
2400	61	0.94
3060	70	1.20
3660	75	1.39
4500	80	1.61
5400	86	1.97
7200	94	2.81

7. Neutral hydrolysis of poly(n-propyl styrenesulfonate), cont'd.

Temperature 90°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	19	0.21
600	34	0.42
900	46	0.62
1200	51	0.71
1500	60	0.92
1800	67	1.11
2100	71	1.24
2400	74	1.35
3000	80	1.61
3600	86	1.97
4500	91	2.41
5400	96	3.22

8. Neutral hydrolysis of poly(isopropyl styrenesulfonate) in 90/10 (v/v) DMSO/H₂O.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	14	0.15
1200	21	0.24
1800	28	0.33

-continued-

8. Neutral hydrolysis of poly(isopropyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
2700	36	0.45
3600	44	0.58
5400	55	0.80
7200	65	1.05
11100	78	1.51
13800	84	1.83
20400	93	2.66

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	11	0.12
600	22	0.25
900	28	0.33
1200	34	0.42
1800	42	0.54
2700	54	0.78
3600	63	0.99
4680	72	1.27
5400	75	1.39
7200	84	1.83
9000	90	2.30
10860	95	3.00

8. Neutral hydrolysis of poly(isopropyl styrenesulfonate), cont'd.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	16	0.17
600	32	0.39
900	37	0.46
1200	45	0.60
1500	50	0.69
1800	55	0.80
2580	65	1.05
3000	71	1.24
3600	77	1.47
4560	84	1.83
5400	87	2.04
7200	94	2.81
9000	98	3.91

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	21	0.24
600	41	0.53
900	49	0.67
1200	55	0.80
1500	62	0.97
1800	69	1.17
2100	73	1.31
2400	76	1.43
3000	83	1.77
3600	87	2.04

-continued-

8. Neutral hydrolysis of poly(isopropyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
4500	94	2.81
5400	96	3.22
7380	98	3.91
9000	99	4.61

9. Neutral hydrolysis of poly(methyl styrenesulfonate-co-styrene)
in 90/10 (v/v) DMSO/H₂O.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	6	0.06
600	11	0.12
1200	21	0.24
2100	32	0.39
2700	40	0.51
3600	49	0.67
4500	56	0.82
5400	60	0.92
7200	70	1.20
9120	78	1.51
11400	84	1.83
12600	86	1.97
14400	89	2.21
18000	94	2.81

9. Neutral hydrolysis of poly(methyl styrenesulfonate-co-styrene),
cont'd.

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	10	0.11
600	18	0.20
900	24	0.27
1200	30	0.36
1500	35	0.43
1800	40	0.51
2400	49	0.67
3000	56	0.82
3600	62	0.97
4500	70	1.20
5400	75	1.39
7200	83	1.77
9000	87	2.04
10800	91	2.41
14700	95	3.00

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	13	0.14
600	27	0.31
900	37	0.46
1200	43	0.56
1800	55	0.80
2400	63	0.99
3000	72	1.27
3660	77	1.47
4500	83	1.77
5400	88	2.12
7200	93	2.66
11400	98	3.91

9. Neutral hydrolysis of poly(methyl styrenesulfonate-co-styrene),
cont'd.

Temperature 75°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	19	0.21
660	37	0.46
900	44	0.58
1200	54	0.78
1500	60	0.92
1800	67	1.11
2100	70	1.20
2400	73	1.31
3000	79	1.56
3600	86	1.97
4500	91	2.41
5400	94	2.81

10. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium
styrenesulfonate) in 90/10 (v/v) DMSO/H₂O.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	14	0.15
600	24	0.27
900	31	0.37

-continued-

10. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
1200	38	0.48
1800	48	0.65
2700	62	0.97
3600	71	1.24
5400	81	1.66
7200	88	2.12
11400	95	3.00
14400	98	3.91

11. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O.

Temperature 55°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	5	0.05
600	7	0.07
1200	14	0.15
1800	19	0.21
2700	28	0.33
3600	35	0.43
5400	49	0.67
7200	61	0.94
9000	70	1.20
10800	77	1.47
14400	86	1.97
18600	93	2.66
21600	95	3.00

11. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate), cont'd.

