

**AN INVESTIGATION OF THE COMMERCIAL APPLICATIONS OF  
ACRYLAMIDE BASED WATER SOLUBLE POLYMERS**

**AN INVESTIGATION OF THE COMMERCIAL APPLICATIONS OF  
ACRYLAMIDE BASED WATER SOLUBLE POLYMERS**

by

**VIC STANISLAWCZYK, B.Eng.**

**A Thesis**

**Submitted to the School of Graduate Studies**

**in Partial Fulfilment of the Requirements**

**for the degree**

**Master of Engineering**

**McMaster University**

**May 1985**

MASTER OF ENGINEERING (1985)  
(Chemical Engineering)

McMASTER UNIVERSITY  
Hamilton, Ontario

TITLE:                   An Investigation of the Commercial  
                          Applications of Acrylamide Based Water  
                          Soluble Polymers

AUTHOR:                 Vic Stanislawczyk, B.Eng (McMaster)

SUPERVISOR:            Dr. A.E. Hamielec

NUMBER OF PAGES:     xiv , 117

## ABSTRACT

In part I of this dissertation, several cationic polyacrylamides were tested under different conditions for their ability to improve the retention of fines in papermaking. A dynamic drainage jar was used to simulate the turbulence encountered in the papermaking process. Several factors, including temperature, the amount and intensity of turbulence, the additive concentration and the presence of impurities were found to affect fines retention with polymers present. A polymer made by Nalco Chemicals proved to be superior to a commonly used polymer, Percol 292 for a standard fine paper pulp. It was thought that further retention improvements might be possible by tailoring the charge density and molecular weight of polyacrylamide retention aides for the specific papermaking system they are intended for. Novel approaches to retention such as those employing combinations of an anionic polymer, a cationic polymer and zirconium oxychloride were thought to show promise as well.

In part II of this dissertation several broad polyacrylamide molecular weight standards were prepared by inverse suspension and solution processes on pilot plant equipment at the McMaster Institute for Polymer Production Technology. They were characterized by laser light scattering and viscometry at McMaster, and externally by other methods. Although the polyacrylamides prepared compare favourably to currently available commercial standards when both are analysed by SEC, further analysis

must be done to be certain of the molecular weight averages.

A relationship is presented to provide for simpler and more accurate light scattering analysis in the future. This relationship relating  $\bar{M}_w$  to the second Virial coefficient may be used to eliminate some uncertainty in the often scattered plots encountered when calculating molecular weights for polyacrylamides analysed by light scattering.

## ACKNOWLEDGEMENTS

This research would not have been possible without the time, ideas, funding and guidance of its many contributors.

Dr. A.E. Hamielec, my supervisor, was a source of countless ideas and guidance. Perhaps more important was his enthusiasm for polymers and his encouragement of new ideas. It is hoped that these attitudes are reflected in this work, and in any future work that I may encounter as an engineer.

Dr. Bob Pelton, formerly of the Pulp and Paper Research Institute in Montreal, contributed his time and guidance to the first portion of this research. The ideas and relevant practical information he supplied helped greatly in areas in which I am somewhat lacking.

I extend my gratitude to Mrs. Angie Vanderlaan, and fellow students Mr. Vlado Hruska and Mr. Dave Hunkeler for their helpful suggestions and their assistance with much of the experimental work in this study. Nalco Chemical Company, Allied Colloids and The Pulp and Paper Research Institute of Canada generously supplied many of the materials and polymers used. The Natural Sciences and Engineering Research Council kindly funded this research both through scholarships and grants for the purchase some of the expensive equipment used.

Finally, I wish to express my appreciation to students and staff at McMaster in general. Many of their contributions were in the form of ideas or assistance, but indirectly, their friendly attitudes, and their participation in many social activities served to create an environment which furthered this work and made it more enjoyable.

## Table of Contents

PART I	FINES RETENTION IMPROVEMENT IN PAPERMAKING USING WATER SOLUBLE POLYMERS	
1.	Introduction	2
2.	Background	4
2.1	Polymer Structures Studied	6
2.2	Mechanisms of Fines Retention	7
2.3	Scope of This Research	14
3.	Experimental	15
4.	Results and Discussion	20
4.1	Reproducibility	20
4.2	Variables Which Affect Retention on the Drainage Jar	22
4.2.1	Impeller Speed (Turbulence)	22
4.2.2	Turbulence Time	24
4.2.3	Temperature	24
4.2.4	pH Effects	27
4.2.5	Polymer Concentration	30
4.2.6	The Effects of Impurities	31
4.3	Comparing Different Cationic Polymers	35
4.4	Some Ideas on Polymer Property Effects	37
4.5	Novel Approaches to Improved Fines Retention	39
4.5.1	Anionic Cationic Synergism	39
4.5.2	Zirconium Oxychloride as a Retention Additive	40
4.6	Recommendations	44
5.	Conclusions	46
6.	References	48
PART II	THE PREPARATION AND CHARACTERIZATION OF BROAD POLYACRYLAMIDE MOLECULAR WEIGHT STANDARDS	
1.	Introduction	51
2.	Scope of Research	52
3.	Theory	53
3.1	Modes of Polymerization	55
3.2	Characterization	56
3.2.1	Low-Angle Laser Light Scattering	56
3.2.2	Size Exclusion Chromatography	58
3.3	Calibration of SEC	59
3.3.1	Narrow Standards	59
3.3.2	Broad Standards	60

4.	Experimental	63
4.1	Ampoule Runs	63
4.1.1	Preparation for Analysis	67
4.2	Reactor Runs	68
4.2.1	Inverse Micro Suspension Runs	68
4.2.2	Solution Runs	71
4.3	A Note on Reactor Clean Up	71
5.	Results and Discussion	72
5.1	Laser Light Scattering	72
5.2	Ampoule Runs	77
5.2.1	Molecular Weight Measurement	82
5.3	Reactor Runs	86
5.3.1	Inverse Suspension Runs	86
5.3.2	Solution Runs	90
5.4	The Second Virial Coefficient and its Relationship to $\bar{M}_w$	104
5.5	Recommendations	106
6.	Conclusions	107
7.	References	108

#### APPENDICES:

A	SEC Calibration Using Broad Standards Example	110
B	Reduced Specific Viscosity Determination	114



## List of Tables

I-1	Typical Headbox Solids Content	5
I-2	Nalco Polymers : Technical Data	19
I-3	Reproducibility	21
I-4	Retention with Newsprint White Water Present	34
I-5	Performance of Nalco Polymers	36
I-6	Retention Levels with Zr as an Additive	42
I-7	Retention with TiO <sub>2</sub> Present	43
II-1	Guide to Selecting Maximum Polymer Concentration and Correct Filter Size	78
II-2	Light Scattering Analysis of Ampoules	83
II-3	SEC Elution Times for Ampoule Polymers	85
II-4	Inverse Suspension Recipes	87
II-5	Molecular Weight Analysis of R2 by Laser Light Scattering	91
II-6	Solution Polymerization Recipes	93
II-7	Light Scattering Analysis of Solution Polymers	98
II-8	A Comparison of Different Analysis Methods on Polyacrylamide Standards	102

## List of Figures

I-1	The Papermaking Process	3
I-2	"Patch" Model Adsorption	8
I-3	"Patch" Model Flocculation	10
I-4	"Loop" Model Flocculation	11
I-5	Anchor Mechanism	13
I-6	Dynamic Drainage Jar	16
I-7	Fines Retention vs. Impeller Speed	23
I-8	Fines Retention vs. Turbulence Time	25
I-9	Fines Retention vs. Temperature	26
I-10	Fines Retention vs. pH - Percol 292	28
I-11	Fines Retention vs. pH - Nalco 7664	29
I-12	Retention vs. Polymer Concentration	32
I-13	Comparison of Percol 292 with Nalco 7664 at Several Concentrations	38
I-14	Zr Application in Fines Retention	41
I-15	Possible Application of Zirconium Oxychloride in a Paper Mill	45
II-1	Calibration Using Broad Standards	62
II-2	Ampoule Dimensions	64
II-3	Vacuum Apparatus for Ampoule Experimentation	66
II-4	Pilot Plant Batch Reactor	69
II-5	Refractometer Calibration	73
II-6	Calculation of $dn/dc$	74
II-7	Drifting Signal Due to Small Filter Size	76
II-8	Noisy Signal Due to Large Filter Size	76
II-9	Conversion vs. Time - A Comparison With and Without CTA in Ampoules	80
II-10	Size Exclusion Chromatograph of 10 min. Ampoule	81
II-11	Adsorption Confirmation in SEC Analysis	84
II-12	Size Exclusion Chromatograph of R3	92

II-13	Size Exclusion Chromatograph of R12	95
II-14	Comparison to Polysciences Standards	99
II-15	Log A <sub>2</sub> vs. Log $\bar{M}_w$	105

## NOMENCLATURE

- A - a constant in the expression for a calibration curve
- $A_1, A_2, A_3$  - constants in gel-effect termination expression
- $A_2$  - second Virial coefficient
- $A_n$  -  $n^{\text{th}}$  Virial coefficient
- C - polymer concentration in light scattering analysis
- [C] - chain transfer agent concentration
- $c_1, c_2, c_3, c_4$  - constants defining cubic calibration curve
- CTA - chain transfer agent
- D - attenuator transmittance in light scattering calculations
- $dn/dc$  - change in refractive index with concentration (light scattering analysis)
- $G_0$  - photomultiplier signal for incident light beam (LALLS)
- $G_\theta$  - photomultiplier signal for scattered light at a given angle
- [I] - initiator concentration
- K - an intermediate value in light scattering calculations
- $K_{AA}$  - Mark Houwink constant for polyacrylamide
- $k_d$  - initiator decomposition rate constant
- $k_{fC}$  - transfer to chain transfer agent rate constant
- $k_{fm}$  - transfer to monomer rate constant
- $k_p$  - propagation rate constant
- $k_p'$  - propagation rate constant for CTA radical
- $K_{peo}$  - Mark Houwink constant for polyethylene oxide
- $k_R$  - kinetic rate constant for reaction of caged radical to form initiator (6)
- $k_t$  - termination rate constant

$k_{t_0}$	- termination rate constant at zero time
$k_x$	- kinetic rate constant for the reaction between monomer and caged radicals
	(6)
$l'$	- length parallel to incident beam (LALLS)
$M$	- molecular weight
$[M]$	- monomer concentration
$M_{AA}$	- molecular weight of polyacrylamide
$\bar{M}_n$	- number average molecular weight
$M_{peo}$	- molecular weight of polyethylene oxide
$\bar{M}_w$	- weight average molecular weight
$n$	- solvent refractive index (LALLS)
$N$	- Avogadro's number
$[P]$	- polymer concentration
$P_m$	- polymer chain with m monomer units
$P_\theta$	- particle scattering function (LALLS)
$R_g$	- radius of gyration of a polymer molecular (LALLS)
$\bar{r}_n$	- number average chain length
$R_{n^0}$	- radical with n monomer units incorporated
$R_p$	- polymerization rate
$\bar{r}_w$	- weight average chain length
$R_\theta$	- Rayleigh factor (LALLS)
$R_\theta$	- Rayleigh factor for polymer solution
$R_{\theta s}$	- Rayleigh factor for polymer solvent
SEC	- size exclusion chromatography
T	- temperature

$v$  - elution volume

$x$  - conversion

### Greek Symbols

$\alpha_{AA}$  - Mark Houwink constant for polyacrylamide

$\alpha_{peo}$  - Mark Houwink constant for polyethylene oxide

$\beta$  - exponent in calibration curve equation

$\beta$  - molecular weight development parameter

$\lambda$  - laser beam wavelength

$\pi$  - 3.14159265

$\sigma'$  - the solid angle over which the scattered light is viewed (LALLS)

$\Phi(v)$  - calibration curve function (SEC)

$\theta$  - parameter used in broad calibration calculations

$\tau$  - molecular weight development parameter

PART I  
FINES RETENTION IMPROVEMENT IN PAPERMAKING  
USING WATER SOLUBLE POLYMERS

## 1. INTRODUCTION

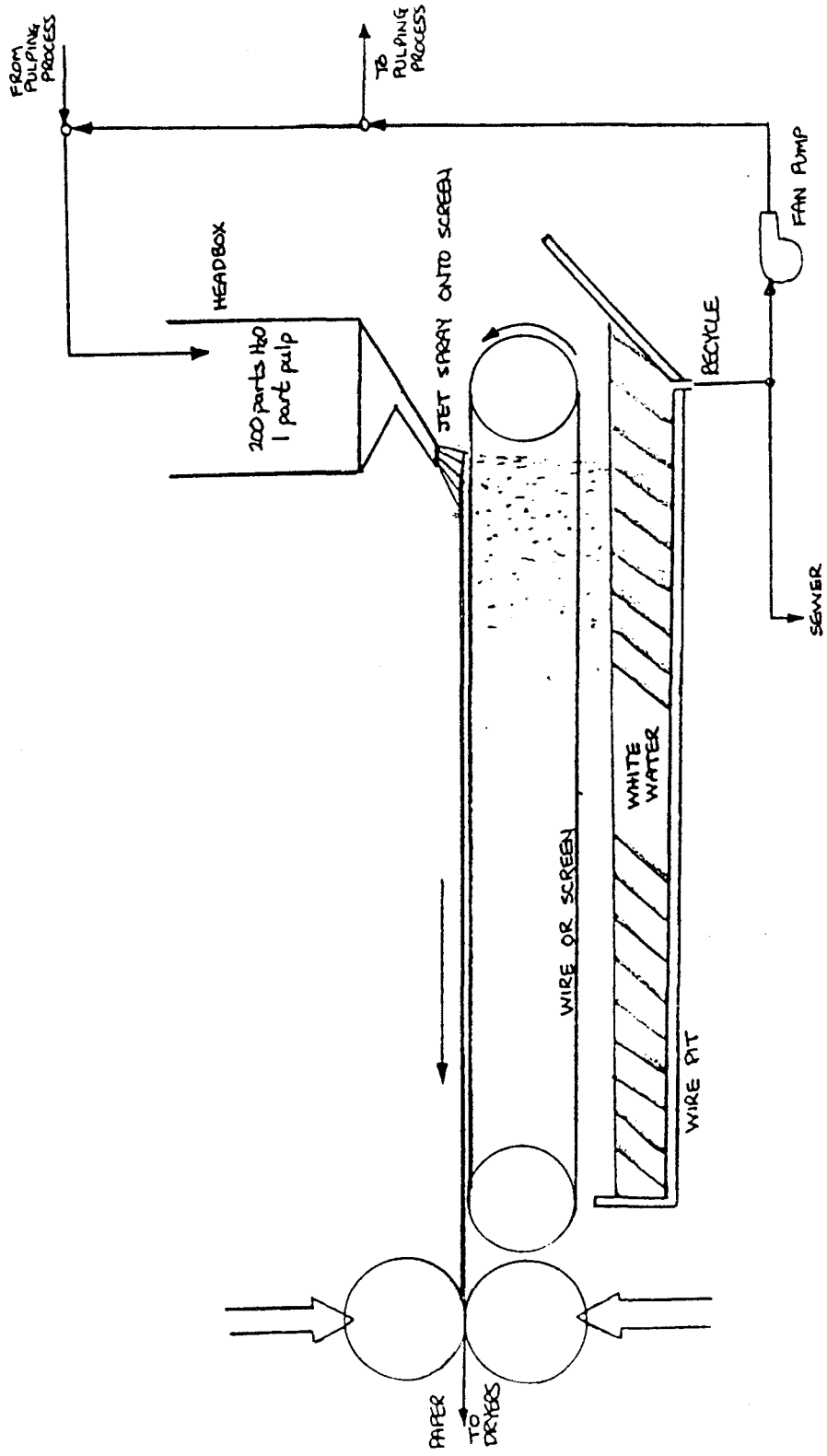
Paper is made by spraying a mixture of approximately 1 part wood pulp and 200 parts water onto a metallic or plastic screen, commonly called the wire. The wire may move at velocities of 60 kph or more. The force of the jet spray, the gravitational force and the movement of the wire combine to drain most of the water from the mixture, leaving a moist sheet of paper capable of supporting its own weight. Figure I-1 illustrates this process and points out some of the important papermaking equipment.

Because most pulps contain fibres and particles having a wide distribution of sizes, some solid material passes through the wire and into the wire pit along with the water drained from the pulp. This mixture of water and finer pulp material is named white water for its characteristic off-white to brown colour. The solid material passing through the wire includes colloidal pulping products, finer wood fibres and fibre fragments, and sometimes expensive pigment additives depending on the nature of the paper being made. Many years ago, much of this solid material, commonly called fines, was simply disposed of. In more recent times increasingly stringent environmental constraints and concerns about lost raw materials dictated measures to reuse white water in the pulping process to cut solid waste. However, high recycle rates tended to concentrate dissolved materials along with fines and colloids in the head box. This often adversely affected paper machine performance and paper quality.

A partial solution to this problem is the use of alum ( $\text{Al}_2\text{SO}_4 \cdot 17\text{H}_2\text{O}$ ), which is thought to aid slightly in the retention of fines, while improving machine operation. In the late 1940's, with the synthesis of water soluble polymers, it was discovered that certain types of polymers improved the retention of fines. Research in the area of synthetic water soluble polymers has been growing rapidly since 1960 (13). Today synthetic polymers are used



Figure I-1 The Papermaking Process



extensively in the manufacture of higher grades of paper, and are beginning to find their way into the production of cheaper papers such as newsprint.




## 2. BACKGROUND

Pulp can be divided into three components; fibres, fines and dissolved materials including fine colloids. The fines fraction can be broadly defined as any undissolved material in the headbox capable of passing through a 200 mesh screen (7). This classification includes fragments of wood fibres, clay and calcium carbonate or titanium dioxide or any other pigment additives. The fines content of a certain pulp can be determined by repeatedly filtering the pulp in water through a 200 mesh screen with agitation until the filtrate is free of solids. Often water must be added several times to achieve this end. The filtrate is then again filtered through a small pore filter, say 1 micron, to separate fines from the dissolved materials and fine colloids. Because of the formation of a mat on the fine filter, and the poorly defined filter size for this separation, the size distinction between fines and fine colloids is poor.

However, the physical effects these groups have on polymer additives may be very important. Table I-1 shows some typical composition breakdowns for two different pulp types, newsprint and higher grade bleached fine paper pulp. These figures are subject to very large variations and are meant only to illustrate the importance of surface area on polymer retention aid effectiveness.

All pulp fibers and particles have a slight anionic charge at papermaking pH ( of the order of  $-1.6 \text{ Coul/cm}^2$  (11)) produced by dissociated carboxylic acid groups and the proton exchange between hydroxyl groups and water in the cellulose contained in wood materials (19). Fillers and pigments tend to distribute themselves according to surface area. Thus the fines fraction will contain both loose filler and pigment, and a large amount of adsorbed filler

Table I-1 Typical Headbox Solids Content

		<u>Fraction:</u>		
		fine colloids / dissolved	finer	fibres
				
Newsprint	mass %	20	20	60
	area %	very high	moderate	low
Fine Paper	mass %	apx. 0	30	70
	area %	low	high	low

and pigment. Hence there is a high dollar value to this fraction in situations where fillers and pigments are used.

Cationic polymer additives adsorb primarily through charge interactions with particle surfaces (31). In many instances polymer adsorption is partially or mostly irreversible (37). Because smaller particles make up a large proportion of the surface area, a cationic polymer additive will tend to adsorb mostly onto the fines fraction in the absence of even smaller fine colloids in any appreciable quantity. Flocculation occurs when a polymer molecule adsorbs onto more than one particle (by mechanisms to be discussed later). When fines flocculate, the fines retention in a system improves. In systems with high dollar value additives this can lead to a substantial cost savings and an improvement in paper properties. When fine colloids "flocculate", however, the increase in particle size is not large enough to significantly reduce particle passage through the wire. In fact in systems with large amounts of fine colloids, very large amounts of cationic polymer must be added to achieve a reasonable improvement in fines retention. The presence of substantial quantities of fine colloids explains the general failure of cationic retention aides in newsprint systems.

## 2.1 POLYMER STRUCTURES STUDIED

Research has been conducted using many different groups of water soluble polymers including polyethyleneimine (29,9,8), polyethyleneoxide (24,25,27,32) and cationic starches (4), but polyacrylamides have been used most extensively industrially in cleaner systems because of their effectiveness at low dosage levels (due largely to the high molecular weights possible) and reasonable cost (15). Most of the work in this research was thus limited to acrylamide based polymers.

Polyacrylamide retention aides can be subdivided into four groups, cationic, anionic nonionic and amphoteric. Nonionic polyacrylamides are usually the simple

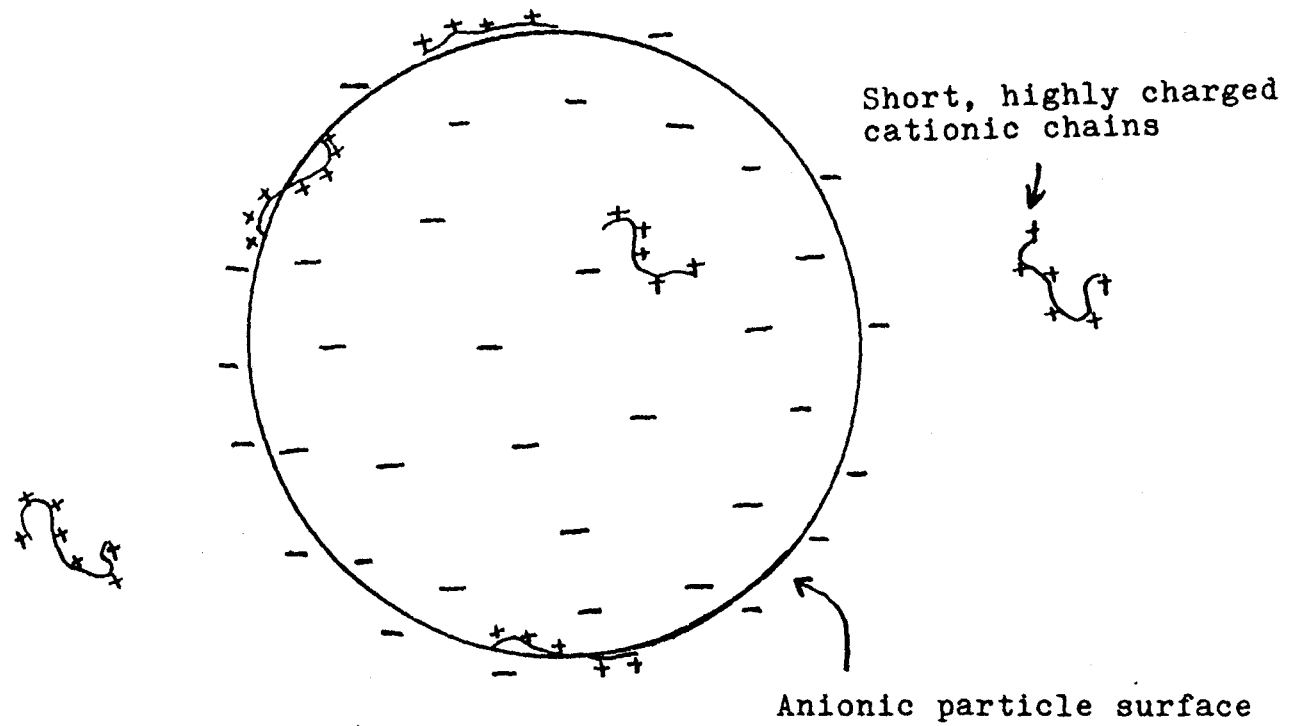
homopolymer. When dissolved in water they do not show appreciable ionic charge. Anionic polyacrylamides are generally copolymers of acrylamide and acrylic acid. Acrylic acid is a weak organic acid, and as such imparts a negative ionic charge to a polymer molecule containing it. Cationic polyacrylamides are usually copolymers of acrylamide and an acrylic monomer containing a quaternary ammonium group. The ammonium group imparts a positive charge when the polymer is dissolved in water. Amphoteric polymers contain both positively and negatively charged groups in individual polymer molecules. Steric difficulties prevent charges from neutralizing. Each of these classes of polymer improve retention in a different manner.

## 2.2 MECHANISMS OF FINES RETENTION

As stated previously, fines retention improvement involves flocculation of fine particles onto other fine particles or fibres. The increased particle size due to flocculation decreases the passage of particles through the papermaking wire resulting in increased fines retention.

Flocculation effects using cationic polymers have been explained using two flocculation mechanisms. In the case of low molecular weight cationic polymers or polymers with high charge densities ( that is a high amount of cationic monomer incorporated into the polymer chain ), the "patch" model has been used to explain retention effects (11,35). Figure I-2 (12) illustrates the adsorption of short, highly cationic polymer chains onto an anionic pulp particle. The patch model assumes the polymer molecule adsorbs relatively flat with few protruding loops or tails. This flatness and the mostly irreversible nature of adsorption allow the polymer molecule to be considered as part of the surface of the particle. The localized cationic charges change the nature of the double layer around the particle, destabilizing the particle with respect to an anionic surface close by, say another fine particle. This

Figure I-2 "Patch" Model Adsorption



destabilization causes flocculation, shown in Figure I-3. The mechanism often repeats several times, forming conglomerates of fines and fibres.

In the case of high molecular weight polymers with specific charge densities dependent on many papermaking conditions, a second flocculation model has been used (10). Such polymers are thought to adsorb only partially to a particle, with portions of the molecules extending away from the particle surface. Steric effects prevent total adsorption. The extended portions of molecules are referred to as loops and tails. Flocculation occurs because these loops and tails can adsorb onto other anionic particles nearby. This flocculation mechanism is shown in Figure I-4.

The two aforementioned modes of flocculation produce flocs with different characteristics. Patch model flocs, or soft flocs, break easily if turbulence is introduced to the system, loop model (hard) flocs do not. If broken, patch model flocs tend to reform when turbulence subsides (35,6). If loop model flocs are broken with high turbulence, reflocculation does not occur to original levels. This observation can be explained by the flattening of polymer loops after flocs are broken. Turbulence would assist in overcoming steric difficulties loop model molecules have in adsorbing totally onto a particle surface. If turbulence is high enough to flatten adsorbed molecules, reflocculation would result mostly from weak patch model adsorption. Generally loop model adsorption is desired over patch model adsorption in the paper industry as flocs must be able to withstand the turbulence of being sprayed onto a rapidly moving wire.

Anionic polyacrylamides may also be used to improve fines retention. The advantages of anionics are lower cost and the possibility of synthesizing polymers with molecular weights higher than cationic polyacrylamides. The major disadvantage lies in the tendency to slow the drainage of water through the forming sheet of paper, necessitating a machine speed slowdown or other measures to counteract this effect.

Figure I-3 "Patch" Model Flocculation

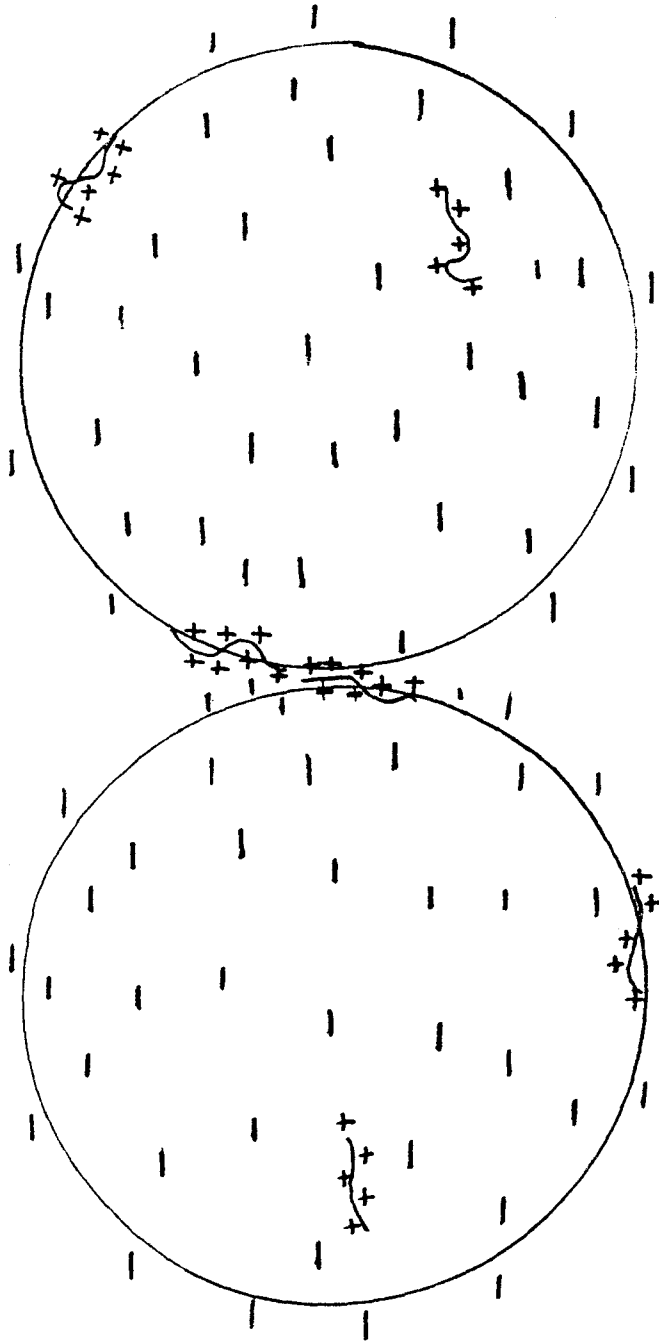
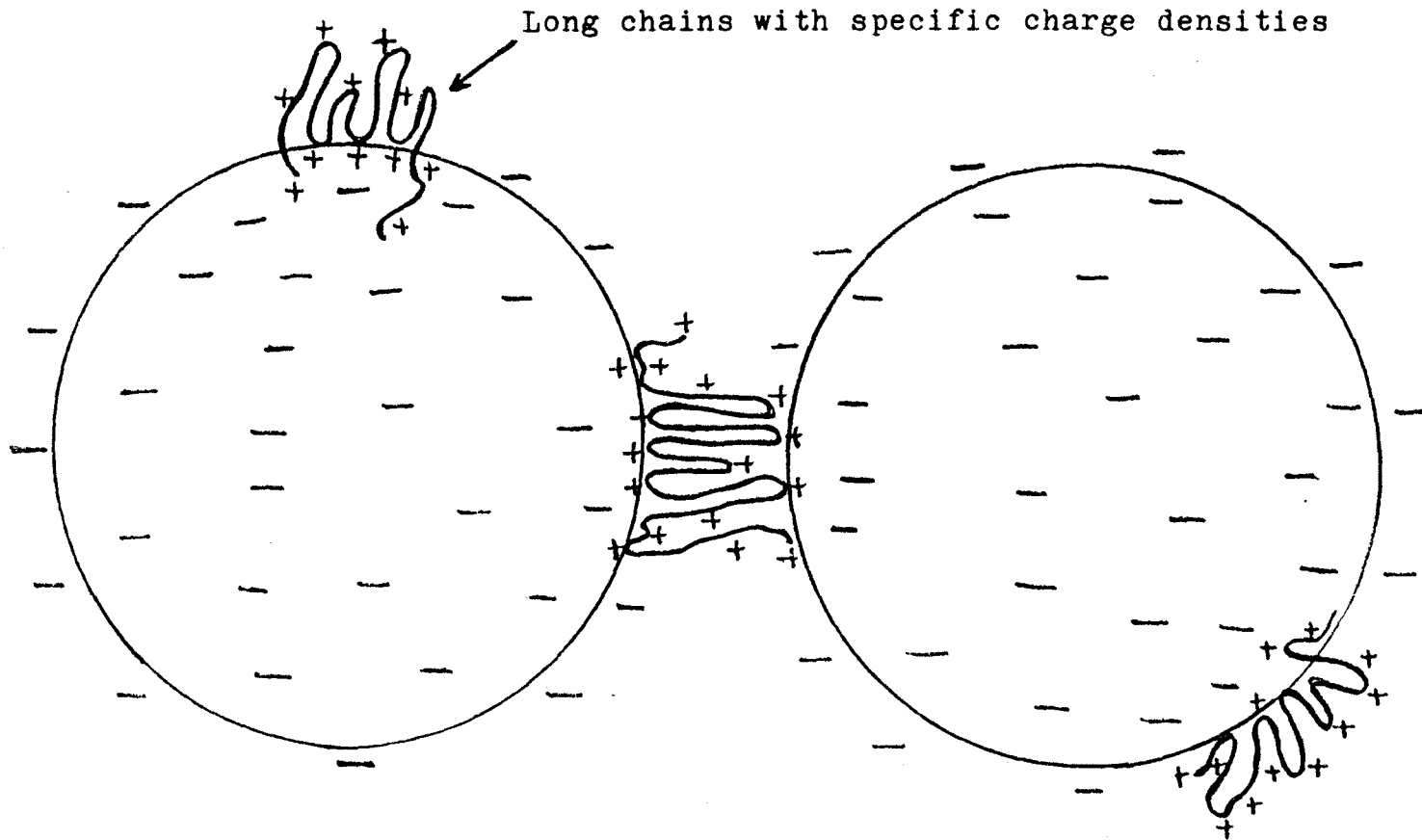




Figure I-4 "Loop" model flocculation



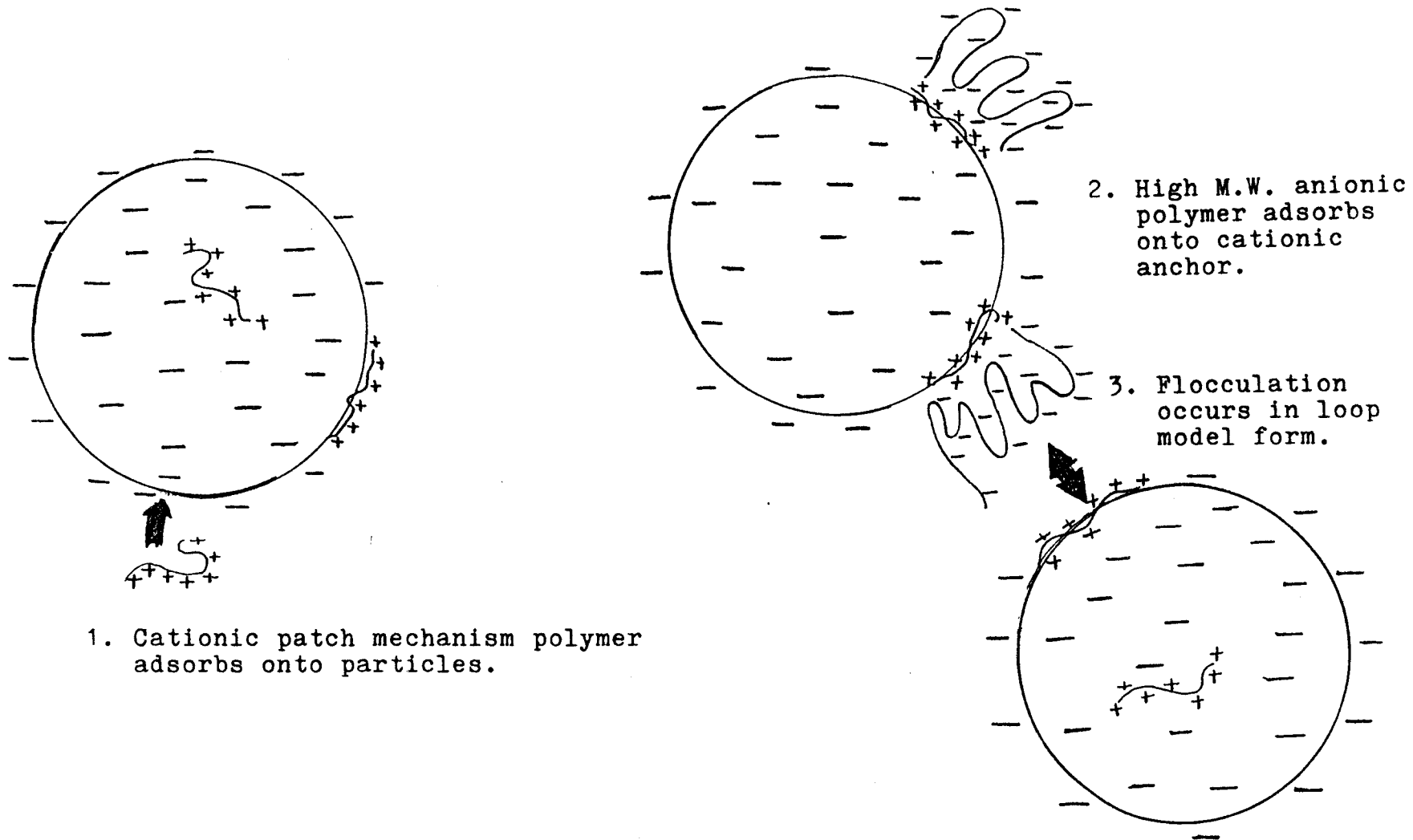
Because pulp particles are anionic (filler and pigments may not be), adsorption of anionic polymers must be facilitated by the addition of a cationic species on which the anionic chain may anchor. Multi-valent metal ions, such as  $Al^{3+}$ , or patch model cationic polymers may be employed successfully. These two schemes are illustrated in Figure I-5. With a suitable anchor, high molecular weight anionic polymers will form loops and tails under certain conditions, forming the strong flocs desirable in papermaking. However, factors such as cationic additive type and concentration, anionic polymer concentration and certain papermaking conditions must be carefully controlled to achieve good retention levels. This is often difficult to do in an industrial situation.

Nonionic polyacrylamides generally do not improve retention as substantially as cationic polymers. Polyacrylamide homopolymers adsorb onto particles weakly by hydrogen bonding (15).

Amphoteric polyacrylamides are a relatively recent addition to the broad range of retention aids available. The degrees of anionic and cationic charge vary with the pH of the solution (36). There is little published information concerning the mechanisms by which such polymers improve retention.

Of the four classes of polyacrylamide based retention aids, cationics have found the most widespread industrial application. There is however, a lack of information in the literature concerning structural and composition effects on polymer effectiveness as a retention aid. In other words, other than trial and error approaches in which different polymers, often with poorly defined structural features, were tested as retention aids, substantial work has not been published on optimizing cationic polymers on a molecular level in order to optimize fines retention. Lindstrom (18) has shown that white water turbidity was lowest when cationics with high molecular weight and molar charge densities between 3.1% and 10.8% were employed. However turbidity measures do not quantitatively indicate fines

Figure I-5 Anchor Mechanism



retention. Arvela et al (3) showed a decrease in white water solids content with an increase in cationic polymer molecular weight. But the polymers they used had a charge density of 80%. Such polymers would perform as patch model flocculants. Besides not being the optimal type of retention aid in papermaking, patch model polymers might give less pronounced increases in retention with increases in molecular weight. In fact Arvela et al observed reversible flocculation with the three cationics they studied, as is common with patch model flocculants.

Also lacking somewhat is research on the external factors which influence a polymers effectiveness as a retention aid, although there has been some work done in this area. Moore (20) concentrated on the effects the zeta potential of a furnish, controlled with Alum, had on a specific cationic polymer's performance at a specific pH. Pelton and Allen (23) studied the effects certain ionic impurities had on polymer effectiveness. Tay (32) and Pelton et al (25) looked at the detrimental effects impurities inherent in newsprint white water had on cationic acrylamides. Lindstrom (18) did some research on the effects of pH on polymer effectiveness, and also the effects polymer concentration has on white water turbidity.

### 2.3 SCOPE OF THIS RESEARCH

The purpose of this research is to find polymeric retention additives which perform better than those commonly used, and to ascertain why these additives perform better in hopes of developing an additive which is optimized for the system studied.

To achieve this objective, the structural features which make a particular additive perform well must be understood. Also, the papermaking conditions which have an effect on additive performance must be understood.

There are no "custom tailored" polymers with all the desirable structural features for such research currently available, nor can such polymers be synthesized in the time allotted for this research. Thus industrially produced polymers with a variety of features were

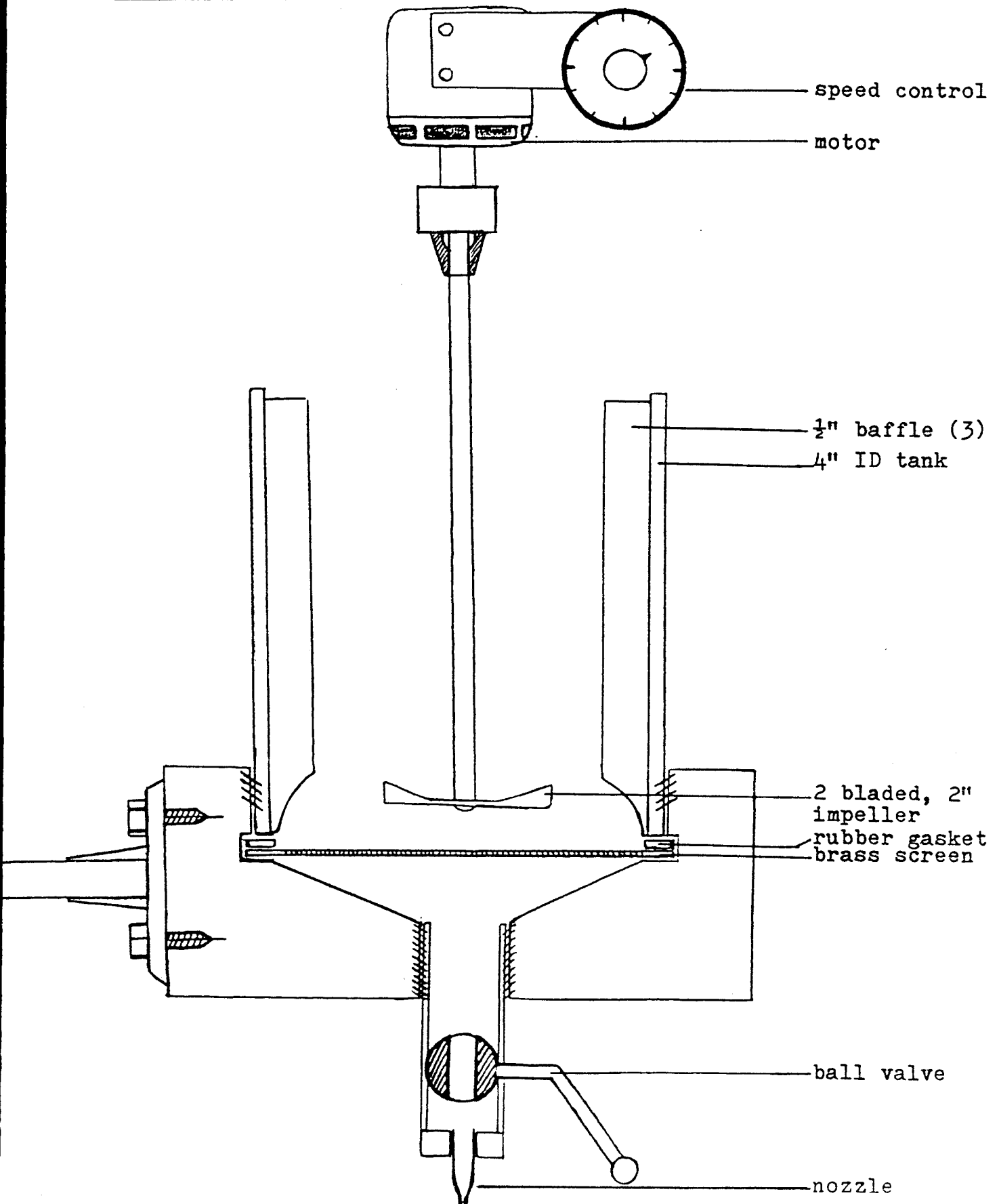
used as the best alternative. Many of these polymers are used in small quantities for applications other than fines retention, and have not been thoroughly tested as retention aids.

Also combinations of anionic and cationic polymers, a novel approach to fines retention which has shown some promise in the literature, were tried as alternatives to cationic polymers alone. It is possible that a novel retention system such as this could supersede cationic polymers in improving fines retention.

### 3. EXPERIMENTAL

As it is both economically and experimentally impractical to evaluate polymers under a variety of conditions on an actual paper machine, a laboratory device called a dynamic drainage jar (Figure I-6) is used to simulate important aspects of the papermaking process. The turbulence created on a paper machine can be approximated using an impeller in a baffled jar. Tam Doo (30) reports that the dynamic drainage jar can produce fibre wall shear stresses comparable to those found on a paper machine. During a run a portion of the swirling mixture of pulp and water is drained through a standardized brass screen. The filtrate, or white water is collected and later filtered through a membrane (1.2 micron) leaving only the fines. By relating the amount of fines passing through the screen to the amount capable of passing through ( the fines content ), the percent fines retention can be calculated. The drainage jar may be operated in two modes; with or without a 25mL pipette nozzle as the exit for the filtrate. Without the nozzle, a mat of fibres can form on the screen. With the nozzle in place, the flow rate of filtrate is reduced so as to minimize the formation of fibre mats. The elimination of mat formation is desirable so a comparison of polymers may be made based on their flocculation efficiency, without any filtration effects present, and because better reproducibility would be expected with a well defined screen pore size free of a fibre mat (26,22). Though a polymer which encouraged screen plugging would give improved fines

**FIGURE I-6**      Dynamic Drainage Jar



retention, such a polymer would likely not be an acceptable retention aid because it would also slow drainage. Also mat formation would produce an uneven flow of fines with time, making the white water collection volume an important consideration in determining fines retention. Despite the advantages of running with the nozzle in place, both modes are commonly used in paper industry testing. Most of the runs conducted in this research employed the nozzle, however some early runs were done without the nozzle in place. These early runs employed only cationic retention aids, and involved constant white water volume collection, thus the results are thought to validly compare the retention aids used, and to validly demonstrate trends when a single cationic retention aid is used under a variety of conditions. A comparison of results using this mode and the mode with the nozzle in place is not quantitatively valid though.

It has been demonstrated that the dynamic drainage jar can successfully predict the performance of pulp additives on paper machines. This device has thus been accepted as a laboratory apparatus for comparing additives and studying their effects under specific papermaking conditions (5,7,10,34).

The best procedure for evaluating retention aids for a specific papermaking machine would involve using actual headbox stock in the drainage jar. The general applicability of the results for such experimentation would be in question, however, because there are many differences between different papermachine stocks. Indeed, the fluctuation in an individual papermachine stock may be large enough to invalidate general application of results. Such things as pulp makeup and consistency, fines content and amounts of fillers and pigments added, and water supply variations may change the type of polymer required to achieve optimal retention. Also, should an actual headbox stock be employed, replication of results might prove difficult over longer time intervals as the original stock could be depleted, or could undergo aging processes, and new stock might be somewhat different. Because of

these problems, it was thought best to use pulps diluted in distilled water. The first pulp used, which was immediately available, was spruce thermomechanical pulp (TMP) obtained from the pilot plant pulping process at Abitibi-Price Research in Sheridan Park, Ontario. The second was a bleached 50% hardwood/ 50% softwood pulp obtained from the Pulp and Paper Research institute in Pointe Claire, Quebec. This pulp is used as a standard by the institute and affiliated organizations for research of this type.

Fillers such as  $\text{TiO}_2$  were not used in retention tests. It is recognized that the retention of such additives may be more important than the retention of pulp fines. However, the difficulties associated with measuring metallic additives, such as ashing, would require a great deal of time. Also, different fillers and pigments might behave differently with different additives, necessitating many runs with an assortment of additives present for a thorough investigation. Two runs were conducted with  $\text{TiO}_2$  to ascertain the effectiveness of a novel approach to retention with additive present.

The polymers used were obtained from various sources. Percol 292, a common cationic retention aid and the accompanying technical data (2) were obtained from Allied Colloids in Mississauga, Ontario. A sample of high molecular weight polyethylene oxide was obtained from Abitibi-Price Research in Sheridan Park, Ontario. Nalco Chemical of Naperville, Illinois sent several experimental and commercial polymers along with the technical data listed in Table I-2.

The polyethylene oxide and Percol 292 polymers were in solid form. All of the Nalco polymers were in inverse emulsion form. Inverter was supplied by Nalco to facilitate the dissolution of their emulsion polymers.

Alum was obtained from Fisher Scientific. Zirconium oxychloride was obtained from BDH chemicals. Water was distilled and deionized through a Barnstead "Nanopure" cartridge system.



Table I-2 Nalco Polymers : Technical Data

Nalco Code	Cationic Monomer	mol %	RSV	Process
CX 322	DMAEM•MSQ	5	10.4	#1
CX 305	DMAEM•MCQ	10	16.0	#1
CX 396	DMAEM•MCQ	10	15.0	#2
CX 397	DMAEM•MCQ	15	12.3	#2
CX 398	DMAEM•MCQ	27	12.1	#2
CX 316	DMAEA•MCQ	8	18.4	#1
CX 292	DMAEA•MCQ	15	8.9	#1
CX 296	DMAEA•MCQ	34	9.1	#1
CX 315	DMAEA•MCQ	50	9.8	#1
7664	DMAEM•MSQ	3.85	14.0	?
7654	DMAEM•MSQ	7.70	14.0	?
N770	anionic	35 NaAc	46	?

RSV stands for reduced specific viscosity.  
See Appendix B for details.