Temperature 60°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	7	0.07
600	11	0.12
1200	21	0.24
1800	30	0.36
2700	41	0.53
3600	52	0.73
4500	61	0.94
5400	68	1.14
7200	80	1.61
9000	84	1.83
10800	91	2.41
12600	93	2.66
14400	96	3.22

Temperature 65°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	9	0.09
600	16	0.17
900	26	0.30
1200	33	0.40
1800	47	0.63
2400	56	0.82
3000	65	1.05
3600	72	1.27

-continued-

11. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
4500	79	1.56
5400	86	1.97
6300	88	2.12
7200	93	2.66
9000	98	3.91

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	13	0.14
600	27	0.31
900	38	0.48
1200	49	0.67
1800	62	0.97
2400	73	1.31
3000	80	1.61
3600	87	2.04
4500	91	2.41
5700	96	3.22
7200	98	3.91

12. Acidic hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O (1:1 HCl:ester).

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	15	0.16
600	26	0.30
900	37	0.46
1200	46	0.62
1800	63	0.99
2400	76	1.43
3000	83	1.77
3600	87	2.04
4500	94	2.81

13. Basic hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 100% H₂O (2:1 NaOH:ester).

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	16	0.17
600	27	0.31
900	36	0.45
1200	47	0.63
1800	62	0.97
2400	73	1.31
3000	82	1.71

-continued-

13. Basic hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
3600	87	2.04
4500	91	2.41
5400	93	2.66
7200	98	3.91

14. Neutral hydrolysis of poly(methyl styrenesulfonate-co-sodium styrenesulfonate) in 50/50 (v/v) DMSO/H₂O.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	16	0.17
600	30	0.36
900	42	0.54
1200	49	0.67
1800	63	0.99
2400	74	1.35
3120	81	1.66
3600	84	1.83
4500	91	2.41
5400	95	3.00
7200	98	3.91

15. Neutral hydrolysis of poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H₂O. $M_v = 41,000$.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	17	0.19
600	28	0.33
900	38	0.48
1200	45	0.60
1500	51	0.71
1800	56	0.82
2100	61	0.94
2400	64	1.02
3000	71	1.24
3600	75	1.39
4500	81	1.66
5400	85	1.90
7200	91	2.41
9000	94	2.81
10800	97	3.51

16. Neutral hydrolysis of poly(methyl styrenesulfonate) in 90/10 (v/v) DMSO/H₂O. $M_v = 52,000$.

Temperature 70°C

-continued-

16. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	16	0.17
600	28	0.33
900	37	0.46
1200	45	0.60
1500	51	0.71
1800	56	0.82
2100	60	0.92
2400	63	0.99
3000	70	1.20
3600	74	1.35
4500	82	1.71
5400	85	1.90
7320	90	2.30
9000	94	2.81
10800	96	3.22

17. Neutral hydrolysis of poly(methyl styrenesulfonate) in 90/10
(v/v) DMSO/H₂O. $M_v = 203,300$.

Temperature 70°C

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
300	16	0.17
600	27	0.31
900	36	0.45
1200	44	0.58
1500	49	0.67
1800	55	0.80

-continued-

17. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

<u>Time (seconds)</u>	<u>p (% hydrolysis)</u>	<u>Ln(100/100-p)</u>
2100	60	0.92
2400	63	0.99
3000	70	1.20
3600	74	1.35
4500	80	1.60
5520	86	1.97
7200	90	2.30
9000	94	2.81
10800	96	3.22

18. Neutral hydrolysis of poly(methyl styrenesulfonate) emulsion in 100% H₂O.

Temperature 80°C

<u>Time (minutes)</u>	<u>p (% hydrolysis)</u>	<u>Comments</u>
5	6	solution cloudy
10	11	" "
20	17	" "
30	22	" "
45	27	" "
60	30	" "
90	36	" "

-continued-

18. Neutral hydrolysis of poly(methyl styrenesulfonate) emulsion, cont'd.

<u>Time (minutes)</u>	<u>p (% hydrolysis)</u>	<u>Comments</u>
120	43	solution cloudy
150	52	
190	61	solution clear
210	73	
240	90	" "
275	99	" "
300	100	" "
330	100	" "
360	100	" "

19. Neutral hydrolysis of poly(methyl styrenesulfonate) in 80/20 (v/v) DMSO/H₂O. Relative viscosity vs. % hydrolysis.

Temperature 50°C

<u>Time (minutes)</u>	<u>p (% hydrolysis)</u>	<u>Relative Viscosity</u>
10	5	1.48
30	18	2.32
50	26	2.58
80	36	2.83
120	47	2.84
180	59	2.85
240	66	2.85
360	79	2.84

-continued-

19. Neutral hydrolysis of poly(methyl styrenesulfonate), cont'd.

<u>Time (minutes)</u>	<u>p (% hydrolysis)</u>	<u>Relative Viscosity</u>
480	85	
660	92	2.74
1200	97	2.72
1800	100	2.66
		2.63

20. Neutral hydrolysis of poly(methyl styrenesulfonate) in 80/20 (v/v) DMSO/H₂O + 0.5 M NaCl. Relative Viscosity vs. % Hydrolysis.

Temperature 50°C

<u>Time (minutes)</u>	<u>p (% hydrolysis)</u>	<u>Relative Viscosity</u>
10	21	1.21
20	26	1.23
60	40	1.36
100	53	1.38
200	66	1.27
360	82	1.26
720	90	1.26
1800	100	1.25