As per instructions supplied, stock solutions of the Nalco and Percol polymers were prepared no more than 48 hours before testing. Concentrations of these solutions were 0.1% active polymer, as suggested by both suppliers. Dissolution involved frequent manual shaking over a period of several hours.

During a typical run, a pulp in "slush" form was weighed and diluted to the required consistency in purified water. The water content of the slush was accounted for in this dilution. The pulp water mixture was then added to the drainage jar with the drain closed. The mixer was set at high speed for exactly 2 minutes to ensure dispersion of the pulp mixture. Mild agitation ( 150 rpm calibrated with digital tachometer ) was then initiated, and the appropriate amount of polymer stock solution was added using a pipette. Mild agitation was continued for exactly 30 seconds. The mixer was then adjusted to the desired run speed, and the filtering process begun. Exactly 100 mL of filtrate was collected in a 100 mL graduated cylinder while the filtration time was recorded. The filtrate was later filtered through a membrane to allow calculation of fines retention for the run.

## 4. RESULTS AND DISCUSSION

### 4.1 REPRODUCIBILITY

Several blank runs were conducted on the drainage jar to establish the level of reproducibility between fines retention measurements (Table I-3). These runs were conducted on the spruce TMP pulp with a measured fines content of 19.16% .

By taking the deviation of each of the measurements from the average for each impeller speed, a pooled variance estimate was calculated. This calculation yielded a variance, as estimated by pooled standard deviation, of approximately 2.0 . Applied to individual fines retention calculations, this level of reproducibility is acceptable. Moreover, little more could be done to increase reproducibility. Such things as the height of the impeller above the brass

Table I-3 Reproducibility

Retention %	Impeller Speed (rpm)			
	520	860	1160	1340
58	58	35	32	
64	56	38	31	
63	56	36		
	57			
avg. 61.7	56.8	36.3	31.5	

$$s_p^2 = \frac{d_1 s_1^2 + d_2 s_2^2 + d_3 s_3^2 + d_4 s_4^2}{d_i}$$

$d_i$  = degrees of freedom for each speed

$s_i$  = standard deviation for each speed

$s_p$  = 2.0 ( pooled variance estimate )

- Notes:
- Consistency = 0.5%
  - Nozzle not used
  - Spruce TMP pulp

screen, the volume of diluted pulp, the cleanliness, pH and temperature of the water and the volume of filtrate collected were all carefully controlled.

For situations in which pulp type, amount of polymer or other conditions were varied, duplicate runs were often conducted to gauge reproducibility. Judging from the agreement from such duplicate runs, reproducibility is of the same order as that in the blank runs shown above.

## 4.2 VARIABLES WHICH AFFECT RETENTION ON THE DRAINAGE JAR

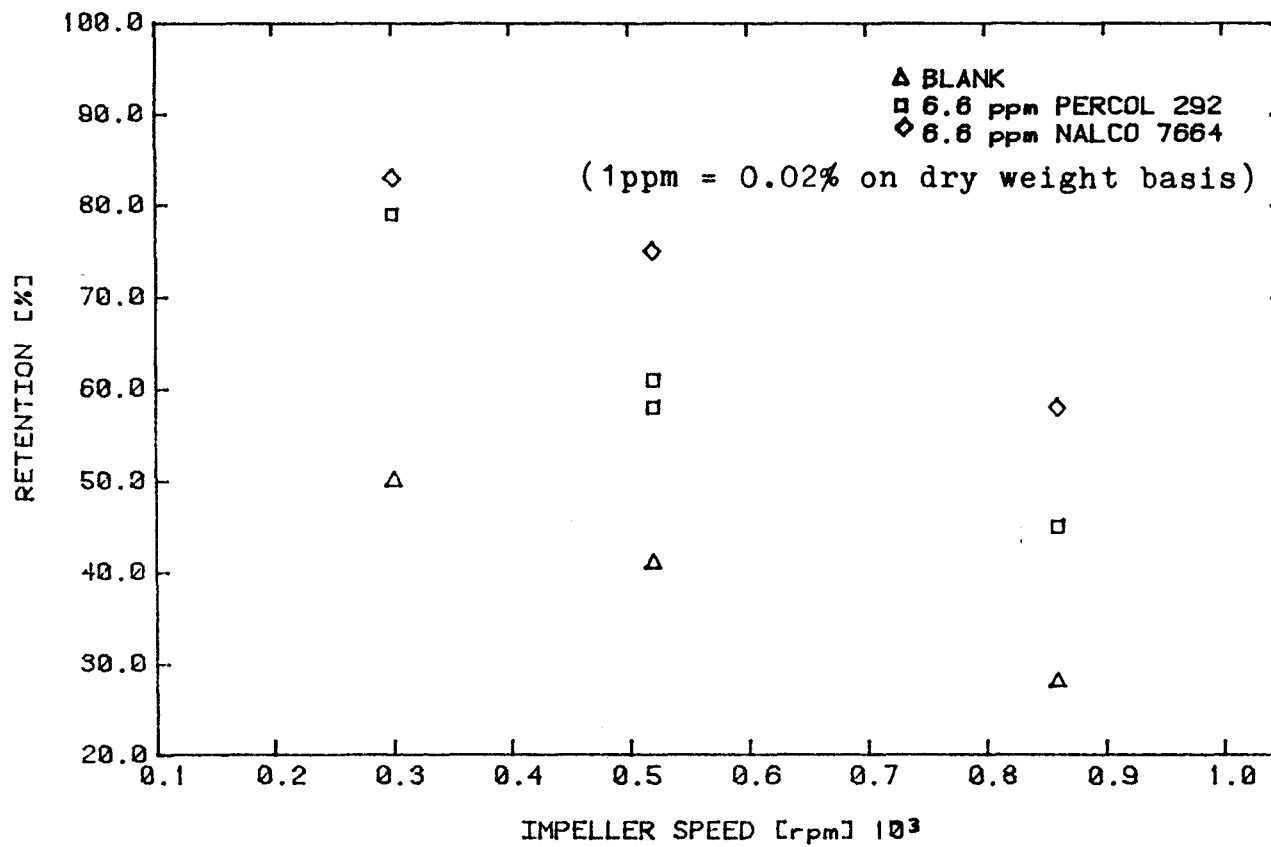
### 4.2.1 Impeller Speed (Turbulence)

Impeller speed has a large effect on retention. Figure I-7 shows a plot of fines retention vs. impeller rpm for a set of blank runs, and for a set of runs using 6.6 ppm Nalco 7664, a high molecular weight cationic polymer. These results can be simply explained by floc break up with high turbulence, resulting in many dispersed fine particles capable of passing through the screen.

It has been suggested that such plots can be used to predict additive performance on an actual paper machine if headbox stock is employed in such a test (1,7,10). The prediction would involve a fines retention measurement on the machine without any retention additives present. This measurement would be used to find a level of turbulence on the drainage jar which gives the corresponding fines retention level. The fines retention level given by the drainage jar additive at this turbulence level predicts the performance of that additive on the paper machine. In this reasearch, confirmation of this prediction method was not possible because of the lack of an available paper machine.

The importance of comparing retention additives at different levels of turbulence is evident, however. Polymer A may perform better on a machine with lower turbulence, while polymer B may do better on a machine with more turbulence, where stronger flocs are

Figure I-7 Fines Retention vs. Impeller Speed



required. Practically, the "corresponding rpm" to real paper machines might be in the 300 to 860 rpm range on the drainage jar used in this research, judging by the blank fines retention at these impeller speeds.

#### 4.2.2 Turbulence Time

Figure I-8 indicates that the time which the polymer retention aid is subjected to turbulence before drainage is begun can have an effect on the fines retention for that run. To minimize this effect, drainage was initiated immediately after impeller speed was increased to the experimental level. With the nozzle in place, 100mL drainage times varied by several seconds at most in a series of runs, with an average drainage time of about 2 minutes. During drainage, the drainage jar contents were subjected to turbulence, but because the drainage times between runs varied little, the effect of turbulence time is seen as a very minor source of error.

#### 4.2.3 Temperature

Paper machines are generally run at temperatures exceeding ambient for various reasons. Figure I-9 indicates that fines retention changes with temperature for a particular additive. Note that retention at 50 C, a common operating range for a paper machine, is higher than retention at room temperature. The reasons for this are not clear. Perhaps polymer adsorption is enhanced at slightly elevated temperatures, possibly due to less extensive coiling. Lindstrom (17) has data showing enhanced cationic polymer adsorption onto cellulose if temperature is increased slightly from ambient, giving some evidence to back this explanation. Note, however, that there seems to be a drop in retention between 50 C and 70 C in Figure I-9.

Figure I-8 Fines Retention vs. Turbulence Time

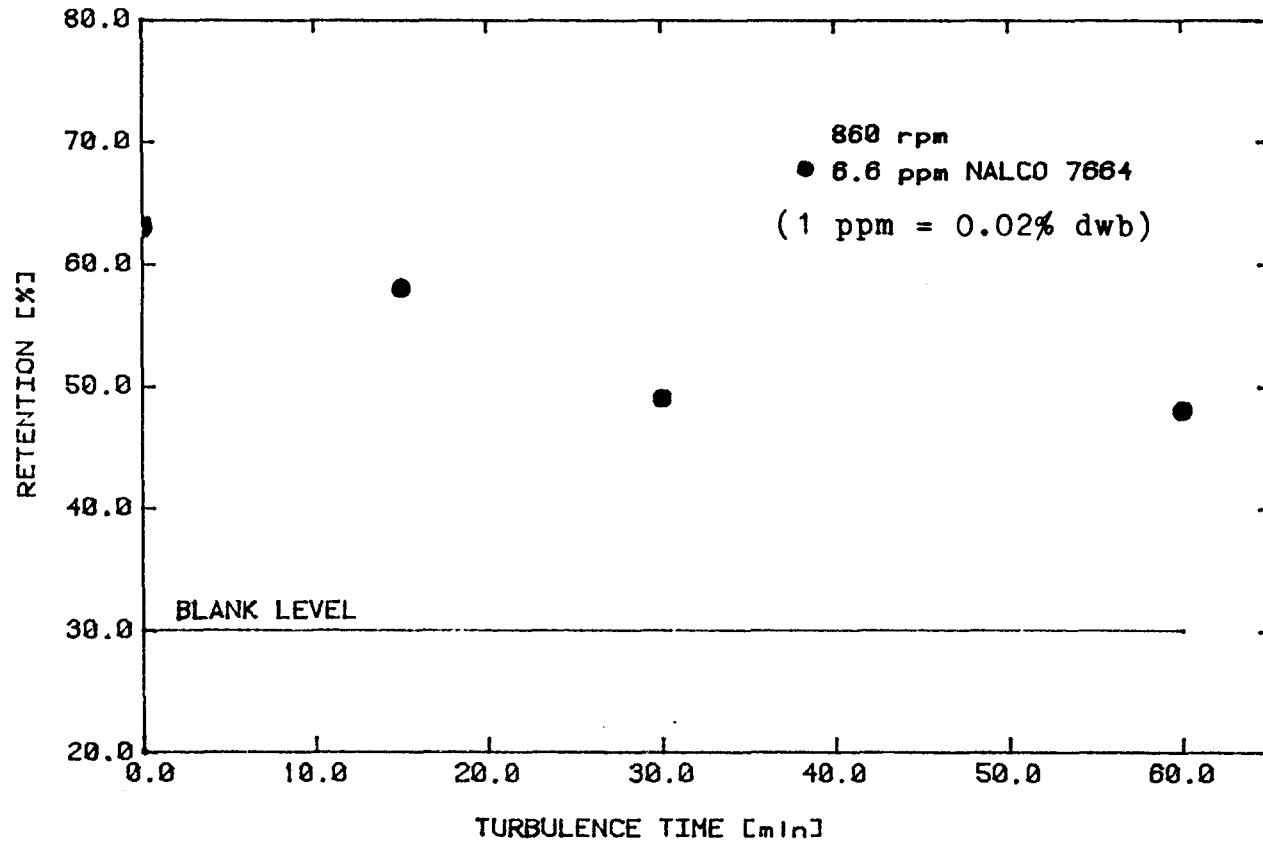
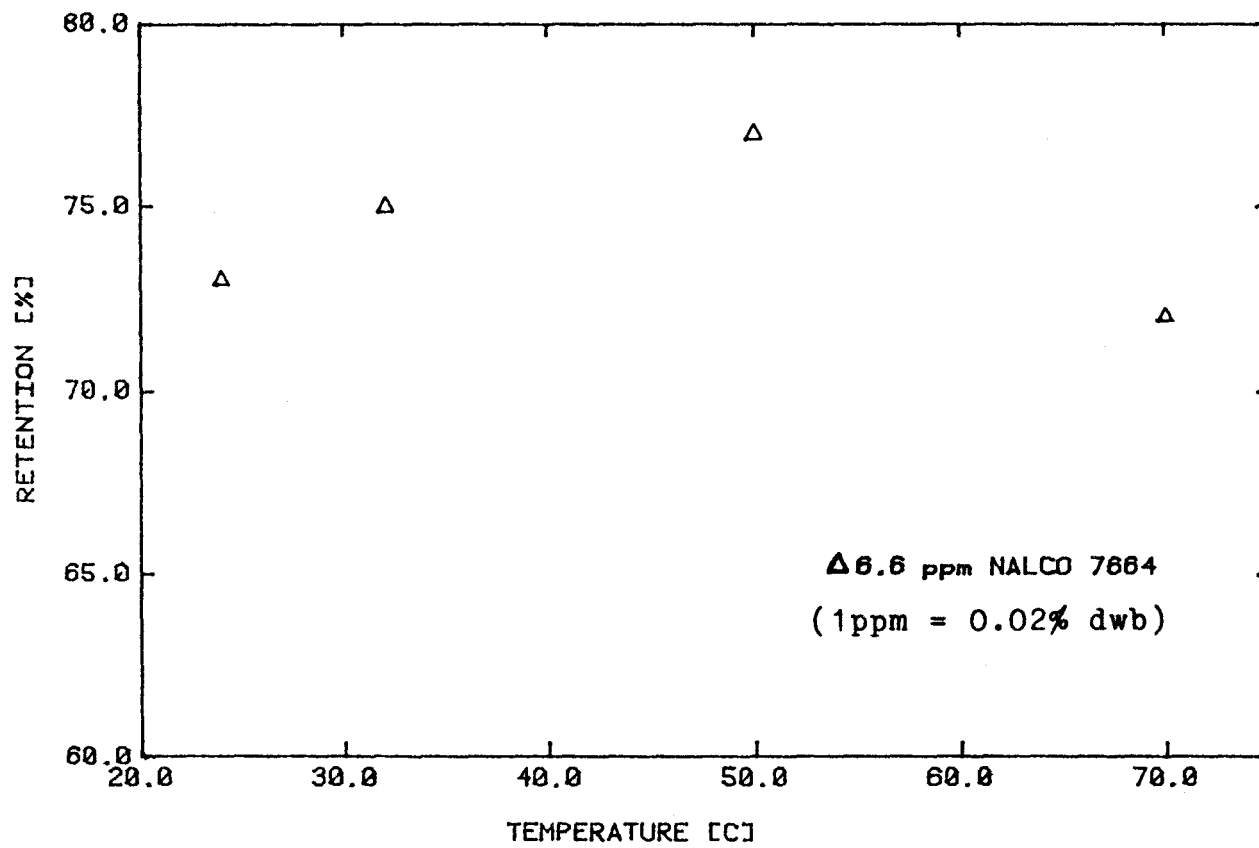


Figure I-9 Fines Retention vs. Temperature





Experimentation was conducted at 22 C because of difficulties involved in running the drainage jar at the elevated temperatures common on paper machines, but, perhaps a thorough investigation of retention additives should include a comparison in a range of temperatures because of the possibility of different temperature - retention relationships.

#### 4.2.4 pH Effects

The pH range used in papermaking is quite broad. Traditionally pH has been kept in the 4-6 range, but neutral and alkaline papermaking systems also are used. There can be changes in pH on individual paper machines due to such things as process water pH fluctuations as well. Common cationic retention aids should not be chemically affected over a broad pH range because the quaternary ammonium groups which impart the charge are stable ions, except under severe conditions not normally associated with papermaking. However, Lindstrom (18) published results showing the particular retention aids he used became less effective at pH 4 and substantially less effective at pH 3. Figures I-10 and I-11 show similar results for Percol 292, but not for the Nalco polymer. This information is disconcerting because a flocculants effectiveness might fluctuate if the headbox pH falls.

There are two possibilities with respect to explanations for these results. At low pH, the ionic character of pulp materials changes. Jaycock and Pearson (14) have data showing that the zeta potential of cellulose fibres becomes positive at about pH 3. The anionic charge resulting from dissociated carboxylic acid groups inherent in all wood materials decreases at low pH because certain types of acid groups become undissociated. Such a change might affect the strength of adsorption of a particular type of polymer onto particle surfaces. The Nalco 7664 polymer has a charge density of 3.85 mol%, while the Percol 292 has charge density of 10 mol%. It would seem that a change in the anionic charge on pulp particles should have some effect in the retentions observed for both polymers, which is not the case. A more

Figure I-10 Fines Retention vs. pH - Percol 292

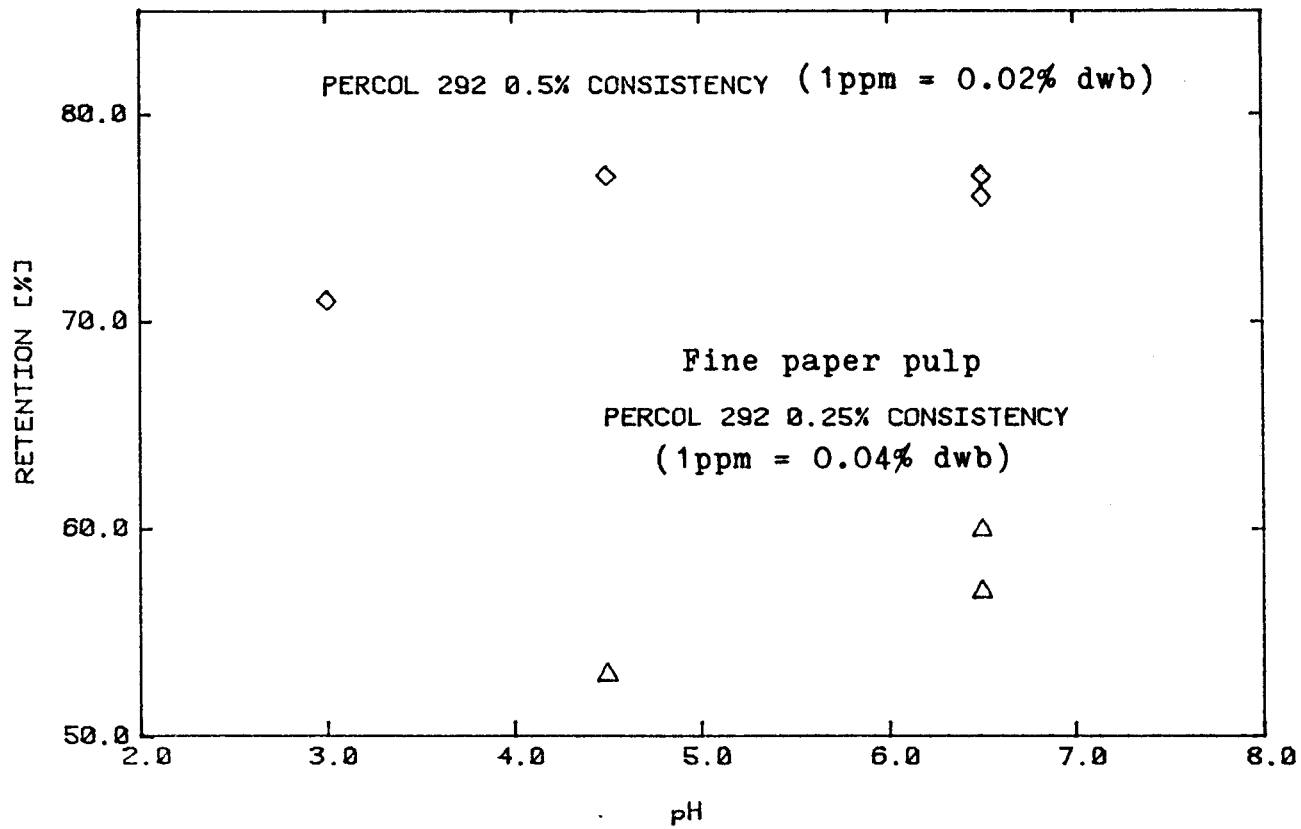
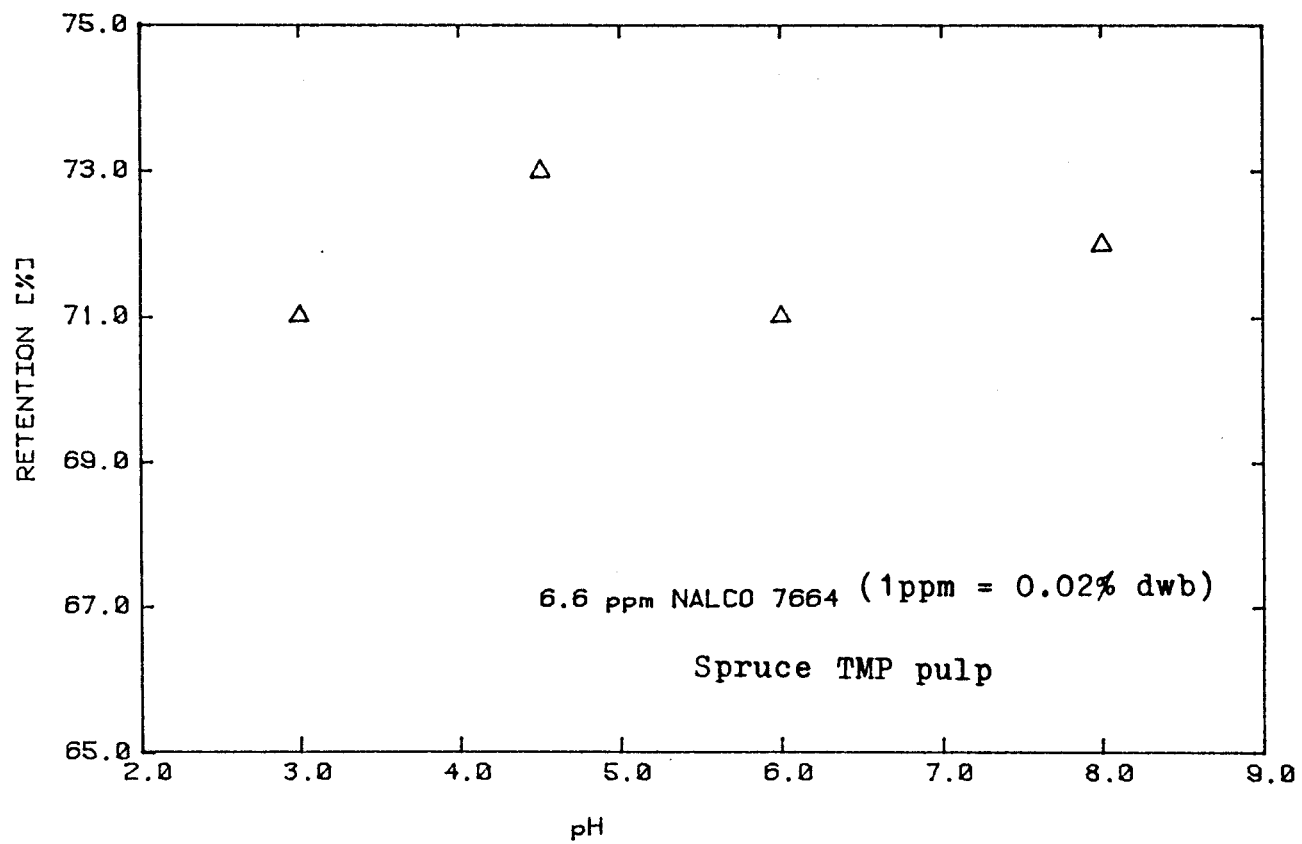


Figure I-11 Fines Retention vs. pH - Nalco 7664



likely explanation for the differences between the pH sensitivities of the two polymers lies in the effects  $H^+$  concentration has on the tertiary structure ( the coiling ) of large, cationic molecules. At low pH molecular coiling should be tighter because the environment around the molecule has many  $H^+$  ions. However, a molecule with a higher cationic content may experience a relatively large compression with a drop in pH, while a lower charge density molecule may not compress to the same extent. Tighter coiling would tend to cause adsorption with less extensive looping, and thus tend to lower retention. Still one would expect to see some loss in fines retention for the lower charge density polymer at low pH. Certainly more work is necessary in this area to determine if polymer pH sensitivity is somehow dependent on cationic content.

In this research, the pH of solutions containing spruce TMP pulp was generally kept at 4.5, a common pH for papermaking with pulp of this type. With the 50/50 hardwood/softwood bleached pulp pH was generally kept at 6.5 . In an industrial situation, especially when papermaking pH is low or highly variable, retention aids should be checked for pH sensitivity.

#### 4.2.5 Polymer Concentration

There are two common ways of reporting retention aid concentration in a particular furnish. The first is based on the ratio of polymer mass to the mass of dry pulp present, often expressed as a percent value. Such a value is helpful in cost calculations. The second method of reporting concentrations is in ppm or in milligrams of polymer per litre of furnish. This value is a true concentration, however, the consistency of the furnish must be known to calculate additive cost. Also comparisons can be deceiving if furnish consistencies are not stated. In this research both methods are reported where possible.

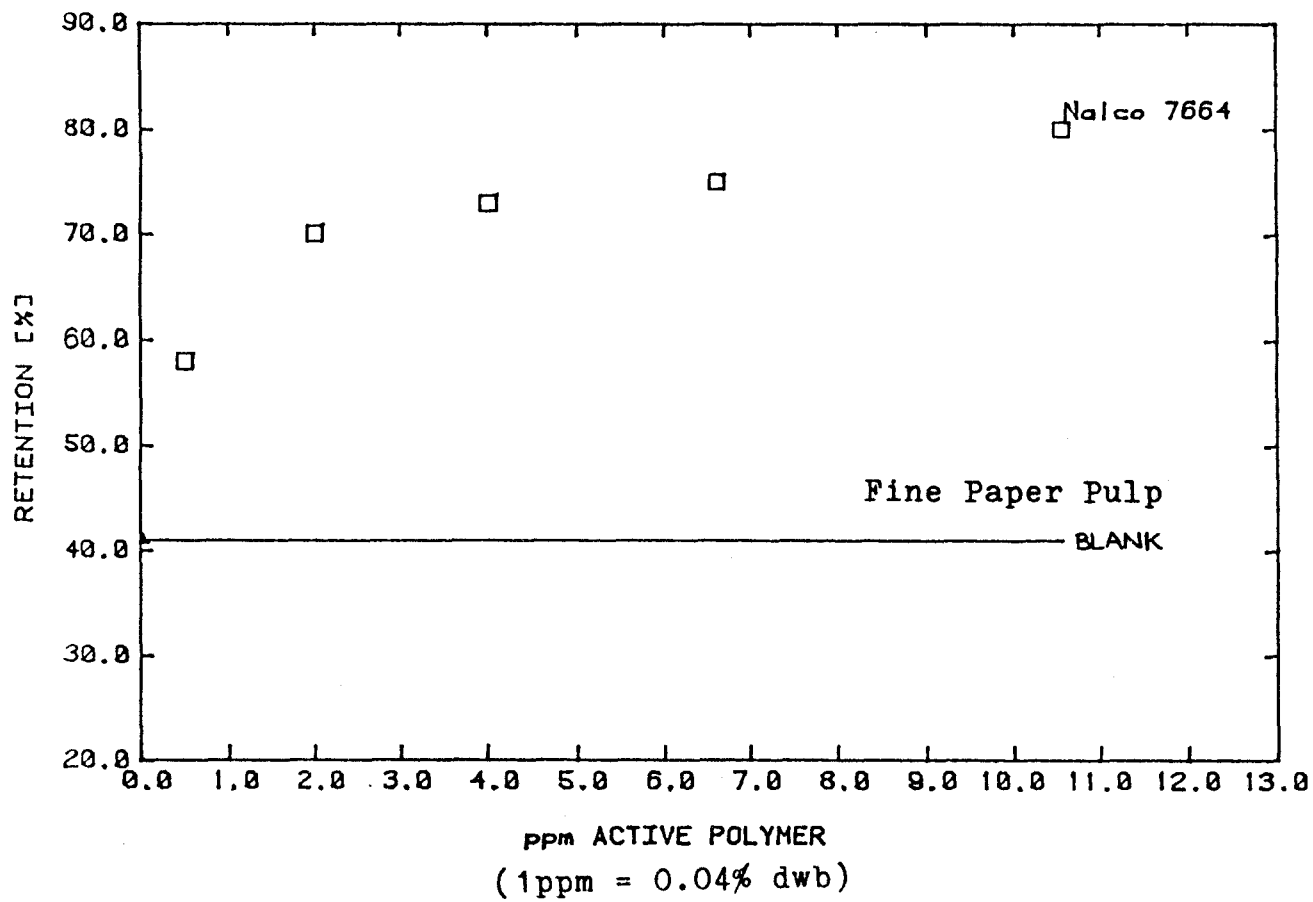
Figure I-12 shows how fines retention varies with concentration of a cationic polymer. There is a large retention improvement with the addition of a small amount of additive. Large additions do not substantially improve retention over an addition of about 2 ppm. In fact, Lindstrom (18) has shown that retention can be detrimentally affected at even higher additive concentration. Concentrations much greater than those looked at in Figure 12 would thus offer little advantage in papermaking. In fact, because the cost of polymer is very high with respect to the cost of the paper produced, and because more often than not the profit margin in papermaking is quite small, there is considerable advantage to operating at a low concentration with some compromise in fines retention. A comparison of retention additives must thus be done at a range of concentrations, as there are different cost constraints at different papermaking mills which dictate how much polymer may be added.

#### 4.2.6 The Effects of Impurities

As previously stated, the majority of runs were conducted in distilled deionized water for the sake of consistency. This is not a realistic method of comparing flocculants because impurities will exist to varying degrees in all papermaking systems. In fact dissolved and colloidal impurities have prevented the use of polyacrylamide based polymers on a large scale in the manufacture of newsprint, a particularly dirty system. Many successful drainage jar tested retention aids have failed at the mill because of the failure to account for the impurities present. Literature has also indicated that ionic impurities such as metal salts have detrimental effects on cationic retention aid performance (23,4). Again, a thorough test of a retention aid should involve using actual headbox stock after the aids' competence in a clean system has been established.

A few runs were conducted using newsprint white water to dilute relatively clean spruce TMP pulp. These tests were meant to approximate a real world newsprint headbox

Figure I-12 Retention vs. Polymer Concentration



stock in newsprint manufacture. Retention dropped nearly to blank levels with polymers that gave significant retention improvements in a "clean" system. Very large additions of cationic polymer did increase retention, but such addition levels would not be economically feasible ( Table I-4 ).

The explanation for these results lies in the nature of the impurities present in newsprint white waters, as mentioned briefly in the background section. Work at Abitibi-Price (28) has shown the existence of fatty acids in white water in appreciable amounts. Wood based colloids are also present. Cationic molecules can interact with both these materials. Though such materials may make up only a relatively small proportion of the total solids by mass percent, they constitute the majority of solid surface area in a typical newsprint system, or in other words, the greatest proportion of anionic groups that the cationic polymers can interact with. Hence, in a dirty system, a great deal of cationic polymer is wasted because it adsorbs mostly irreversibly to fine colloids and dissolved materials, and not to fines as intended.

Polyethylene oxide is a non-ionic polymer which has shown promise in many newsprint systems (24,25). A run conducted with a sample of this polymer ( MW of about 5 million ) showed retention improvement over similar concentrations of cationic polymer for spruce TMP pulp diluted with newsprint white water (Table I-4). However, in a similar run with distilled deionized water as a diluent, no retention improvement was observed. This supports Tay's work (32,33) showing similar results. Tay and Pelton (27) believe polyethylene oxide somehow associates with white water impurities to produce an effective retention aid. Polyacrylamide homopolymers do not seem to follow this route.

Table I-4 Retention with Newsprint White Water Present

Nalco Cationic Polymer #7664 (ppm)	Alum (ppm)	Retention (%)
0	0	44
0	0	48
13.3	0	59
13.3	0	56
20.0	0	64
20.0	96	68
10.0 PEO*	0	62

\* 10 ppm of polyethylene oxide was employed in this run for comparison. The quoted molecular weight of this polymer is 5 million.

Notes: -Spruce TMP pulp diluted with 75 % distilled water and 25 % white water from a newsprint mill (McLaren Co., Masson, Quebec, Oct. 28, 1983. ) was used in these runs.  
-impeller speed = 860 rpm



### 4.3 COMPARING DIFFERENT CATIONIC POLYMERS

Several cationic polymer samples provided by Nalco Chemical Co. of Naperville, Illinois were compared on their ability to improve fines retention at different concentration levels. Percol 292, made by Allied Colloids, was also included in this comparison. These polymers encompassed a broad range of charge densities. All were high molecular weight, but molecular weight varied in the high range, as shown by RSV viscosity measurements. Table I-2 shows the Nalco codes for each of the polymers studied, along with other pertinent information as given by the supplier. Absolute molecular weights can not be easily determined for such polymers because of the cationic charge. Gel permeation chromatography is difficult to use because of the adsorption of cationic species onto common column packings. Also the lack of appropriate standards would pose problems if the adsorption problem could be overcome. Light scattering is not always effective in determining cationic polymer molecular weight.

Table I-5 shows the performance of the Nalco polymers. Polymers CX316 and CX396 are clearly superior to the other polymers studied. It is, however, difficult to conclude which structural properties give these polymers an advantage over the others. Both CX316 and CX396 have charge densities within the 3 - 10% range Lindstrom (18) thought to be optimal for the furnish he used. Both these polymers also have higher viscosities than the other Nalco polymers, however. Indeed, these polymers may also differ in molecular weight distribution and charge density distribution, properties which could have bearing on retention aid effectiveness. As far as deciphering the relationships between polymer structure and polymer effectiveness, this data should thus only be used to illustrate some trends.

Comparing polymers CX315, CX296 and CX292, which have similar viscosities but differences in charge density, there seems to be an increase in retention with a decrease in the charge density from 50% to 34%. The distinction between polymers with charge densities of

Table I-5 Performance of Nalco Polymers

Polymer	% Cationic	RSV	Retention		
			2 ppm	4 ppm	6 ppm
CX 316	8	18.4	80	84	85
CX 396	10	16.0	75	82	82
7654	7.70	14.0		80	
7664	3.85	14.0		80	
CX 305	10	16.0	69	77	78
CX 292	15	8.9	73	74	77
CX 296	34	9.1	73	74	75
CX 322	5	10.4	70	73	76
CX 398	27	12.1	69	72	74
CX 397	15	12.3	68	72	73
CX 315	50	9.8	67	67	71

- Notes: - Blank retention = 55%
- Impeller speed = 520 rpm
- Consistency = 0.5 %
- 1 ppm of polymer is equivalent to 0.02 % on a dry weight basis.
- Fine paper pulp ( 50 % hardwood/ 50 % softwood bleached ) was used in these runs.

34% and 17% is less pronounced. It seems that the 15% charge density polymer is less effective than the 34% charge polymer at higher concentration levels.

Looking at polymers CX397 and CX398, the same similarity in retention seems to exist between two polymers with different charge densities but similar molecular weights. Lindstrom's data (18) is not extensive enough to support or disagree with these observations.

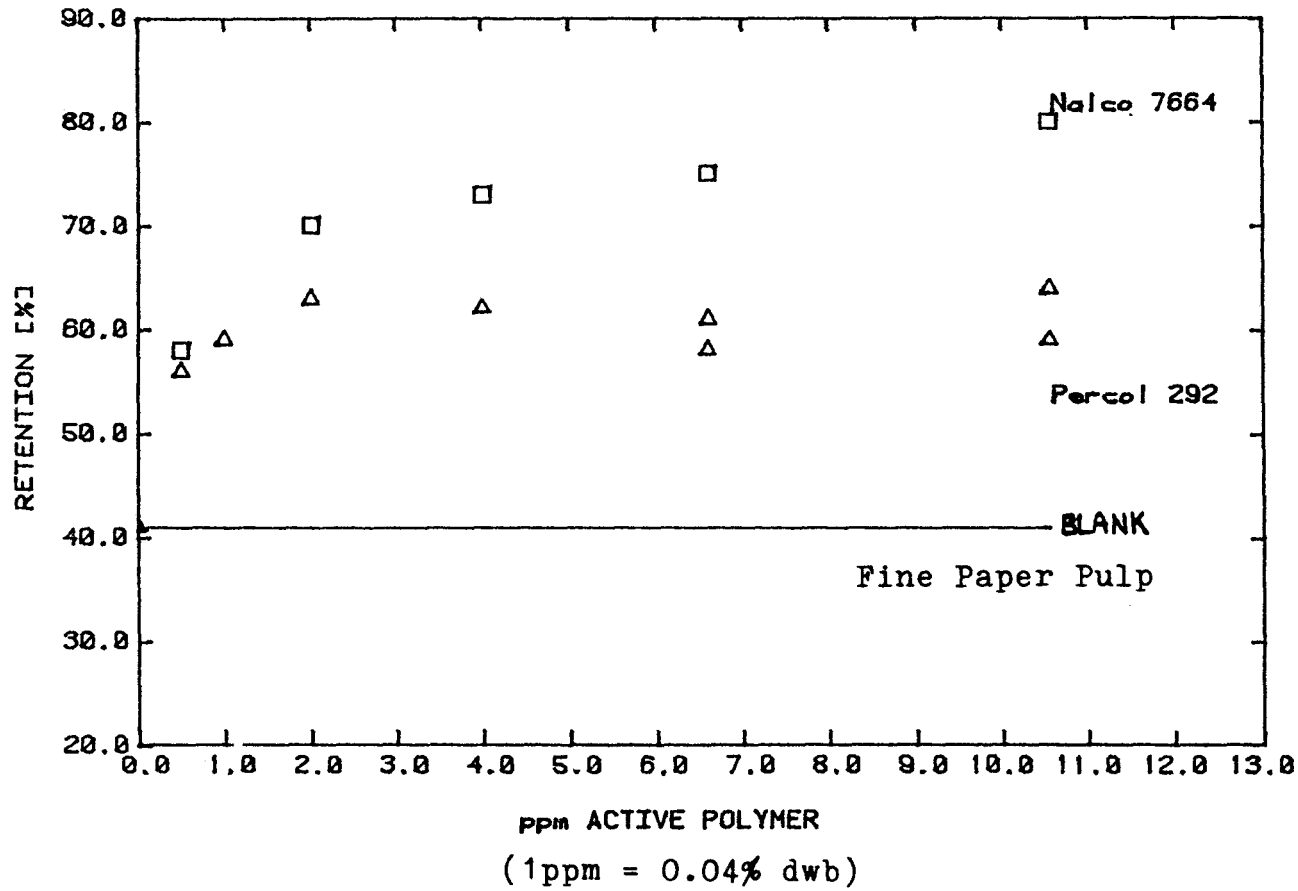
Perhaps the most important revelation from this comparison is the advantage CX316 has over Nalco 7664 which in turn is superior to Percol 292, the commonly used flocculant, as shown by Figure I-13. In fact Nalco 7664 is superior to Percol 292 at all concentration levels. There would undoubtedly be a price difference between CX316 and Percol 292, with the latter being perhaps 1/3 as costly. But it may be possible to reduce polymer dosage such that CX316 becomes the economically favourable additive when a certain retention level is required. Also, it is likely that more widespread use of CX316 would lower its price somewhat.

It must again be stressed that these results apply to a particular furnish, and may not be applicable to specific papermaking systems, though there is likely to be some correlation.

#### 4.4 SOME IDEAS ON POLYMER PROPERTY EFFECTS

Cationic polymers, as stated previously, are copolymers of acrylamide with specific cationic co-monomers. Information on exactly how such polymers are produced by Nalco and Percol is proprietary. The least expensive way to produce such polymers is by a batch process in which both monomers are simply reacted in a well mixed reactor without any inputs during the reaction. Such a process inherently produces copolymerization drift so that the resulting batch of polymer contains a broad composition distribution. The average composition is usually quoted as determined by the ratio of monomers initially added to the reactor, but the

Figure I-13 Comparison of Percol 292 with Nalco 7664 at Several Concentrations



actual breadth of the composition is usually not known. In an extreme case, the copolymer could be essentially a mixture of two homopolymers, polyacrylamide and the homopolymer of the cationic monomer. Polymers with controlled composition drift can be produced by semi-batch processes. Such polymers, if made properly, can have very narrow composition distributions.

A polymer with a broad composition distribution around an optimum charge density would not be expected to perform as well as a polymer in which all molecules have the optimum composition. The reasoning follows from Lindstrom's work and this research showing that polymers with very high and very low charge densities perform poorly as retention aids. Thus a broad composition distribution polymer would contain some molecules which are not serving their purpose of improving fines retention. The intensity of this effect would depend on the actual breadth of the composition distribution, and the relative effectiveness of polymer molecules with compositions somewhat removed from the optimum. Both of these factors are difficult to measure because of the lack of information concerning composition distribution, and thus inadequate information on how molecules removed from the optimum charge density perform.

#### 4.5 NOVEL APPROACHES TO IMPROVED FINES RETENTION

##### 4.5.1 Anionic Cationic Synergism

Anionic polymers, in combination with cationic agents, have shown good results in improving fines retention (5,16,21,34,36). Several runs were conducted with a ratio of approximately 10:1 cationic to anionic polymer concentration, as this ratio has been shown effective in the literature. All of these experiments resulted in poor retention levels; levels that are lower than those with the cationic polymer alone. The cationic polymers used, however, were loop model types, as no highly charged low molecular weight cationic could be

obtained. Patch model polymers were used in the literature. It is also possible that an improper ratio of cationic to anionic polymer was employed for the particular polymers used.

#### 4.5.2 Zirconium Oxide as a Retention Additive

$ZrOCl_2 \cdot 3H_2O$  has been successfully tested as a precipitating agent for dissolved materials in newsprint manufacture. A water soluble powder, this compound forms highly cationic ions and hydrolyzed species which are strongly adsorbed by anionic materials. It was thought that  $ZrOCl_2$  might provide strong cationic anchors on fines particles at fairly low concentration levels. The testing scheme used is shown diagrammatically in Figure I-14. Table I-6 shows retention levels for various combinations of Zr/ anionic/ cationic. Retention values along the x-axis are standard cationic runs with no recycle.

Visually, when anionic polymer was added to the Zr/anionic laced fines, flocculation occurred almost immediately. The results for 6.6 ppm cationic/ 2ppm  $ZrOCl_2$  / 1.3 ppm anionic show a very large improvement over the base case 6.6 ppm cationic run (92% retention vs. 74% retention). Note that the retention level seems quite "peaked" with respect to cationic polymer concentration.

Two runs were conducted with  $TiO_2$  present to ascertain the effectiveness of this novel approach in the retention of an expensive additive. These results are presented in Table I-7. As well as improving overall fines retention (retention of pulp and additive fines), the ash content of the retained pulp increased from 1.8 % to 2.9 %, an increase of more than 50%. Thus this novel approach seems to result in much better  $TiO_2$  retention. The time involved in this type of retention measurement, and the difficulty maintaining a uniform stock dispersion of  $TiO_2$  in water prevented further tests.

Such a novel system is likely not economically feasible because of the relatively large amounts of chemicals used. Nevertheless, the papermill equivalent of such a process is

**Figure I-14** Zr Application in Fines Retention

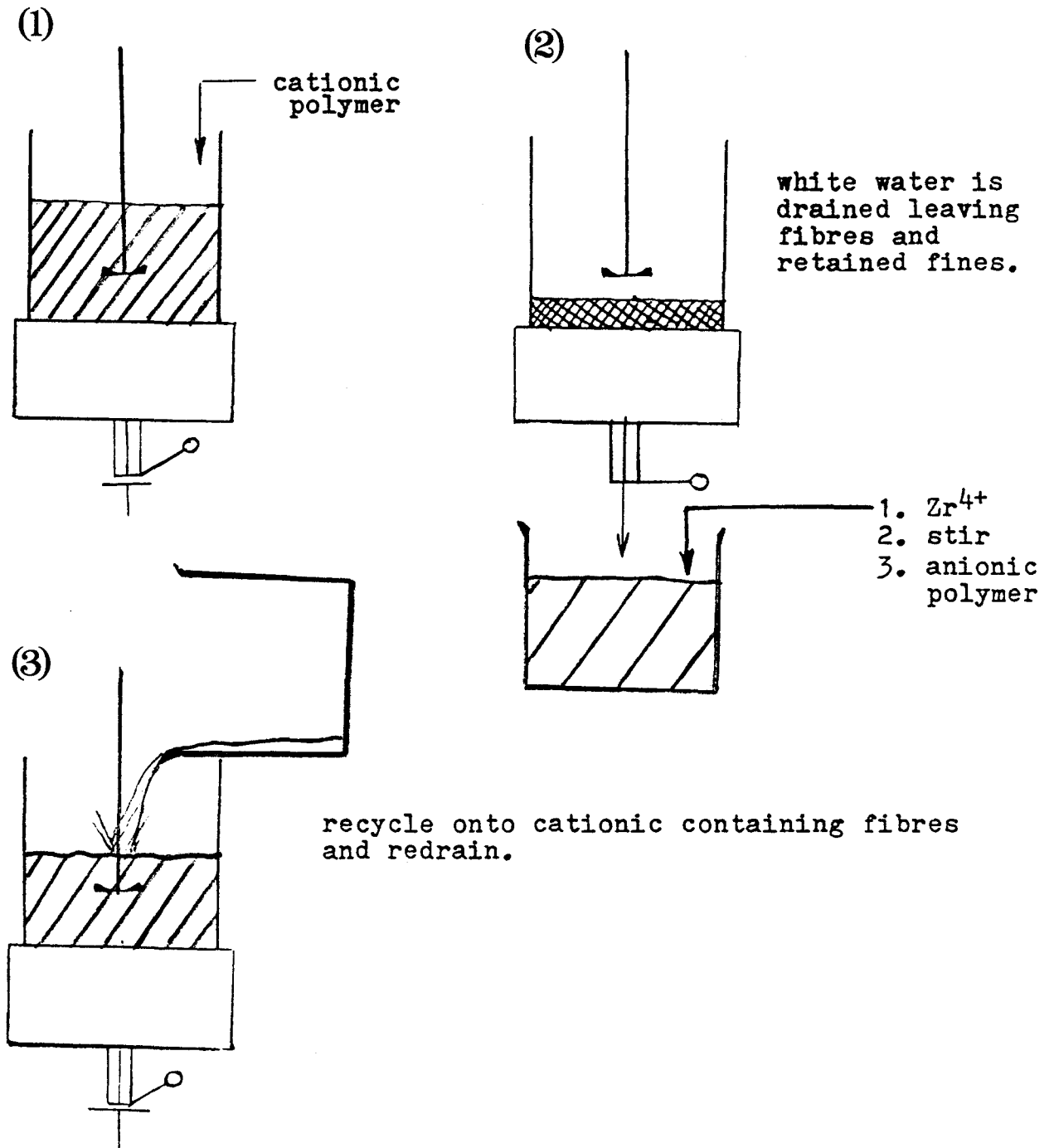


Table I-6 Retention Levels with Zr as an Additive

<u>ZrOCl<sub>2</sub>·3H<sub>2</sub>O</u> (ppm)	<u>anionic</u> Nalco 330 (ppm)	<u>cationic</u> Nalco 7664 (ppm)	<u>Retention</u> (%)
0	0	0	41
0	0	0.5	58
0	0	2.0	70
0	0	4.0	73
0	0	6.6	74
0	0	10.6	80
0	0.3	3.3	61
0	0.7	6.6	78
4.0	0.4	4.0	72
4.0	0.7	2.6	70
4.0	0.7	6.6	86
4.0	1.3	6.6	83
2.0	0.4	4.0	74
2.0	1.3	7.9	85
2.0	1.3	5.3	78
2.0*	0.7	6.6	87
2.0*	0.7	6.6	87
2.0	1.3	6.6	92
2.0**	2.0	6.6	89
2.0**	2.0	6.6	89

\*,\*\* repeat runs

Notes: - method as per Figure I-14  
 - consistency = 0.25%  
 - 1ppm = 0.04% dwb  
 - impeller speed = 520 rpm  
 - fine paper pulp used



Table I-7 Retention with TiO<sub>2</sub> Present

<u>ZrOCl<sub>2</sub>·3H<sub>2</sub>O</u> <u>(ppm)</u>	<u>anionic</u> <u>Nalco 330</u> <u>(ppm)</u>	<u>cationic</u> <u>Nalco 7664</u> <u>(ppm)</u>	<u>total fines</u> <u>retention</u> <u>(%)</u>	<u>ash content</u> <u>of retained</u> <u>pulp (%)</u>
0	0	6.6	65	1.8
2.0	1.3	6.6	93	2.9

- Notes:
- consistency = 0.25 %
  - 1 ppm = 0.04% on a pulp dry weight basis
  - fine paper pulp used
  - 5 mL of a 1 % suspension of TiO<sub>2</sub> was added to the drainage jar prior to any mixing of the pulp.
  - impeller speed = 520 rpm

shown in Figure I-15. In general, such an approach to fines retention would be difficult to implement on an actual paper machine because of the problems associated with maintaining additive levels at optimums. However, the very positive results shown are thought to warrant further investigation, perhaps with different polymers which could be more effective at lower dosages, and with Alum to replace  $ZrOCl_2$ .

Attempts to mix anionic polymer with  $ZrOCl_2$  prior to introduction into a pulp furnish resulted in no visible flocculation, whereas subsequent addition of anionic polymer to a zirconium laced furnish did result in visible flocculation. The addition of  $ZrOCl_2$  is thought to crosslink the anionic polymer, making it insoluble. If such a mixture could be made without substantial crosslinking, an effective substitute for cationic retention aids could result. Attempts to hinder crosslinking by introducing large amounts of NaCl, or by lowering pH seemed to help somewhat, but the resulting "pseudo cationic" polymers did not perform nearly as well as the other cationic retention aids used.

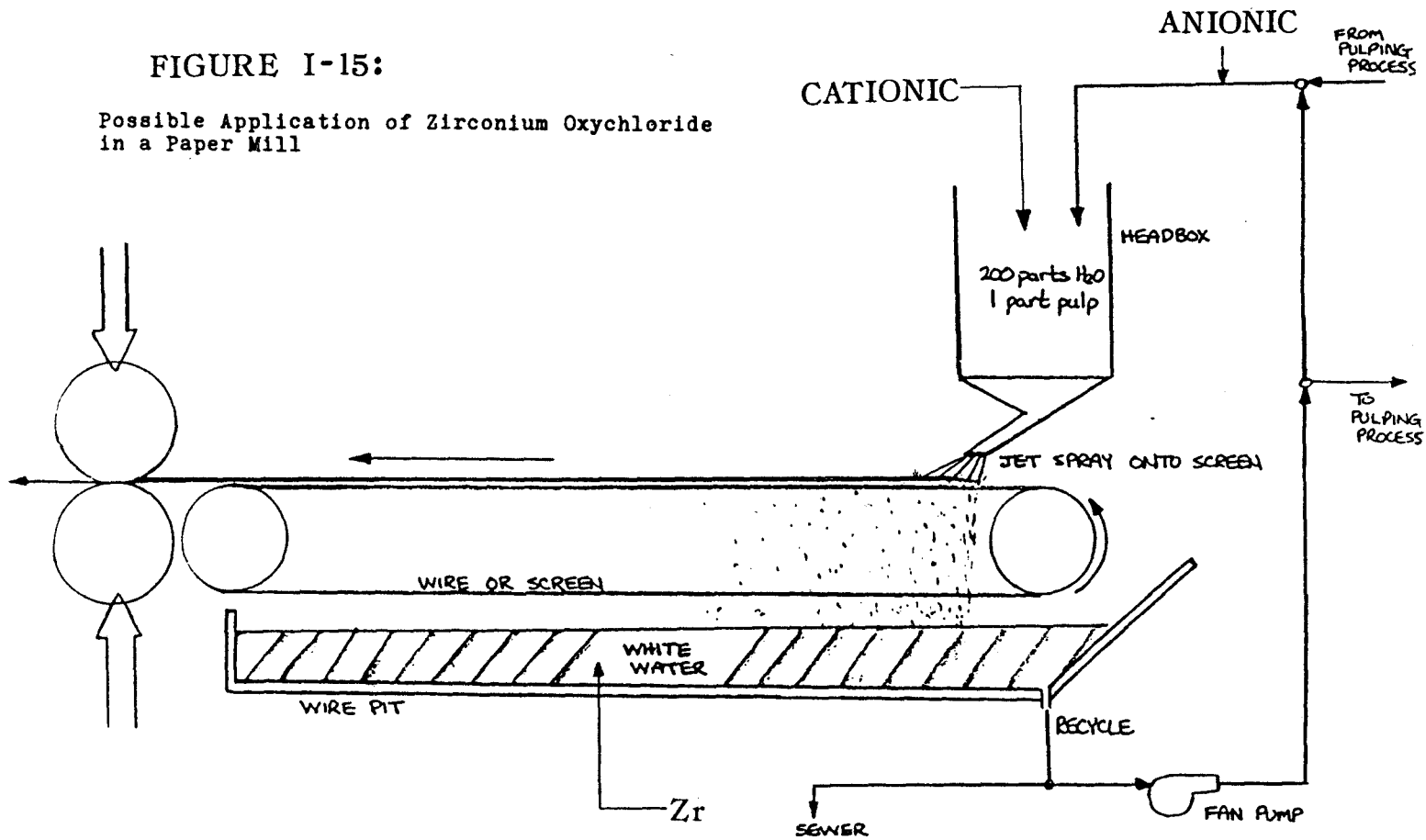
#### 4.6 RECOMMENDATIONS

Perhaps the most difficult problem with the results is the confounded effects of polymer molecular weight and polymer charge density. To resolve these effects, narrowly charge distributed polymers with similar molecular weights, and a set of polymers with a given charge and a variation in molecular weight should be studied. It is thus recommended that such polymers be synthesized before further research is begun.

Research with these polymers would reveal the optimal charge density for a particular system, and also give information on the effects of molecular weight and straying away from the optimal charge density. In other words retention vs. molecular weight and retention vs. charge density plots could be prepared.

FIGURE I-15:

Possible Application of Zirconium Oxychloride  
in a Paper Mill



Still, a big problem would be the applicability of these results to systems with different pulp types or conditions. It is very unlikely that the polymer optimized for the pulp used in this research would be optimal for all pulp types and papermaking conditions. However, it is very likely that such a polymer would perform significantly better than the currently used polymers on many papermaking machines, especially those with similar pulps and conditions to those employed in the research. Hence there is some commercial value to optimizing a polymer in a particular system. The actual optimization for a papermachine is not really a research matter, and should be left to the paper company or the polymer manufacturer.

There is a chance that cationic polymers could be replaced by a novel retention approach such as the Zr/anionic/cationic combination. Finding an economically feasible novel system and optimizing it might be of interest. But whether such an approach would work on a large scale is a difficult question to speculate on. The problem of very concentration dependent retention might be very difficult to solve at an actual mill. In the near future at least, the optimization of simple cationic retention aids holds greater promise as far as economic feasibility and ease of implementation on a large scale.

## 5. CONCLUSIONS

The data shown has indicated several methods of increasing fines retention for a particular furnish over fines retention obtainable with a common commercial flocculant, Percol 292. The more effective methods include the use of cationic polymers CX316 and CX396 made by Nalco Chemicals, and the use of a Zr/anionic/cationic tertiary system. It must be remembered that although these results show promise, more work must be done with actual headbox stocks to ensure that the improved retention methods are applicable to real

papermaking furnishes. Certainly the costs and ease of implementation of new retention aids must be considered before spending time testing them on real furnishes.

The structural aspects of cationic polymers which increase retention are less clearly indicated by the data presented. The polymer which performed best, Nalco CX316, had the highest molecular weight, as indicated by the viscosity, and a charge density of 8 mol %. Other data shows that polymers with high viscosities and charge densities in the 3 - 25% range seem to perform well, though not as well as CX316. Because of the lack of polymers "tailored" for this research, however, it is difficult to ascertain the relative effects of changes in molecular weight and changes in charge density. Indeed, different molecular weight and charge density distributions in the polymers studied could have significant influences on results.

Several papermaking conditions were shown to affect the performance of certain polymer retention aids. The amount of turbulence, the time subjected to turbulence, the temperature, the papermaking pH, the concentrations of impurities, the concentration of retention aid, and the makeup of the pulp are some of the factors which can influence the effectiveness of retention aids, and perhaps dictate the type of retention aid which performs best.

The most important conclusion from this work is the apparently large room for improving fines retention over that possible with commonly used Percol 292. Optimizing polymers for a particular system represents the upper limit to improving fines retention. In commercial terms, this would involve "custom tailored" polymers, or at least a large line of polymers with different features. However, there may be much gained by simply changing to currently available polymers which are more toward the optimum than those in use.

## 6. REFERENCES

- (1) Abson, D., et.al., *Tappi*, 63(6), 55-58 (1980).
- (2) Allied Colloids Co., Technical Data Bulletin PD292/1, Mississauga, Ont. (1984).
- (3) Arvela, P., et.al., *Tappi*, 58(11), 86-89 (1975).
- (4) Avery, L.P., *Tappi*, 62(2), 43-46 (1979).
- (5) Britt, K.W., *Tappi*, 56(10), 46-50 (1973).
- (6) Britt, K.W., *Tappi*, 56(3), 83-86 (1973).
- (7) Britt, K.W. and Unbehend, J.E., *Tappi*, 59(2), 67-70 (1976).
- (8) Britt, K.W., et.al., *Tappi Journal*, 64-66, Nov. 1 1982.
- (9) Das, B.S. and Lomas, H., *Pulp and Pap. Mag. Can.*, 74(8), 95-100 (1973).
- (10) Frankle, W.E. and Sheridan, J.L., *Tappi*, 59(2), 84-88 (1976).
- (11) Gossens, J.W.S. and Luner, P., *Tappi*, 59(2), 89-94 (1976).
- (12) Gregory, J., *J. Colloid Interface Sci.*, 42(2), 448-456 (1973).
- (13) Hoover, M.F., *J. Macromol. Sci.-Chem.*, A4(6), 1327-1417 (1970).
- (14) Jaycock, M.J. and Pearson, J.L., *J. Colloid Interface Sci.*, 55(1), 181-190 (1976).
- (15) Klass, C.P., et.al., "Polyelectrolyte Retention Aids", Merck & Co. Inc., Rahway, N.J.
- (16) Klugness, J.H. and Exner, M.P., *Tappi*, 63(6), 73-76 (1980).
- (17) Lindstrom, T. and Soremark, C., *J. Colloid Interface Sci.*, 55(2), 305-311 (1976).
- (18) Lindstrom, T., et.al., *Trans. Tech. Sect.*, 3(4), 114-118 (1977).
- (19) Lindstrom, T., et.al., *Tappi*, 57(12), 94-96 (1974).
- (20) Moore, E.E., *Tappi*, 58(1), 99-101 (1975).
- (21) Moore, E.E., *Tappi*, 59(6), 120-122 (1976).
- (22) Pelton, R.H., verbal communication, 1984.
- (23) Pelton, R.H. and Allen, L.H., *Paprican Report PPR351*, January, 1982.
- (24) Pelton, R.H., et.al., *Pulp Pap. Can.*, 81(1), T9-15 (1980).

- (25) Pelton, R.H., et.al., *Svensk Papperstidning*, 83(9), 251-258 (1980).
- (26) Pelton, R.H., et.al., *Pulp Pap. Can.*, 80(12), T425-429 (1979).
- (27) Pelton, R.H., et.al., *Tappi*, 64(11), 89-92 (1981).
- (28) Stanislawczyk, V., "Analysis of Paper Mill Water Samples", McMaster University - Abitibi-Price Cooperative Research Report, 1983.
- (29) Strazdins, E., *Tappi*, 57(12), 76-80 (1974).
- (30) Tam Doo, P.A., et. al., *Paprican Report PPR424*, April 1983.
- (31) Tanaka, H., et.al., *Tappi*, 62(1), 41-44 (1979).
- (32) Tay, C.H., *Tappi*, 63(6), 63-66 (1980).
- (33) Tay, C.H., verbal communication, 1984.
- (34) Unbehend, J.E., *Tappi*, 60(7), 110-112 (1977).
- (35) Unbehend, J.E., *Tappi*, 59(10), 74-77 (1976).
- (36) Unbehend, J.E. & Britt, K.W., "Pulp and Paper: Chemistry and Chemical Technology", 3rd ed., vol.3, Ch.17, 1593-1607, John Wiley and Sons Inc. (1981).
- (37) Walkush, J.C. & Williams, D.G., *Tappi*, 57(1), 112-116 (1974).
- (38) Woods, D.R., "Surfaces, Colloids and Unit Operations", vol.2, McMaster University (1983).

PART II  
THE PREPARATION AND CHARACTERIZATION OF  
BROAD POLYACRYLAMIDE MOLECULAR WEIGHT STANDARDS



## 1. INTRODUCTION

Non-ionic polyacrylamide is a commonly used water soluble polymer with several applications. It can be an effective flocculant in certain systems. Low molecular weight polyacrylamides can be employed as particle stabilizers in emulsion and suspension polymerization. High molecular weight polyacrylamides have the ability to create a viscous aqueous solution at relatively low concentrations. Of more importance than the acrylamide homopolymer are the numerous co and higher order polymers which employ acrylamide in their synthesis. Important industrial polymers in this group include cationically and anionically substituted polyacrylamides which have applications in tertiary oil recovery and flocculation.

There has been extensive research done on the kinetics of acrylamide polymerizations (6,14), and to a lesser extent on copolymerizations of acrylamide. This research includes the measurement and modelling of polyacrylamide molecular weight. The polymers produced in the kinetic studies mentioned above had very high molecular weights ( $\bar{M}_w$  values of about 7 000 000) characteristic of these types of polymerizations.

There are applications of acrylamide polymers which require controlled molecular weights. In oil recovery, the molecular weight distribution of polymer flooding agents must be tailored for each reservoir (7). Often flocculants are synthesized with very high molecular weights so the polymer can adsorb with long loops and tails onto the particles which are to be flocculated. There are applications, however, for "patch" model flocculants, or polymers which adsorb with minimal looping. To prepare such a polymer, a low molecular weight is desirable. As mentioned some particle stabilizers are also low molecular weight acrylamide polymers. In situations where polyacrylamides must be dissolved from solid form, controlled

molecular weights may be required to avoid the slow dissolution associated with large polymer chains.

To a certain extent molecular weight may be controlled by monomer concentration, initiator concentration and reaction temperature. Large changes in these variables are needed, however, to substantially alter molecular weight. Furthermore process constraints may prevent major tampering with these variables. A chain transfer agent, or CTA, can have drastic effects on molecular weight at relatively low addition levels. Common CTAs are simply compounds containing a labile hydrogen which is easily abstracted by a growing polymer radical. The concentration of such agents gives direct control of molecular weight without necessitating changes in reaction conditions.

Chain transfer agents can have an effect on the kinetics of a polymerization, especially when diffusion controlled termination dictates reaction rate. This effect, and the study of how CTAs may be used to control molecular weight represent the basis of this research. Equally important is the characterization of polymers produced with CTA present. Laser light scattering and size exclusion chromatography (SEC) were used to characterize the polymers prepared. Characterization in itself presents a challenge in this study, as will be discussed later.

## 2. SCOPE OF RESEARCH

A common CTA, ethanol mercaptan, was employed to vary the molecular weight of polyacrylamides prepared both in ampoules and in a 1 gallon pilot plant batch reactor. The polymers produced were characterized both by laser light scattering and SEC. A set of ampoule runs was compared to data presented by Kim (6) without CTA present. Ampoule molecular weight data was used to give approximate CTA levels needed in the batch reactor to give a polymer of the desired weight average molecular weight.

One of the objectives of the pilot plant runs was to produce broad molecular weight standards in relatively large quantities. Ideal polydispersities of broad standards would be close to 2. These polymers would serve to calibrate the SEC at McMaster, and also be sold elsewhere for profit as highly characterized standards.

Because of the availability of light scattering data for many acrylamide polymers of varying molecular weights, it was thought that future light scattering work might be simplified somewhat by finding an empirical relationship between  $\bar{M}_w$  and  $A_2$ , the second virial coefficient (see Theory, pg.57). Such a relationship could improve the accuracy of light scattering analysis, while reducing analysis time.

### 3. THEORY

Kim (6) presents a thorough theoretical background on the kinetics and molecular weight development for polyacrylamide free radical solution polymerization. This background will be briefly summarized and modified here, but for the most part will not be repeated.

The rate of polymerization of acrylamide,  $R_p$ , is given as:

$$R_p = k_p \left( \frac{k_d}{k_t} \right)^{1/2} [I] \left( \frac{k_x}{k_R + k_x[M]} \right)^{1/2} \quad [1]$$

for the purpose of modelling. To model the gel effect shown by increases in reaction rate at high conversion,  $k_t$ , the termination rate constant is defined as:

$$k_t = k_{t0} \exp(A_1 x + A_2 x^2 + A_3 x^3), \quad \text{where } A_i = a_i + b_i T \quad [2]$$

More importantly in this research, Kim has modelled the molecular weight development neglecting termination by combination reactions, so:

$$\tau = \frac{k_t R_p}{k_p^2 [M]^2} + \frac{k_{fM}}{k_p} \quad [3]$$

and

$$\bar{r}_N = \frac{x}{\int_0^x \tau dx} \quad [4]$$

$$\bar{r}_w = \frac{2}{x} \int_0^x \left( \frac{1}{\tau} \right) dx \quad [5]$$

The addition of a CTA promotes a transfer reaction in which the growth of polymer radicals is stopped. A dead polymer chain and a new radical are formed:



Polymerization kinetics will be affected if the activity of the CTA radical is different from that of the polymer radical (1). With transfer agent present:

$$\tau = \frac{k_t R_p}{k_p^2 [M]^2} + \frac{k_{fM}}{k_p} + \frac{k_{fC}}{k_p} \cdot \frac{[C]}{[M]} \quad [7]$$

If the transfer to CTA term is large with respect to the first two terms, as is the case with a relatively high concentration of strong CTA, then  $\tau$  is controlled by the transfer to CTA ,

$$\text{if } [C] \cdot k_{fC} \text{ large} \quad \tau \approx \frac{k_{fC}}{k_p} \frac{[C]}{[M]} \quad [8]$$

Since weight average molecular weight is proportional to  $2/\tau$ , a strong chain transfer agent can be used to directly control molecular weight. Note that  $\tau$  is dependent on  $[C]/[M]$  for a given transfer agent. The concentration of monomer decreases during a batch reaction, as does the concentration of CTA since both are consumed in the reaction. However, these decreases are not proportional, leading, in theory, to a drift in molecular weight with time. With most chain transfer agents, this drift is expected to go towards lower molecular weights with higher conversions because only one molecule of CTA is consumed in the transfer of a radical from a polymer chain containing many monomer molecules. Thus molecules of polymer being produced at the beginning of a batch should have higher molecular weights than molecules produced towards the end of the batch.

### 3.1 MODES OF POLYMERIZATION

One of the simplest ways to produce polyacrylamides is by free radical solution polymerization in water. The limitation of this process is solution viscosity. High molecular weight polyacrylamides can limit monomer concentrations to 1 or 2% by weight. Higher viscosities can lead to poor mixing and insufficient heat transfer. Low molecular weight polymers, however, present little problem in solution polymerizations.

Recently, inverse emulsion, or more correctly, inverse micro suspension processes have been used to more effectively handle high molecular weight water soluble polymers. These processes employ an oil phase in which droplets of water/ monomer mixture are suspended. Initiators may be water soluble or oil soluble. Oil soluble initiators have the advantage of providing greater control of radical concentrations because of higher oxygen solubility in the oil phase. The introduction of an air pulse into the reactor can slow or stop polymerization temporarily. Surfactants or surfactant blends give stability to water phase droplets. Water soluble CTAs may be employed for molecular weight control. Suspension processes in general have the advantage of good heat transfer under conditions which would produce very high viscosities in solution polymerizations. Major disadvantages include the cost of oil and surfactant along with the more involved processing needed should dry polymer be desired.

Polymer purification and preparation for analysis by SEC and light scattering poses a different problem for each of these polymerization methods. Purity must be very high and monomer content must be low, yet care must be taken to avoid the loss of polymer molecular weight fractions. Also residual CTA, surfactant, initiator and in the case of suspension polymerization, oil must be removed. Further complicating the picture is the removal of water, as the polymer must be dry to best facilitate analysis by light scattering and SEC. The methods used to meet these ends are discussed in the experimental section.

## 3.2 CHARACTERIZATION

### 3.2.1 Low-Angle Laser Light Scattering (LALLS)

In light scattering analysis, a series of filtered polymer solutions differing in concentration are passed through a laser beam. Detectors measure the intensity of scattered light at different angles. The Rayleigh factor,  $R_\theta$ , can be calculated from:

$$R_\theta = \left( \frac{G_o}{G_\theta} \right) (D/\sigma' \ell') \quad [9]$$

where,

$G_\theta$  = photomultiplier signal for scattered light at a given angle

$G_o$  = photomultiplier signal for incident beam of light

$D$  = attenuator transmittance

$\sigma'$  = the solid angle over which the scattered light is viewed

$\ell'$  = the length parallel to the incident beam

$D, \ell', \sigma'$  are constants which can be found with instrument calibration.

The weight average molecular weight of a polymer can be calculated from:

$$\frac{KC}{R_\theta} = \frac{1}{M_w P_\theta} + \frac{2A_2C}{P_\theta} + \frac{3A_3C^2}{P_\theta} + \dots \quad [10]$$

where,

$$K = 2\pi^2 n^2 (dn/dc)^2 (1 + \cos^2\theta) / \lambda^4 N$$

C = polymer concentration

n = solvent refractive index

$\lambda$  = laser beam wavelength

N = Avogadro's number

$A_n$  = virial coefficient

$\frac{dn}{dc}$  = change in refractive index with concentration

$P_\theta$  = particle scattering function

$\bar{M}_w$  = weight average molecular weight of polymer

A simplified expression for  $P_\theta$  proposed by Debye is given by:

$$P_\theta = 1 - (16\pi^2/3\lambda^2) R_g^2 \sin^2(\theta/2)$$

where  $R_g$  is radius of the gyration of a polymer molecule. In cases where  $R_g < 1$  and  $\theta$  approaches 0,  $P_\theta \approx 1$ . Thus in LALLS, with low angles and low polymer concentrations:

$$\frac{KC}{R_\theta} = \frac{1}{\bar{M}_w} + 2A_2 C \quad [11]$$

where,

$$R_\theta = \underbrace{\bar{R}_\theta}_{\text{polymer solution}} - \underbrace{\bar{R}_{\theta s}}_{\text{solvent}} \quad [12]$$

The determination of weight average molecular weight involves the measurement of the scattering of a series of polymer solutions of different concentration. Plotting  $KC/R_\theta$  vs C should give a straight line with a slope of  $2A_2$  and an intercept of  $1/\bar{M}_w$ .

The refractive index of the solvent employed may be found in the literature or determined experimentally using a laser differential refractometer. The refractometer is also

used in determining  $dn/dc$ , and in cases where the polymer is not dry polymer concentration may also be measured if a calibration curve is available.

Polyacrylamide binds water tenaciously (11), especially when the polymer is not finely ground. Vacuum drying at 40 or 50 C will not remove all of the water, while the higher temperatures (200 C) recommended by Molyneux (11) are likely to cause polymer degradation and thus changes in molecular weight. Hence, the refractometer, in conjunction with a calibration curve, seems to be one of the better methods to determine concentrations of polyacrylamide solutions.

### 3.2.2 Size Exclusion Chromatography

SEC employs a packed column capable of hindering the travel of certain sized molecules passing through it. Usually a packing with carefully prepared pores is used. Large molecules do not enter as many of the pores because of their size; the smallest molecules may enter all of the pores. Thus a solution containing a mixture of molecules may be separated by a column or series of columns with the appropriate pore sizes. The larger molecules will elute first, with successively smaller molecules eluting as time passes. More often than not, interactions will exist between the packing surface and the molecules to be separated. If the packing surface and polymer have like charges, the electrostatic repulsion will cause exclusion from the pores. If the packing and polymer have opposite charges, electrostatic attraction will cause adsorption. Both of these effects may be overcome by the addition of surfactants and electrolytes to the mobile phase.

Many packings, in combination with certain polymers, experience the problem of adsorption. Active packing surface sites may encourage hydrogen bonding, hydrophobic and/or ionic interactions. Adsorption is indicated if the monomer unit of a polymer species elutes after a non-adsorbing species of similar molecular weight. Adsorption can be tackled by



adding to the polymer solution a species which will adsorb preferentially to active surface sites on the packing, thus blocking surface interactions. Some non-ionic surfactants such as Tergitol NPX with glass packings have been successfully employed for this purpose with SEC analysis of acrylamides (7). Often a trial and error approach is necessary to find a surfactant which is effective on a certain packing.

Adsorption must be eliminated in order to ensure size separation and apply calibration methods accurately in SEC.

### 3.3 CALIBRATION OF SEC

#### 3.3.1 Narrow Standards

The availability of narrow MWD polymer standards offers a great advantage in SEC analysis. A series of such standards can be injected into the instrument under analysis conditions to provide several peak elution times for different molecular weights. By assigning the standard molecular weights to these elution times, an equation, usually cubic, can be derived to represent polymer molecular weight as a function of elution time. This equation is commonly called a calibration curve. Analysis of subsequent samples is simple; weight average, number average and peak molecular weights as well as polydispersity can be calculated easily and from the information provided in the calibration curve. The main requirement for such an analysis is a calibration curve which has been calculated accurately over the entire elution range of the samples to be analysed. In other words, a set of standards must have a molecular weight range which encompasses that of all the polymer samples to be analyzed.

Moreover, the accuracy of the calibration curve suffers as the dispersity of the standards deviates from unity. Often narrow standards are not available commercially for the polymer of interest. Preparation of such standards is possible for polyacrylamide, but the

methods involved, such as fractional recrystallization, are very time consuming, and require great care.

### 3.3.2 Broad Standards

In cases where narrow standards are unavailable, or present a considerable problem in synthesis, SEC calibration with broad standards may be practical. The method involves using a calibration curve derived from narrow molecular weight standards soluble in the same mobile phase as the polymer to be analysed. Polyethylene oxide standards may be used for polyacrylamide calibration. If the calibration curve given by these standards is:

$$M_{\text{peo}} = \phi(v) \quad [13]$$

where  $M_{\text{peo}}$  is polyethylene oxide molecular weight,  $v$  is elution volume and  $\phi(v)$  is a function of elution volume, then the polyacrylamide calibration curve may be written as:

$$M_{\text{AA}} = A \phi^\beta(v) \quad [14]$$

where

$$A = \left( \frac{K_{\text{peo}}}{K_{\text{AA}}} \right)^{1/(1+\alpha_{\text{AA}})} \quad [15]$$

$$\beta = (1 + \alpha_{\text{peo}})/(1 + \alpha_{\text{AA}}) \quad [16]$$

where  $K$  and  $\alpha$  are Mark-Houwink constants. The polyethylene oxide calibration curve may be represented as a cubic,

$$\log M_{\text{peo}} = c_1 + c_2 v + c_3 v^2 + c_4 v^3 \quad [17]$$

The constants are calculated using a least squares fit to  $\log M$  vs  $v$  data for a series of narrow standards. Thus,

$$M_{AA} = A(10^{c_1 + c_2 v + c_3 v^2 + c_4 v^3})^{\beta} \quad [18]$$

$$\log M_{AA} = \log A + \beta(c_1 + c_2 v + c_3 v^2 + c_4 v^3) \quad [19]$$

$$\log M_{AA} = \underbrace{(\log A + \beta c_1)}_{\theta} + \beta c_2 v + \beta c_3 v^2 + \beta c_4 v^3 \quad [20]$$

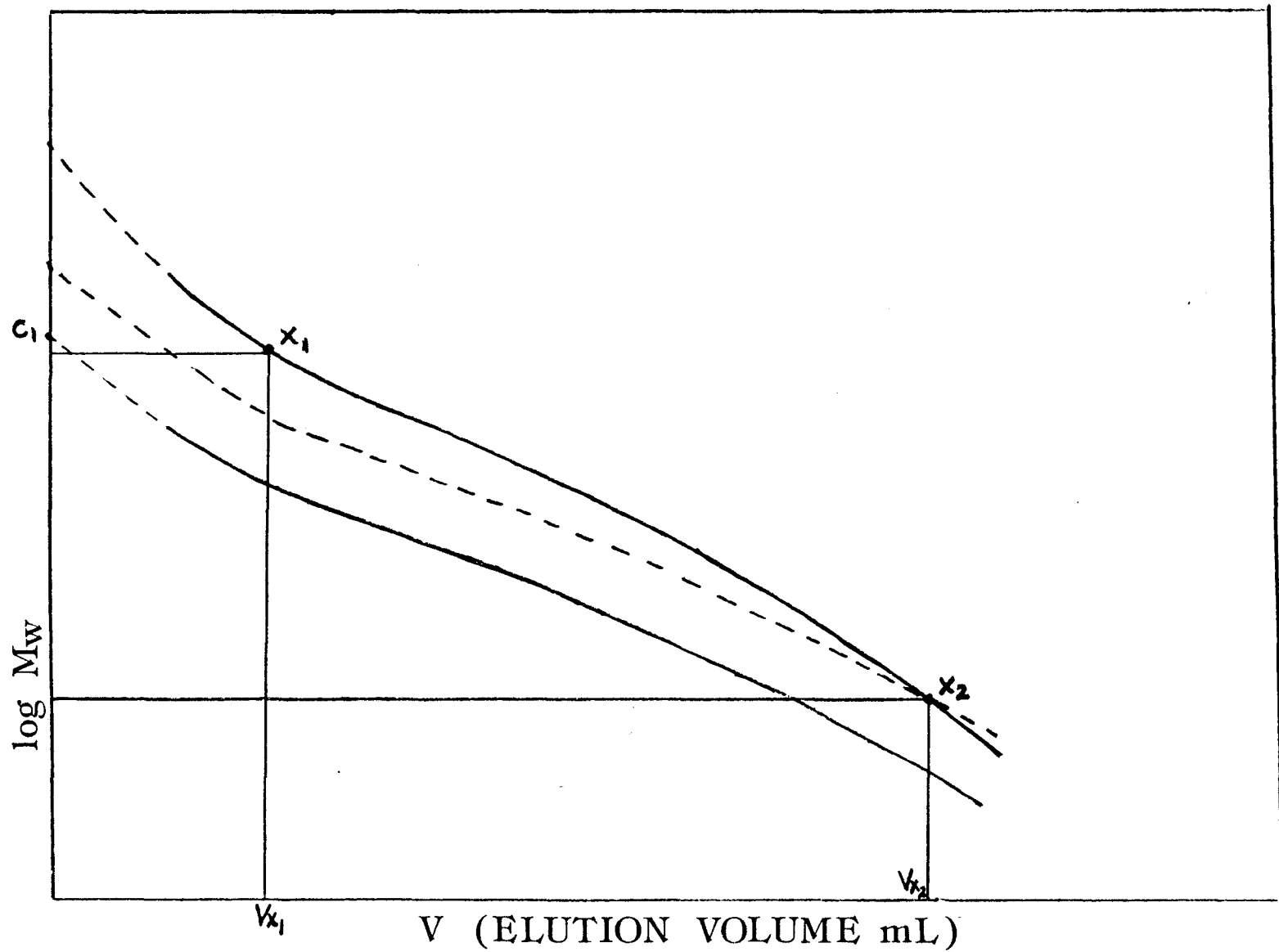
On a semi-log plot these manipulations can be interpreted more clearly. A hypothetical  $\phi(v)$ , a cubic, is shown in Figure II-1, a plot of  $\log M$  vs  $v$ . In equation above, the constant term enclosed in square brackets represents the intercept of the calibration curve for polyacrylamide, where  $c_1$  represents the intercept for polyethylene oxide.  $c_2$ ,  $c_3$  and  $c_4$  dictate the "shape" of the curve for PEO. Note that if  $c_2$ ,  $c_3$  and  $c_4$  are each divided by a constant, the "shape" of the curve will be unaltered, although the slope will.

Consider now two points representing the weight average molecular weights of two broad polyacrylamide standards, marked "x", of which chromatograms have been obtained. The first step in obtaining the calibration curve is to adjust the  $\theta$  parameter by trail and error such that, when polyacrylamide standard 2 is analysed with the new calibration curve it has the correct molecular weight. This step is depicted by the dotted calibration curve. The final step involves a trail and error manipulation of  $c_2$ ,  $c_3$  and  $c_4$  by a constant factor representing  $(1 + \alpha_{peo}/1 + \alpha_{AA})$ . The purpose of this is to increase the slope of the calibration curve without changing the basic "shape" such that when standard x1 is analysed with the new curve, the weight average molecular weight is adequately represented. The  $\theta$  parameter must be adjusted in this process such that:

$$\theta_{\text{new}} = -\beta(c_2 v_{x_2} + c_3 v_{x_2}^2 + c_4 v_{x_2}^3) + \log M_{x_2} \quad [21]$$

This forces the new calibration curve through the point  $x_2$ . The final calibration curve for polyacrylamide is represented by this line.

Figure II-1 Calibration Using Broad Standards



This procedure differs from that given by Chiantore and Hamielec (2), who propose a single variable search computer program to derive the second calibration curve. It is a procedure which would be faster if data acquisition and manipulation were not required (at McMaster, an Apple computer linked to a Varian Vista data station handles chromatogram data and analysis, while a VAX 11/750 is used for variable searches. This necessitates data acquisition, along with data manipulation to satisfy the search program used). It is thought that the method presented here is more efficient because there is no need for data transfer and manipulation. Mark-Houwink constants do not have to be known in either case.

Note that the two polyacrylamide standards used should represent the molecular weight extremes of the standards available, as long as the exclusion limits of the columns are not exceeded. To check the validity of the polyacrylamide calibration curve, other standards with known molecular weights should be used as checks. This step ensures validity between molecular weight extremes.

## 4. EXPERIMENTAL

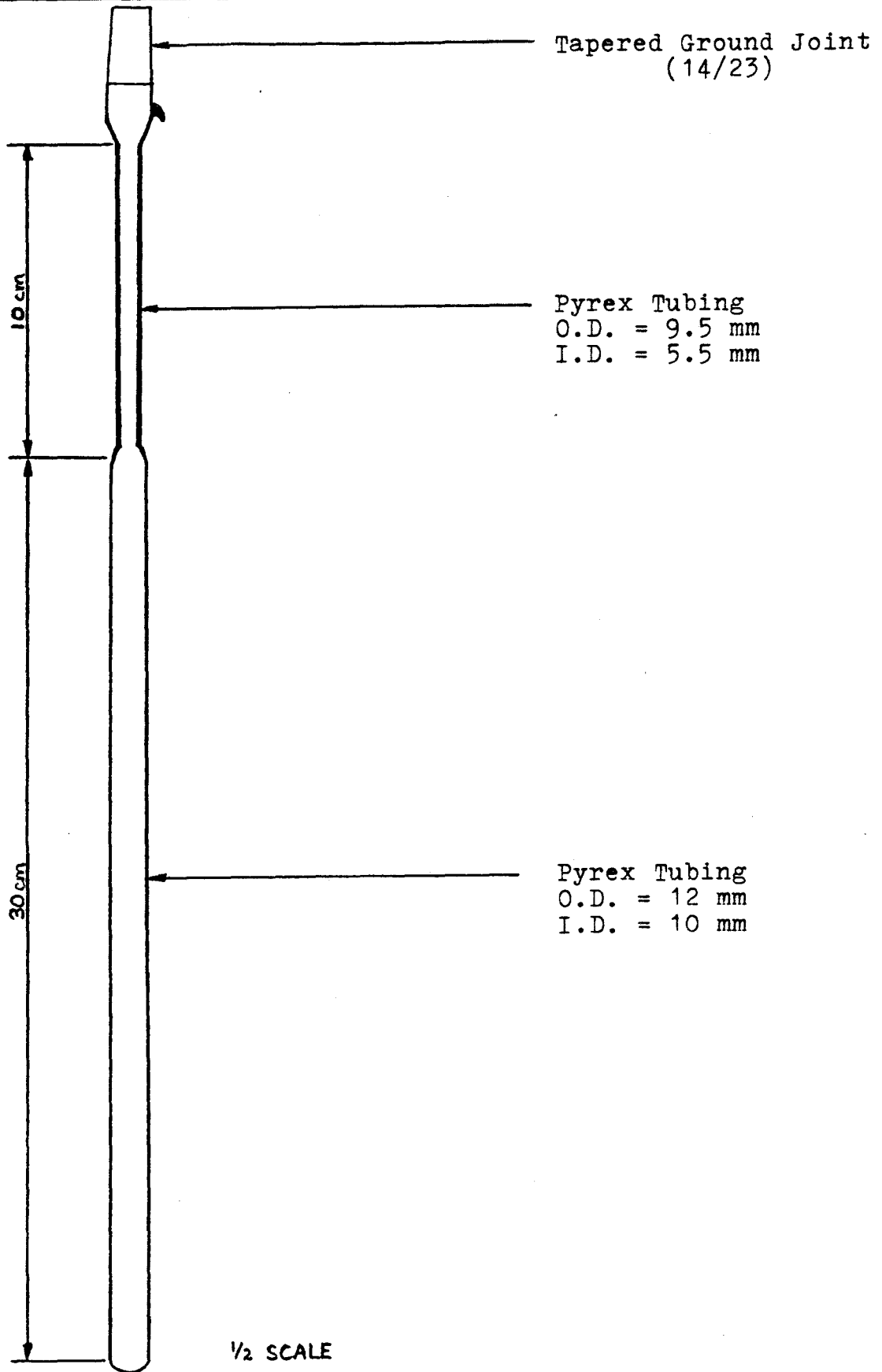
### 4.1 AMPOULE RUNS

Several ampoule runs were conducted to evaluate the effectiveness of ethanol mercaptan at controlling polyacrylamide molecular weight. The ampoules used are shown in Figure II-2.

The initiator, potassium persulphate, was obtained from BDH chemicals, Toronto. Several grams of the initiator were recrystallized twice from distilled deionized water. Between uses the purified initiator was stored in a dark dessicator.

A large quantity (3kg) of acrylamide monomer was obtained from Eastman Kodak Corporation. About 1kg was recrystallized twice from chloroform. The recrystallization procedure involved filling a 4L Erlenmeyer flask with approximately 3.5L of chloroform. The

Figure II-2    Ampoule Dimensions



chloroform was heated moderately on a hot plate while acrylamide was slowly added and dissolved. The mixture was stirred frequently to aid the slow dissolution of the solid acrylamide. When the chloroform solution was close to boiling, a small excess of acrylamide was added so that a small amount of powder remained undissolved after frequent stirring. The flask was then topped up with chloroform and again brought to boiling. About 0.5kg acrylamide total dissolved.

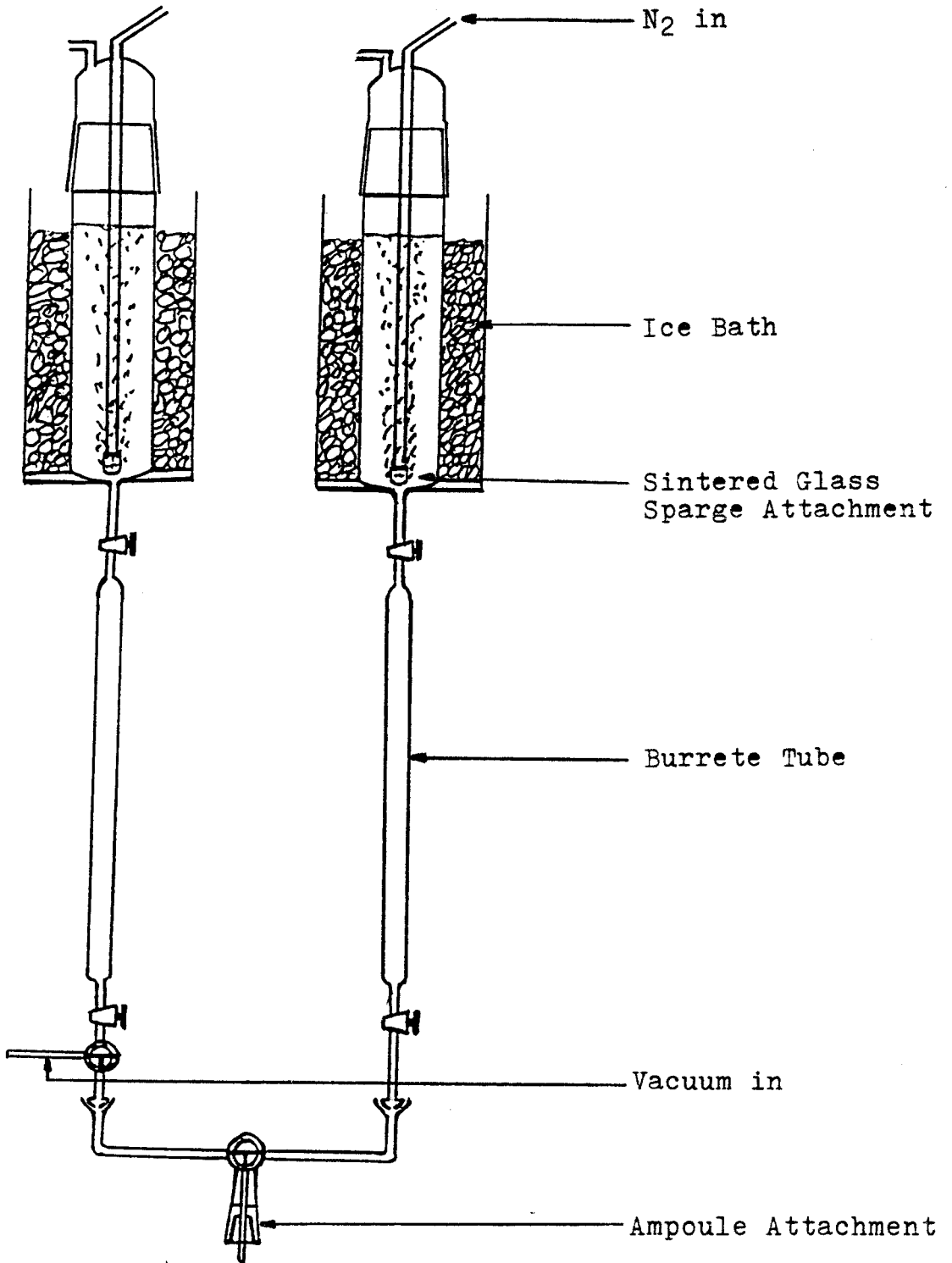
A large heated Buchner funnel was attached to a vacuum filtration apparatus. Medium, chloroform compatible filter paper was used to quickly filter the boiling chloroform solution. The filtrate was cooled on ice for several hours, and the cooled chloroform containing precipitated acrylamide was then again filtered. The precipitate was washed several times in benzene and dried overnight in a vacuum oven at room temperature. A second batch of monomer was recrystallized as above and mixed with the first batch after drying. The combined batch was recrystallized a second time using the same method to give a final batch of product. The purified acrylamide crystals were stored in a dark dessicator until needed.

The chain transfer agent, ethanol mercaptan, was obtained from Aldrich Chemicals. It was not purified in any way. Solutions of acrylamide/CTA and initiator were prepared the morning of an experiment, and stored in tin foil wrapped flasks in the refrigerator until use.

A schematic of the vacuum apparatus is shown in Figure II-3. Solutions were added to the storage vessels shown. Ice was added to the storage vessel jackets. Ultrahigh purity nitrogen, passed through a pyrogallol solution, a calcium chloride dryer, and a dust filter was used to deoxygenate both the acrylamide and initiator solutions. Slow bubbling was continued for about an hour.

Ampoules were vacuum evacuated and filled with recipe dictated quantities of each stock solution as measured by the burette tubes below the solution vessels. After being sealed

**Figure II-3** Vacuum Apparatus for Ampoule Experimentation





under vacuum, ampoules were brought to approximately room temperature by hand warming, and then placed in a controlled temperature oil bath for a selected amount of time. After removal from the oil bath, they were cleaned and immersed in an ice bath for about 1 minute, and then carefully immersed in a flask of liquid nitrogen. After a set of ampoules was completed, a 0.1% solution of hydroquinone was prepared. The cold ampoules were then broken to allow the dissolution of the solid contents in approximately 10 mL of hydroquinone solution in sealed flasks. Distilled deionized water was added to each of the flasks to give 100 mL total volume. Complete dissolution often took several days.

#### 4.1.1 Preparation For Analysis

The polymer/monomer solutions were analysed by light scattering for weight average molecular weight. Some solutions were also analysed by SEC for conversion and molecular weight distribution. For SEC analysis, about 1 mL of each of the ampoule solutions were saved and stored in the freezer until analysis.

Light scattering analysis requires the removal of monomer and other impurities from solution. This involved the addition of methanol to the polymer/ monomer solutions until all of the polymer precipitated. About 1000 mL of methanol were added to each 100 mL solution to ensure that the low molecular weight tail of a polymer sample precipitated. A small amount of aluminum sulphate solution was added to facilitate coagulation of the finely dispersed polymer precipitate. The precipitate was then filtered through medium methanol compatible filter paper under vacuum. The polymer was washed several times in HPLC grade methanol and then dried for at least 48 hours under vacuum at 40 C. The dried polyacrylamide was crushed and stored in air tight bottles for later dissolution and analysis by light scattering.

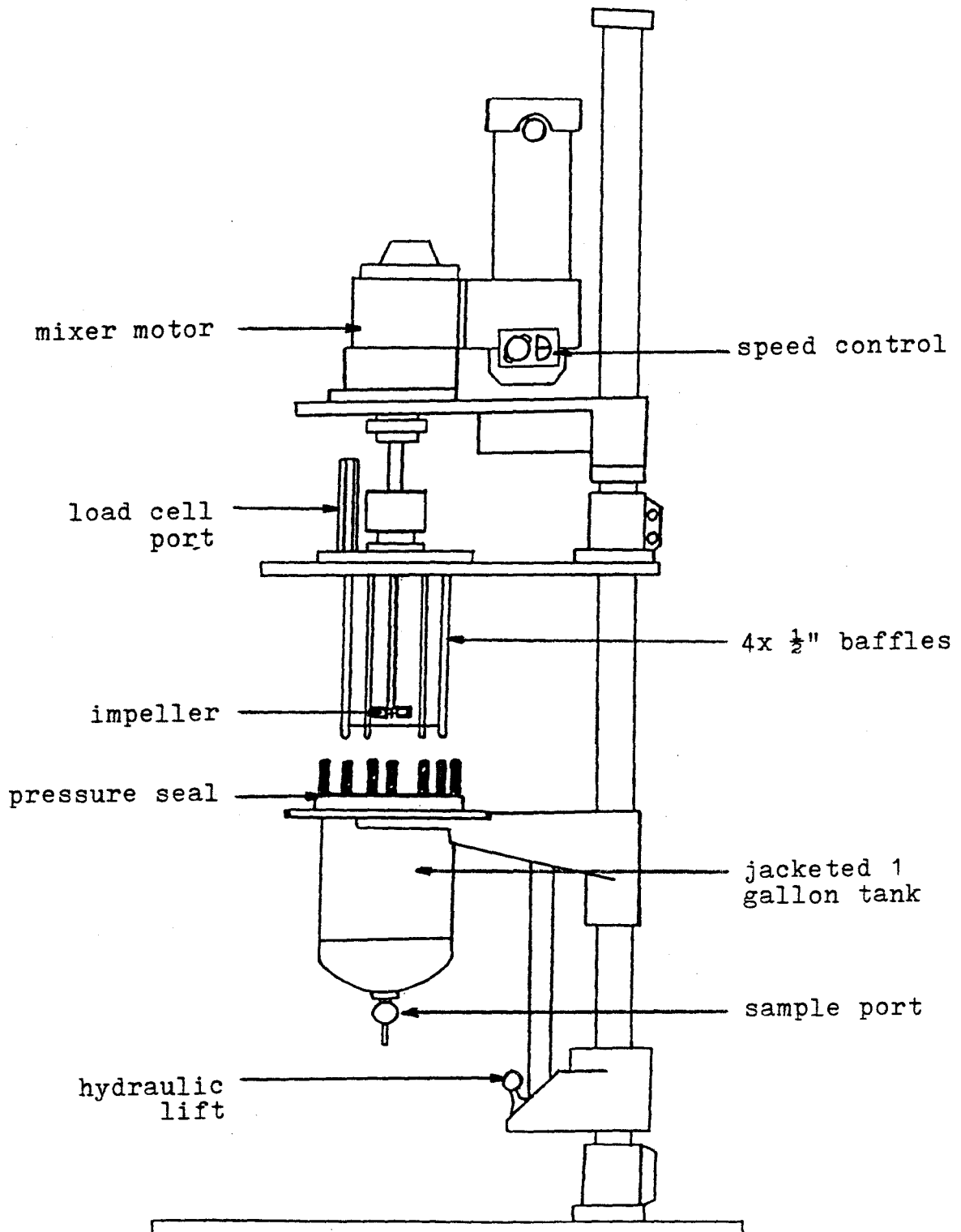
## 4.2 REACTOR RUNS

Solutions containing 50% ( $\pm 2\%$ ) acrylamide inhibited with a copper solution were obtained from Alkaril Chemicals in large quantities (32L). No purification was carried out. Versenex 80, a copper chelating agent was also obtained from Alkaril, along with oil-surfactant mixture used for suspension polymerizations. The contents of the mixture was proprietary information. The reactor used in all runs is pictured in Figure II-4.

### 4.2.1 Inverse Micro Suspension Runs

Seven inverse suspension runs (R2-R8) were conducted on the MIPPT pilot plant equipment. Prior to each run solutions of CTA and initiator were freshly prepared. Acrylamide solution was used undiluted. Versenex 80 was added in the recommended quantities to 2500 grams of acrylamide solution immediately before each run. The acrylamide and 1250 grams of oil phase was then added to the carefully cleaned 1 gallon batch reactor, followed by the CTA solution. In the first run, R2 (R1 was conducted at Alkaril Chemicals for training purposes), the initiator was added after the CTA solution. The mixer was set at the highest possible rate for 1 minute to finely disperse the two phases, and then set to a medium speed for the remainder of the run. In runs other than R2, the initiator was added via a load cell after the reactor had been sealed, deoxygenated (10 psi UHP nitrogen sparge for 20 min, oxygen content  $< 2$ ppm ), and brought to temperature using the reactor temperature controller. It was found that load cell addition of the initiator after temperature equilibration aided in temperature control, and thus likely produced a less dispersed polymer. Nitrogen sparging was continued at a reduced pressure throughout the reaction. The reactor was run as close to isothermal as possible until the controller indicated that the steam valve opening percentage was approximately the same as that before the initiator was added. An increase in temperature to 80 C reduced residual monomer.

Figure II-4 Pilot Plant Batch Reactor



The reactor was then cooled to about 40 - 50 C to allow safe drainage into a large container. The product was a white suspension of polymer in oil if the run was successful. Processing the product involved two steps; separation and purification of the polymer. Centrifugation at 5000 rpm for an hour provided an adequate separation of the oil phase from the polymer. The machine used was a Lourdes Instrument Company refrigerated centrifuge with a capacity of approximately 1 litre. At 5000 rpm the indicated centrifugal force was 4100 times gravity. After centrifugation, the oil was simply drained from the centrifuge bottles leaving a thick paste of polymer. The polymer paste was scraped out of the bottles and mixed into a tank containing approximately 10L of methanol, resulting in a powdery precipitate. The polyacrylamide precipitate was left to soak in the methanol for at least 24 hours to ensure that the larger particles were cleaned of methanol soluble impurities. During this time, residual oil was skimmed several times from the surface of the methanol using paper towels. The polyacrylamide powder was then filtered through a medium filter and washed with HPLC grade methanol. Care was taken in not exposing the filtering polymer to humidity for long periods as this resulted in sticky particles which were very difficult to remove from the filtering apparatus. The purified polymer was dried under vacuum at 40 C until no liquid was observed in the liquid nitrogen condenser. The drying process took from 48 hours to 1 week. The dry polymer was crushed using a mortar and pestel, and then sieved through a flour sifter. Because the polymers produced by the inverse suspension process turned out to have high molecular weights, this sieving step was necessary to allow dissolution in acceptable time periods. The finished polymer was kept in sealed polyethylene bottles to minimize moisture absorption.

#### 4.2.2 Solution Runs

Eight solution polymerization runs were conducted on the pilot plant reactor. As with the inverse suspension runs, CTA and initiator solutions were prepared beforehand. Acrylamide solutions were diluted with distilled deionized water. The expected molecular weight of the product dictated the amount of dilution. Initiator was added from a load cell after deoxygenation and temperature equilibration of the reactor. Reactions were run until steam valve opening values indicated no heat generation.

The polymerization products ranged from syrupy to rubbery in consistency. If a run was successful, the reactor contents were either scraped or poured into a container of methanol (10-15L) to precipitate the polymer. The sticky precipitates tended to form large clumps rather than the powders observed in the inverse suspension runs. The clumps were broken up several times and left to soak in the methanol bath for several days. Vacuum drying took approximately a week at 40 C. It was found that after drying for a day or so, the polymer could be cut into smaller pieces which would not stick together. This step increased the drying rate and aided in later processing.

The dried polymer was crushed into a coarse powder using a clean gravel crusher. After being sieved through a screen with openings of approximately 4mm, the polyacrylamide were stored in tightly closed polyethylene bottles.

#### 4.3 A NOTE ON REACTOR CLEAN UP

Reactor clean up, especially for high molecular weight polymers, can be a very time consuming process. Several steps were discovered to aid this process. The most important measure is the removal of as much polymer as possible before any water is introduced into the reactor. Small amounts of high molecular weight polymer led to very viscous solutions and slow dissolution rates. A paint scraper was found to be very effective in removing most of the

polymer from the reactor walls. The reactor is then best filled with water, heated to 80 C, and left overnight stirring at high speed. Repetition of these steps may be necessary with high molecular weight polymers.

## 5. RESULTS AND DISCUSSION

### 5.1 LASER LIGHT SCATTERING

Characterization by laser light scattering proved to be somewhat difficult for the acrylamide polymers analysed, especially those with high molecular weights. The first problem encountered was the difficulty measuring the dry weight of polymer used to prepare the five solutions recommended for analysis (10). A commercial polymer dried under vacuum for 48 hours at 40 C had between 1.5 and 2.2% water content as indicated by a Karl Fisher titration. The adequacy of this titration method in determining water content is questionable, however. The procedure took over 6 hours because of very slow equilibration. During this time the mixture of polymer and titration solution may have absorbed atmospheric moisture, even though the titration was conducted in a closed bottle. Also, the titration may not have been adequate in measuring tightly bound water, such as that in larger polymer particles.

The same commercial polymer was used in calibrating the laser differential refractometer in order to determine the concentrations of other polymers analysed by light scattering. The resulting plot of refractometer count vs. polymer concentration is shown in Figure II-5.

Figure II-6 indicates the plot used to determine  $dn/dc$  for polyacrylamide. Distilled, deionized water was used as a diluent. The calculated intercept, 0.187, compares favourably with the value of  $dn/dc$  recommended by Kulicke (8), 0.185. Because of the inaccuracy of the intercept calculated,  $dn/dc = 0.185$  was used in all calculations. It is interesting to see the large range of  $dn/dc$  values listed in the literature (11,8). Some values quoted are as low as

Figure II-5 Refractometer Calibration

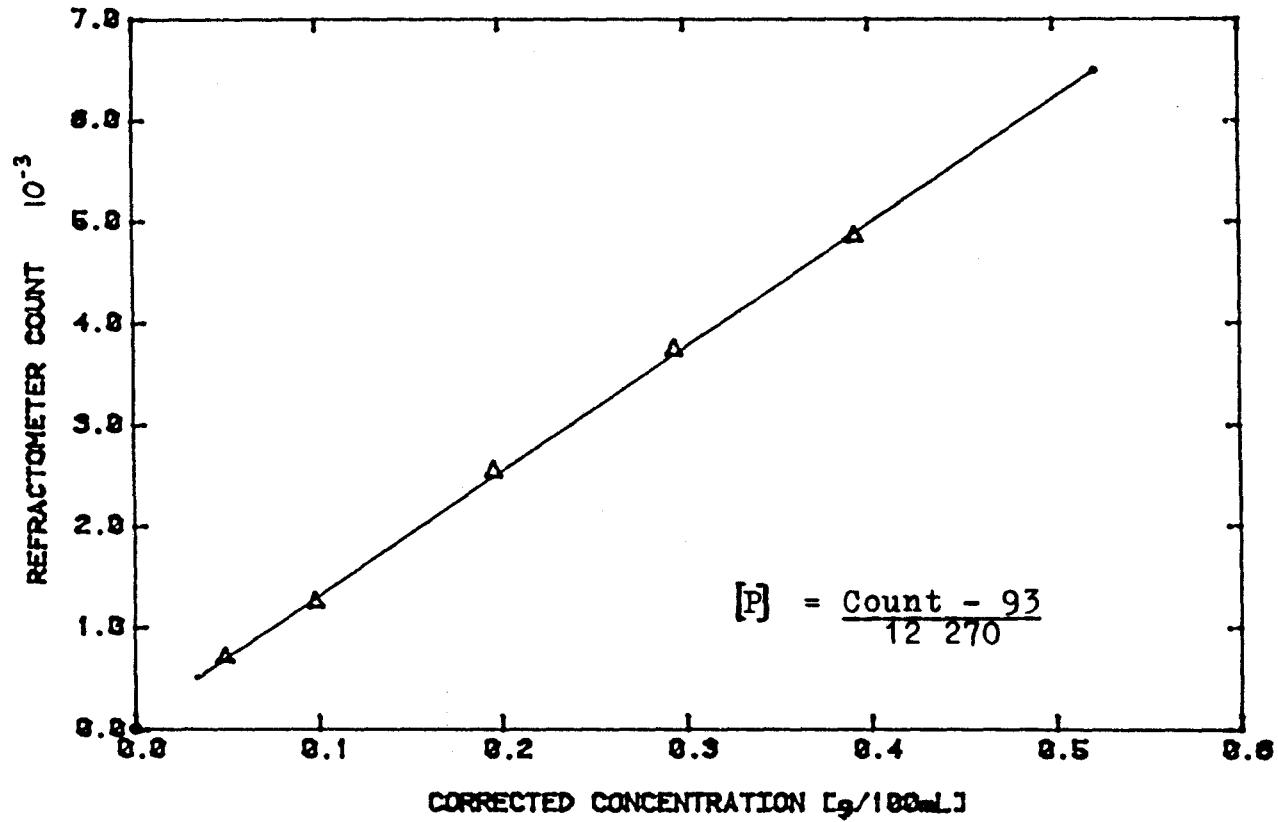
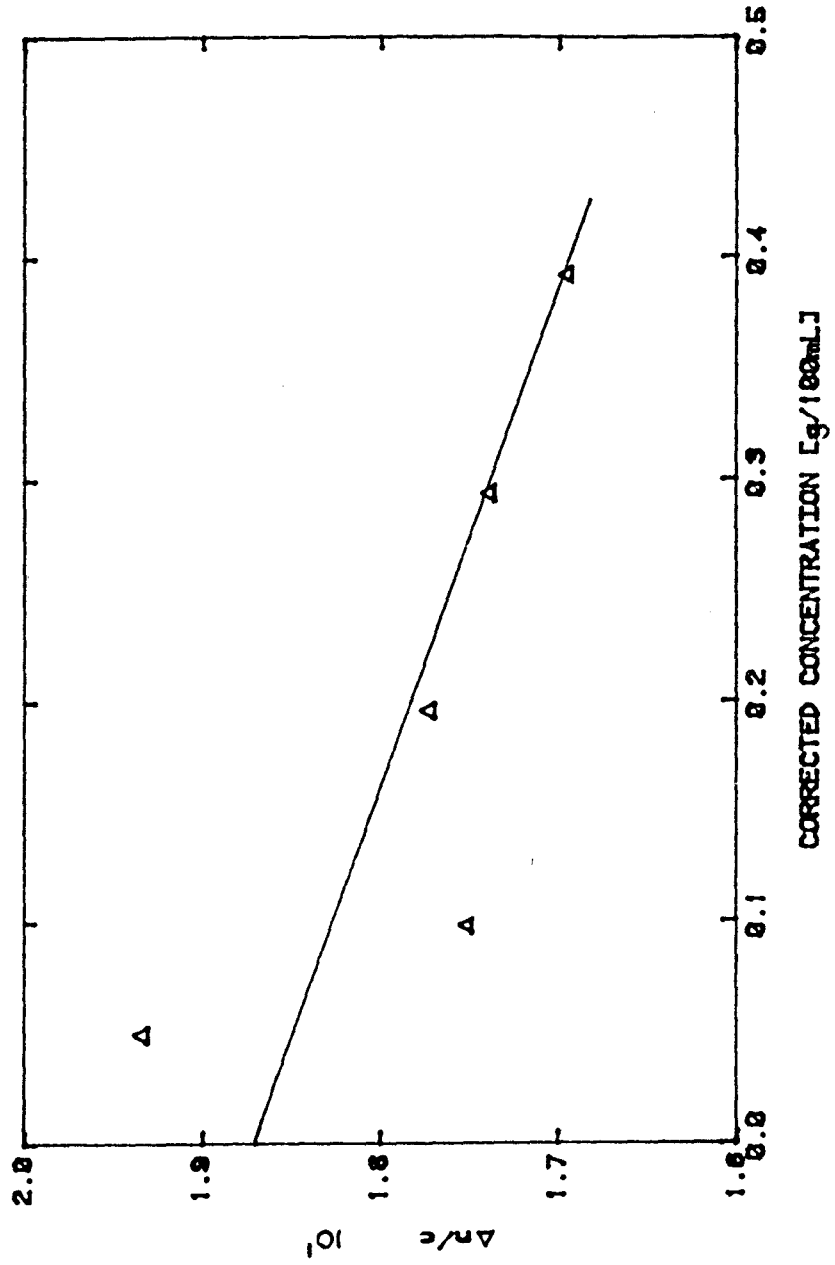


Figure II-6 Calculation of  $dn/dc$





0.142, representing a very large difference in molecular weight results when compared with those which would result with the recommended values ( $\bar{M}_w \propto 1/(\text{dn}/\text{dc})^2$ ). In this research, it was found that polymer water content, if not accounted for, will have a major impact on the calculation of  $\text{dn}/\text{dc}$ . Using a polymer with approximately 2% water content, the  $\text{dn}/\text{dc}$  value based on uncorrected concentration was 0.1835 as compared to 0.187 for the corrected concentration. The 2% water content represents a meticulously dried polymer. Perhaps some of the lower values of  $\text{dn}/\text{dc}$  in the literature are inaccurate because the polymer was not dried, and residual water content was not corrected for.

During acrylamide polymerizations partial polymer ionization can occur due to the formation of carboxylic acid groups along the polymer chain. To counteract the effects this might have on light scattering analysis, the polymers were dissolved in 0.02M sodium sulphate solution. There was however, very little difference in calculated molecular weights when runs using sodium sulphate and those conducted in distilled deionized water were compared. Molyneux (11) states that the presence of salt seems to have little effect on the conformational size of acrylamide.

Two important considerations in obtaining acceptable results were found to be the instrument focus and the filter size chosen for a particular analysis. An improper focus could be seen as a "cloudy" centre dot when looking through the instrument viewport. Visually, the focus can be adjusted with good accuracy if care is taken in the adjustments. However, if during the course of a set of samples the cells must be removed, it is quite easy to forget to refocus the instrument. A focus error seems to manifest itself in lower than expected molecular weights.

Choosing the correct filter size proved to be an even greater problem. Too small a filter resulted in a clean signal, but often produced drift, as shown in Figure II-7. This drift is likely caused by the slow clogging of filter pores by larger polymer molecules resulting in a

Figure II-7 Drifting Signal Due to Small Filter Size

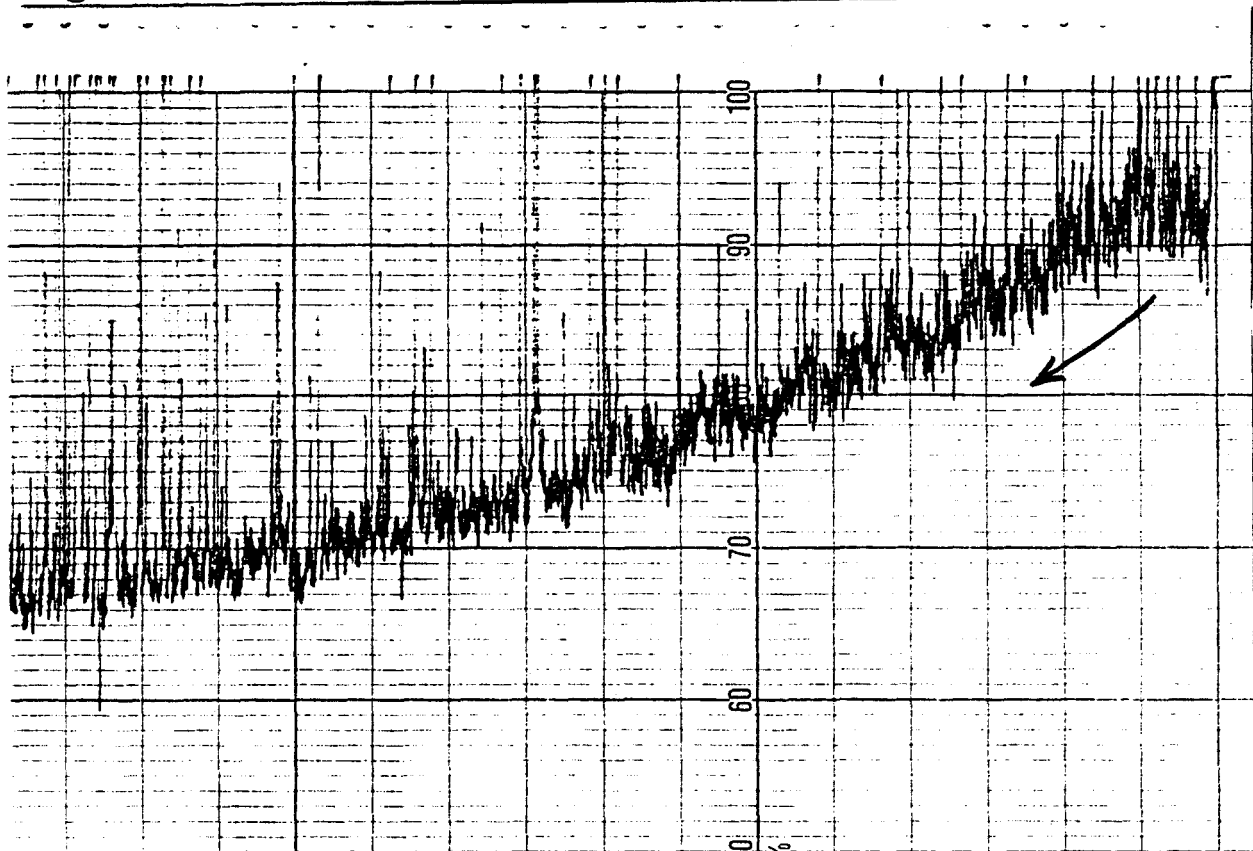
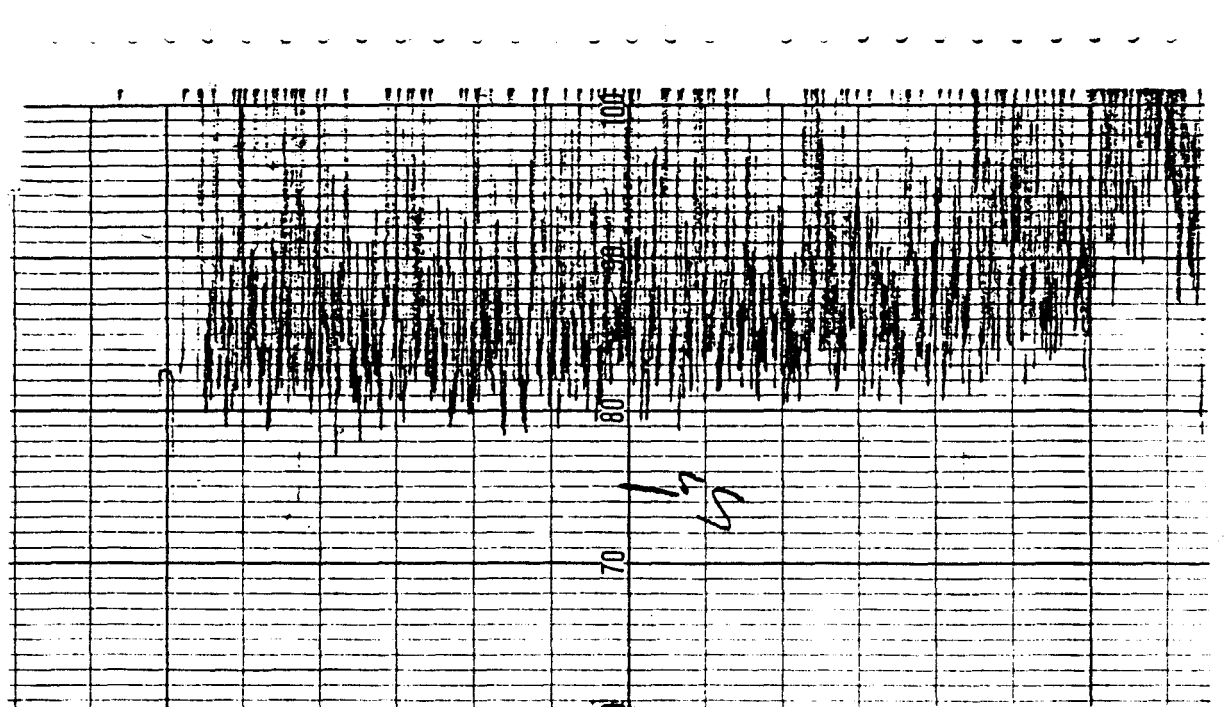


Figure II-8 Noisy Signal Due to Large Filter Size



slowly decreasing pore size with time, and a filtrate containing less of the high molecular weight tail of a sample. This drift along with high back pressures necessitated frequent changes of small pore size filters (often after every dilution of a polymer sample). On the other hand, a filter with too large a pore size gave a noisy signal because of the dust particles and micelles allowed through (Figure II-8). Cells had to be cleaned frequently, sometimes twice per polymer sample, and the location of the beam had to be changed often because of dirty cells. These factors all led to poor  $KC/R_{90}$  plots.

Better results were obtained using a second inline filter before the internal filter on the KMX-6 unit. A rough guide to choosing filter size as well as maximum solution concentration is shown in Table II-1. These values seemed to give the better results in LALLS analysis. It is also recommended that samples be allowed to dissolve for several days with frequent shaking, but no mechanical stirring. Using a magnetic stirrer with high molecular weight polymers is risky because of the possibility of shear degrading polymer molecules. If a stirrer must be used, speed should be kept as low as possible.

As a final note, problems were encountered in light scattering analyses when frequent solvent changes were made on the instrument. Especially if toluene was used as a solvent prior to changeover to water, the signal was noisy regardless of filter size. Also, cells tended to get dirty very quickly. Simply flushing the system in acetone did little to help these problems. It was found, however, that soaking the cells, tubing and syringe for several hours in acetone and then rinsing in distilled deionized water corrected these problems.

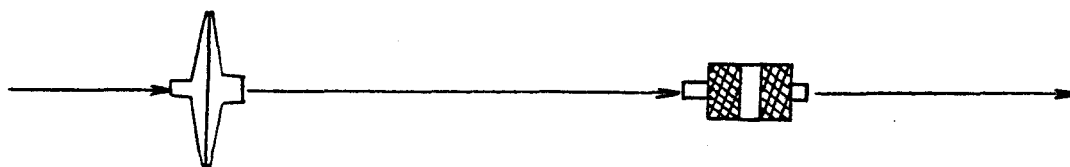
## 5.2 AMPOULE RUNS

Three sets of ampoules were run. The recipes used are as follows:

Table II-1

Guide to Selecting Maximum Polymer  
Concentration and Correct Filter Size

<u>Expected <math>\bar{M}_w</math></u>	<u>1<sup>st</sup> inline filter (<math>\mu\text{m}</math>)</u>	<u>2<sup>nd</sup> filter</u>	<u>[P] max.</u>
20 000	0.2	0.2	1 %
150 000	0.2	0.45	0.5 %
500 000	0.45	0.45	0.5 %
800 000	0.45	0.6	0.4 %
2 000 000	0.45	0.8	0.1 %
5 000 000	0.45	1.2	0.05 %



first filter  
(Millipore cartridge)

2<sup>nd</sup> filter  
(encased in metal  
housing located just  
before cell inlet )

3.4 mol mol/L acrylamide (purified)

$2.6 \times 10^{-4}$  mol/L initiator (purified)

100 or 200 ppm ethanol mercaptan as indicated

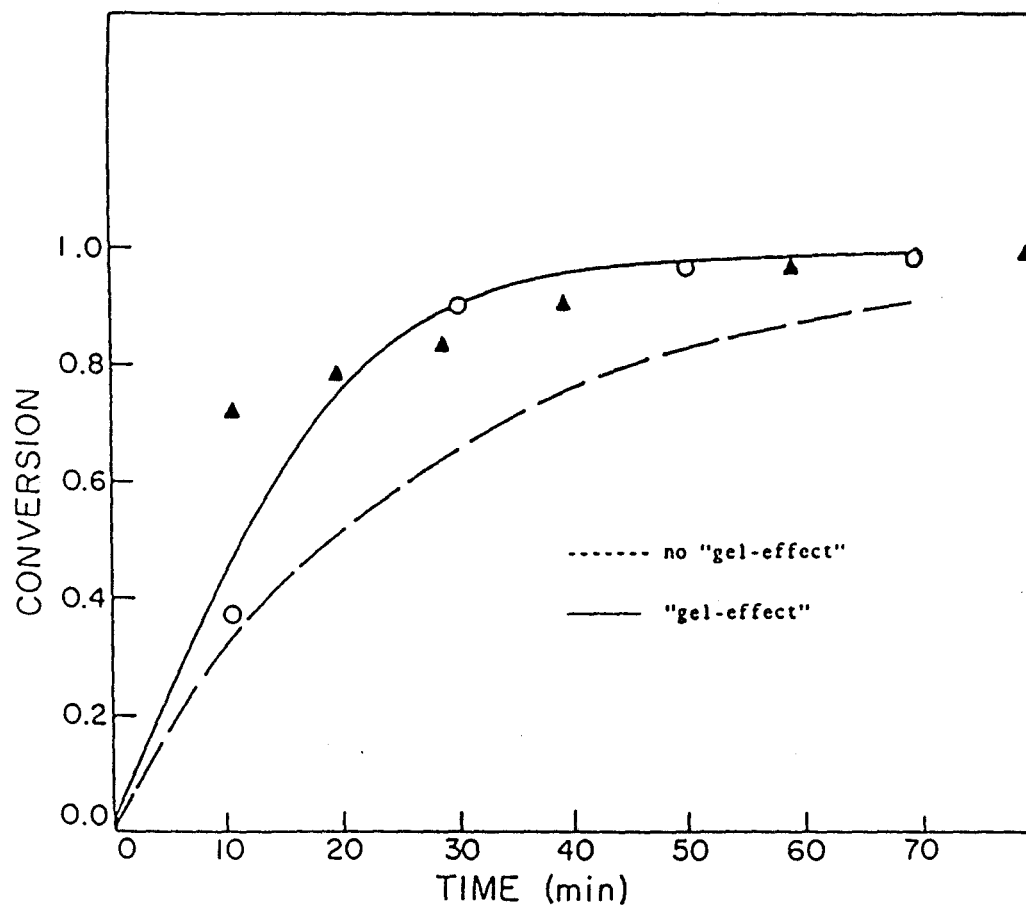
T = 60°C

distilled/deionized water to dilute

For the 100 ppm runs, conversions were measured by SEC and compared to conversion data from Kim (6) without CTA. These data are shown in Figure II-9. Except for the 10 minute point, there is good agreement between the two sets of data. The model predictions used by Kim use a gel-effect equation to describe the rate escalation when the termination reactions become diffusion controlled. In theory, the addition of CTA should reduce the gel effect because lower molecular weight molecules would be less prone to diffusion controlled termination. The 100ppm data points are generally slightly lower than Kim's data points and model predictions, possibly due to a lessening of the gel effect.

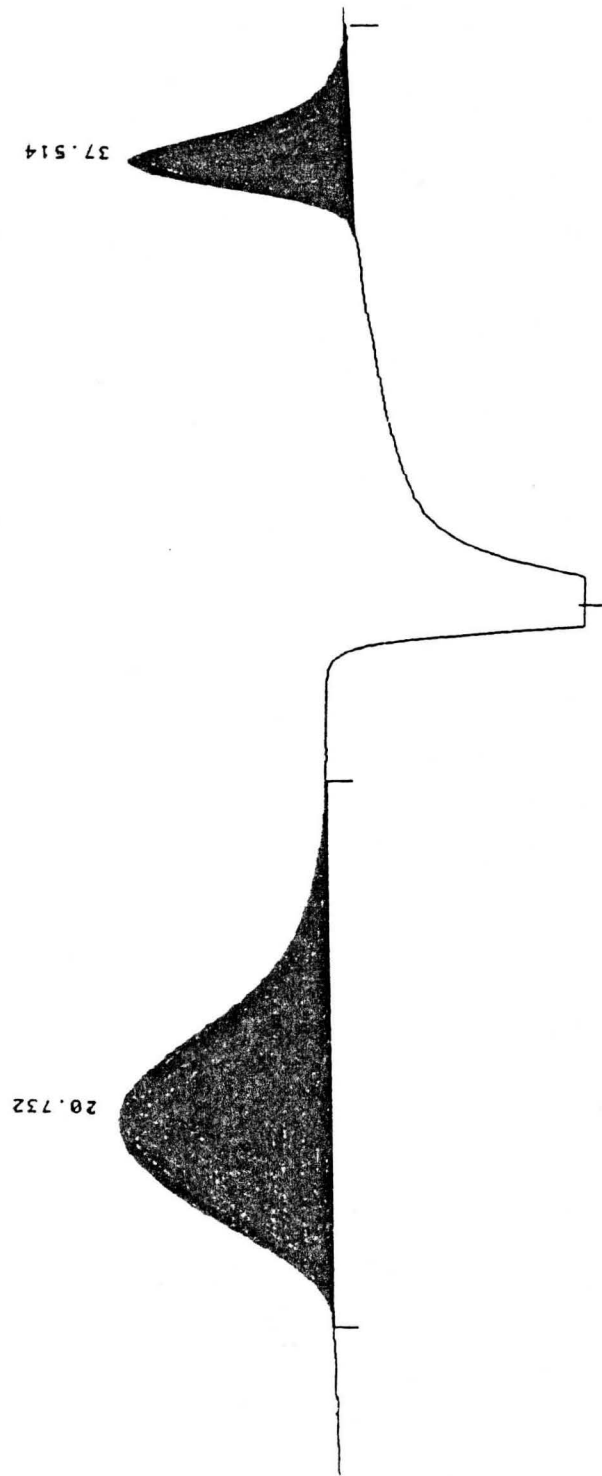
The accuracy of the 10 minute point may be in question. When the polymer from this ampoule was precipitated, it was noticed that there was substantially less solid than other ampoules, an indication of low conversion. It is possible that in the storage of the SEC sample some polymerization occurred. Although all the samples were stored with hydroquinone present in the cold, storage time was close to four months. Especially with a low conversion sample, there should be some concern about possible polymerization during the long storage period. It was however found that the SEC peak for the 10 minute ampoule was not skewed or bimodal as would be expected if post reaction polymerization occurred (Figure II-10).

Figure II-9 Conversion vs. Time - A Comparison with and without CTA in Ampoules



○ Kim (6)  
▲ This Research  
(100ppm CTA)

Figure II-10 Size Exclusion Chromatograph of 10 min. Ampoule



### 5.2.1 Molecular Weight Measurement

Table II-2 shows the results of light scattering analysis on sets of ampoules with 100ppm and 200ppm ethanol mercaptan present. SEC analysis failed in that adsorption was indicated by the elution time of the monomer being greater than the elution time of a similar molecular weight molecule (Figure II-11). The addition of Tergitol NPX, which was effective in preventing adsorption on glass packing (6), did not change the monomer elution time. Nevertheless,  $\bar{M}_w$  elution times, as indicated by the integration routine employed, are shown in Table II-3 for comparison. These values represent the elution times of the weight average molecular weight of the polymer peak with adsorption taking place. The actual values of  $\bar{M}_w$  calculated from calibration with broad standards are invalid because of adsorption. A worked example of the broad calibration method is given in Appendix A to simplify any future SEC calibrations if the adsorption problem is overcome. The elution volumes are meant to show the similarities and trends between ampoules. Also shown are the peak dispersion coefficients. No SEC analysis was conducted on the 200ppm ampoules.

It is interesting to see that  $\bar{M}_w$  seems to increase with conversion for the 200ppm ampoules, contrary to what theory predicts. This trend is not very certain because of the inaccuracy of the light scattering method. At best,  $\pm 10\%$  accuracy can be expected on  $\bar{M}_w$  values, based on errors associated with the instrument alone. The actual errors associated with ampoule reactions, such as the volumetric measurement of the CTA/monomer and initiator solutions using a burette while disregarding the residual volume past the "T" leading to the ampoule could add significantly to the instrument errors.

Perhaps the 100 ppm light scattering data better illustrates this uncertainty. This data set shows no apparent trend between  $\bar{M}_w$  and conversion. The repeat analysis of the 10 min ampoule yielded molecular weights of 392 900 and 479 500, a difference representing



Table II-2 Light Scattering Analysis of Ampoules

<u>Ampoule #</u>	<u>Rxn Time</u>	<u>[CTA]</u>	<u><math>\bar{M}_w</math> LALLS</u>	<u><math>2A_2 \times 10^{-3}</math></u>
#32	10 min	100 ppm	392 900	9.127
#32	10 min	100 ppm	479 500*	8.801
#35	20 min	100 ppm	650 100	9.412
#34	30 min	100 ppm	486 900	8.379
#30	40 min	100 ppm	593 100	9.287
#33	60 min	100 ppm	449 900	8.156
#36	80 min	100 ppm	593 600	7.430
#24	20 min	200 ppm	156 400	9.795
#20	30 min	200 ppm	175 600	9.711
#22	60 min	200 ppm	181 400	9.534

\* repeat measurement

Note :  $\frac{[C]}{[M]} = 4.744 \times 10^{-4}$  for 100ppm ampoules  
 $= 9.488 \times 10^{-4}$  for 200ppm ampoules

Figure II-11 Adsorption confirmation in SEC Analysis

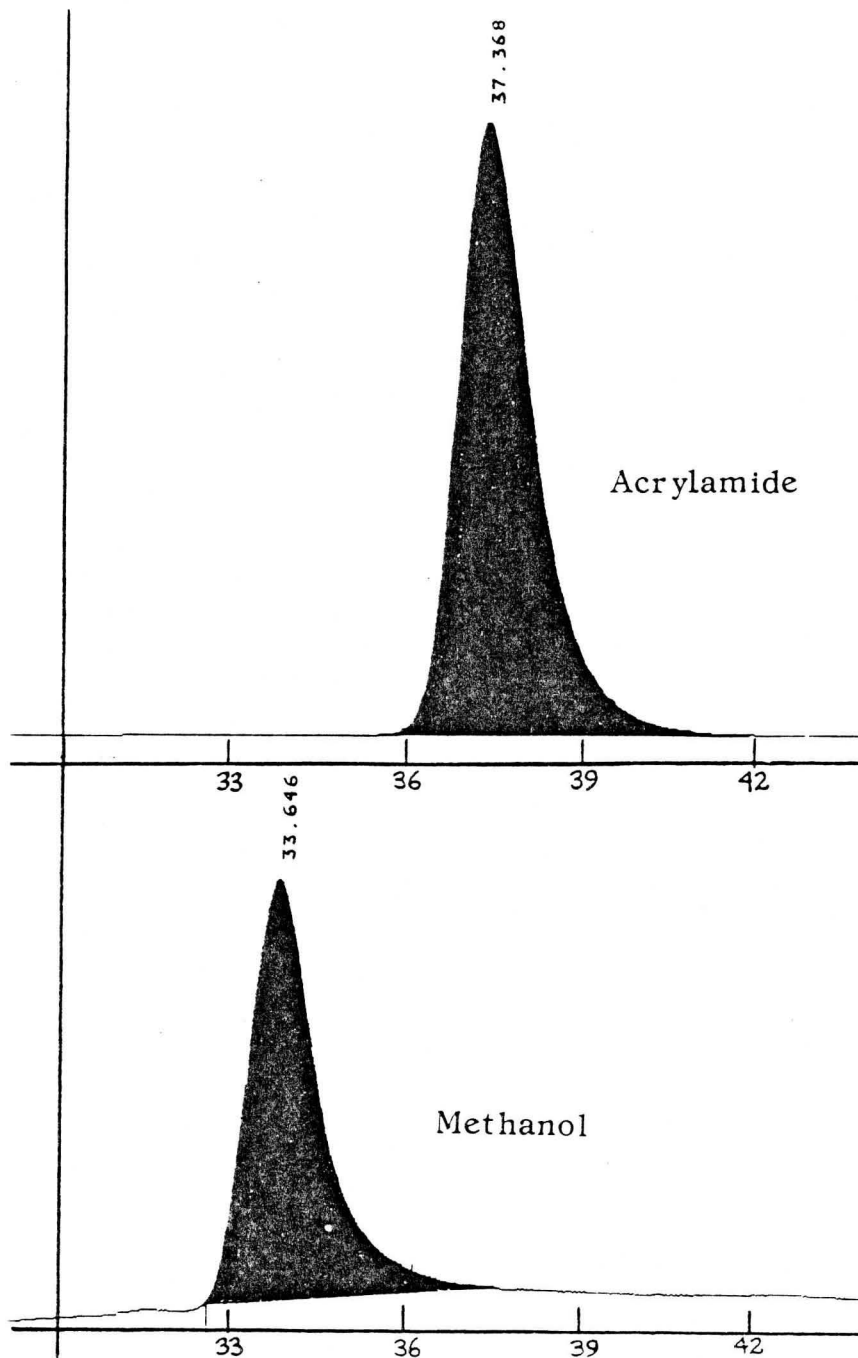


Table II- 3 SEC Elution Times for Ampoule Polymers

<u>Ampoule #</u>	<u>Rxn Time</u>	<u>[CTA]</u>	<u><math>\bar{M}_w</math> Elution Time (min)</u>	<u>Dispersivity*</u>
#32	10 min	100 ppm	20.14	3.032
#35	20 min	100 ppm	20.23	3.595
#34	30 min	100 ppm	20.29	3.955
#30	40 min	100 ppm	20.12	3.931
#33	60 min	100 ppm	20.12	3.684
#36	80 min	100 ppm	20.02	3.548

\* Dispersivity is proportional to polydispersity.

Note:  $\frac{[C]}{[M]} = 4.744 \times 10^{-4}$  for 100ppm ampoules

18% of the higher molecular weight. If any trend is present, it is not evident from light scattering data from this ampoule set.

The SEC data does show an interesting pattern, however. As indicated by elution times, molecular weight seems to decrease to 30 minutes and then increase to the 80 minute ampoule. This could be easily dismissed as coincidence or experimental error except for the trend in polydispersity indices which supports this observation somewhat. The polydispersities increase to the 30 minute ampoule and then decrease, a pattern which would be expected if molecular weight decreases and then begins to increase. The samples were analysed randomly and blindly. Certainly further experimentation and analysis should be conducted to either support or disprove such a trend.

The values of the second Virial coefficient are also indicated in Table II-2. These will be discussed in conjunction with other calculated Virial coefficients later.

### 5.3 REACTOR RUNS

#### 5.3.1 Inverse Suspension Runs

As mentioned previously, runs 2-8, abbreviated R2-R8 were inverse micro suspension runs. No R7 was conducted. Recipes are shown in Table II-4.

R2 was begun with initiator present prior to heating and sparging. It is believed this resulted in a runaway reaction because of the inadequacy of the controller in accounting for the large heat kick associated with the onset of polymerization during reactor heating. The temperature of the reactor reached 104 C before a quantity of hydroquinone solution was added to stop the runaway. It is likely that the reactor was near complete conversion at this time, and thus would not have increased in temperature for much longer. Injection of air into the reactor at about 80 C, a common practice in industry to control runaways, was not effective in slowing the temperature increase. This is likely because the initiator, potassium

Table II- 4 Inverse Suspension Recipes

R1	-	Conducted at Alkaril Chemical for training purposes. Recipe unknown.	
R2	-	1. 2500 g 50 % monomer solution in H <sub>2</sub> O 2. 1250 g oil / surfactant mixture 3. 4.2 g VERSENEX 80 chelating agent 4. 1.077 g CTA - ethanol mercaptan 5. 0.176 g initiator - K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	
R3	-	1. 2500 g 2. 1250 g 3. 4.3 g 4. 0.524 g 5. 0.176 g	R4 - 1. 2500 g 2. 1250 g 3. 4.3 g 4. 0 g 5. 0.176 g
R5	-	1. 2500 g 2. 1250 g 3. 4.381 g 4. 4.019 g 5. 0.175 g	R6 - 1. 2500 g 2. 1250 g 3. 4.2 g 4. 0.293 g 5. 0.176 g
R7	-	Not Conducted	
			R8 - 1. 2500 g 2. 1250 g 3. 4.3 g 4. 0.798 g 5. 0.176 g

Note :  $[C] / [M]$  values for each of these runs are as follows :

R2	-	$9.867 \times 10^{-4}$
R3	-	$4.961 \times 10^{-4}$
R4	-	0
R5	-	$3.682 \times 10^{-3}$
R6	-	$2.684 \times 10^{-4}$
R8	-	$7.311 \times 10^{-4}$

persulphate, is water soluble rather than oil soluble as many industrial inverse suspension initiators are. Oxygen has a greater solubility in the oil phase, hence oil soluble initiators are more easily controlled by air injection.

The suspension resulting from R2 seemed normal, so processing was carried out. At the elevated temperatures observed during this run there is a risk of producing a branched polymer (8). Because polymer R2 dissolved relatively easily, and because SEC analysis indicated a good fit to a calibration curve prepared with other polymers(9), it is thought to be linear, and thus an acceptable standard. A branched polymer would have an  $\bar{M}_w$  ( as measured by light scattering) which is higher than the  $\bar{M}_w$  measured by SEC.

Run 3 was set up to give a polymer of approximately 700 000 molecular weight based on ampoule data. Temperature control was excellent throughout the reaction, with maximum variations of no more than 1 C. Good control was thought to be largely due to load cell addition of the initiator. Reaction time was approximately 4 hours, as judged by steam valve opening values.

Run 4 was set up for a very high molecular weight polymer. Again temperature control was excellent. Unfortunately, the resulting polymer was destroyed during a processing step when a vacuum oven malfunctioned. High temperatures burned the polymer.

R5 was set up to produce a very low molecular weight polymer. Temperature control was good until a point approximately 2 hours into the reaction, when reactor temperature began to rise uncontrollably to about 100 C. Inspection of the reactor revealed that the polymer suspension had inverted. The result was a rubbery mass of polyacrylamide which would not dissolve entirely in hot water. The molecular weight of the polymer, as judged by the viscosity of the partially dissolved solution, was very high. The polymer was thus not processed any further. The inversion of R5, and the observed increases in fouling with increased amounts of CTA may indicate appreciable surface effects caused by the CTA,

resulting in a less stable suspension. This observation has rather important industrial implications, where an inversion of a large batch could cause a very dangerous and uncontrollable runaway. Perhaps the surfactant type or quantity must be tailored to the amount of CTA present to prevent fouling and runaways.

Two more runs, R6 and R8, yielded excellent temperature control. The polymers were not processed, however, because the analysis of small samples from all of the runs indicated all of the products had very high molecular weights. R8, which was expected to give a polymer with a molecular weight of less than 100 000, yielded a polymer with a molecular weight of well over 2 000 000 judging by the viscosity of a 0.05% solution. It seemed that the CTA was not effective in inverse suspension polymerizations, or, at least, the ampoule data was not applicable.

There are thought to be three possible causes for this. Ethanol mercaptan may partition between phases and/or undergo oxidation due to poor oxygen removal in the one gallon reactor. Shelf aging between the times the CTA was used in ampoules and in the reactor may also be possible. When a drop of ethanol mercaptan was added to light mineral oil, it seemed to dissolve, indicating oil solubility. The Handbook of Chemistry and Physics (15) does not have solubility data for ethanol mercaptan in any hydrocarbons, but does indicate that this CTA is soluble in benzene, a fairly non-polar solvent. It is thus likely that ethanol mercaptan is at least partially soluble in mineral oil.

When a large quantity of ethanol mercaptan was added to a beaker of mineral oil and heated to approximately 60 to 80 C, a precipitate, thought to be sulphur, and a second phase, thought to be ethanol, were observed. This indicates that an oxidation process may be occurring at reaction temperatures. Furthermore, a sealed volumetric flask containing an acrylamide solution and 200ppm CTA, intended to give a repeat set of data for the first set of 200ppm ampoules, instead gave unusable data. The polymers produced had molecular

weights of more than a million. This solution was stored in a refrigerator for about 2 weeks prior to use. It is believed that the ethanol mercaptan partially oxidized or aged during storage leading to a concentration of less than 200ppm when the ampoules were run. If aging can occur at refrigerator temperatures over a period of months, shelf aging may also be possible. Thus both oxidation and partitioning processes could be responsible for the ineffectiveness of ethanol mercaptan in inverse suspension polymerizations conducted in the batch reactor.

Of the inverse suspension runs that were purified, only R2 and R3 were analysed by light scattering. Three repetitions were conducted on R2 yielding the molecular weights shown in Table II-5. Two repetitions were conducted on R3. Both gave  $KC/R_0$  plots with unacceptable scatter. The first repetition, in which the polymer sample was left to dissolve with only occasional shaking yielded a molecular weight of over 10 000 000. When the same polymer was dissolved using a magnetic stirrer set for moderate agitation, the molecular weight was measured to be approximately 2 000 000. This difference might be explained by incomplete dissolution in the first case, leaving some high molecular weight gel. With stirring, the polymer likely experienced molecular breakage judging by the decrease in viscosity observed during the approximately 3 days the sample spent on the stirrer, and the large low molecular weight tail shown in the chromatogram of R3 (Figure II-12). It is thus likely that the molecular weight of R3 is between these extremes.

### 5.3.2 Solution Runs

Runs R9-R16 were conducted using the recipes shown in Table II-6. Also shown in the table is an indication of whether the run was successful.

Runs R9,R10,R11 and R16 were fully processed to yield approximately 500 grams of each standard. R12 was processed only partially because it was discovered that the polymer



Table II- 5      Molecular Weight Analysis of R2 by  
Laser Light Scattering

	<u>Repetitions</u>	<u>Average</u>
	1 914 000	
R2    -	1 865 000	1 811 000
	1 653 000	

Figure II - 12 Size Exclusion Chromatograph of R3

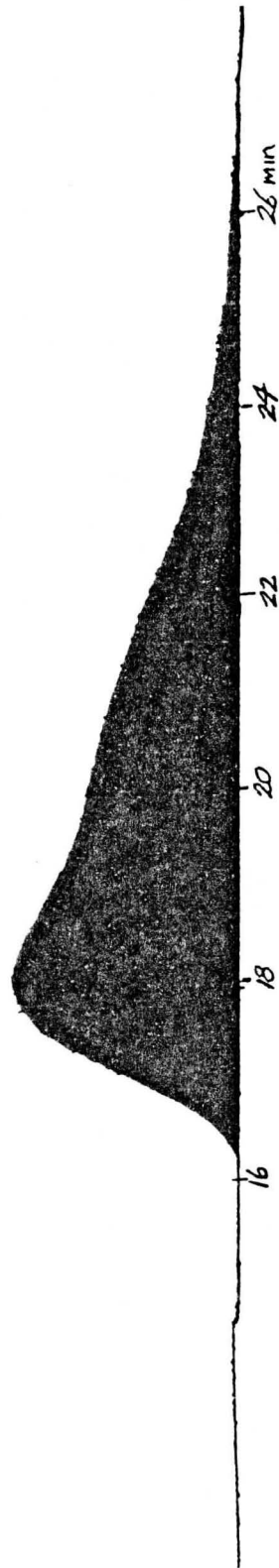
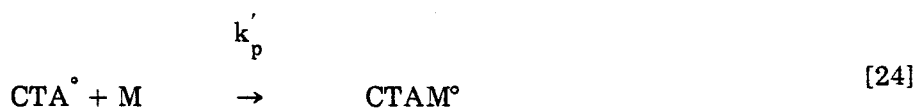


Table II- 6 Solution Polymerization Recipes

Run	<u>g 50% AAM soln</u>	<u>g H<sub>2</sub>O</u>	<u>g CTA</u>	<u>g VER 80</u>	<u>g init.</u>	<u><math>\frac{[C]}{[M]}</math> x10<sup>-4</sup></u>	<u>Comments</u>
R9	1600	2600	2.74	2.7	.300	39.22	Syrupy liquid, good temperature control at 60°C, acceptable standard.
R10	1600	2600	1.75	2.7	.303	25.09	Very viscous liquid, good temperature control, acceptable standard.
R11	1600	2600	1.30	2.7	.301	18.58	Jello like product, high pressure needed to cause product to flow from reactor, good temperature control. Acceptable standard, but broader than others.
R12	2200	2000	9.44	3.7	.302	85.79	Very viscous gel had to be scraped from reactor, good temperature control, bimodal polymer thus not an acceptable standard.
R13	2000	2200	10mL .01% FeCl <sub>3</sub>	0	.524	.0044	Runaway reaction due to high viscosity, rubber like product.
R14	1600	2600	0.1 PrAm	2.7	.303	1.216	Polymerized prior to initiator input, very viscous.
R15	1600	2600	8.00 PrAm	0	.303	97.26	Very viscous but flows slowly under pressure. Not processed. Good temperature control.
R16	1600	2600	11.28	0	.303	161.4	Syrupy liquid, poor temperature control, acceptable standard.

was bimodal by SEC analysis (Figure II-13). R16 was proved difficult to control temperature wise, as the temperature reached 70 C with a 60 C set point. It was decided that a set point change to 65 C would minimize dispersity.

Even though initiator concentrations approximated those used in ampoule runs, reaction times were generally much longer. R9, R10 and R11 took about 2 hours to reach a point where heat generation was small. Likely in part because of the higher temperature, R16 was complete in about 30 minutes. The explanation for the increased reaction times in the cases of R9, R10 and R11 is difficult. It is possible that poor oxygen removal inhibited the reaction somewhat, or that high concentrations of CTA had some effect. In the second situation, CTA molecules may form a more stable radical than the initiator or the monomer, giving a second propagation reaction:

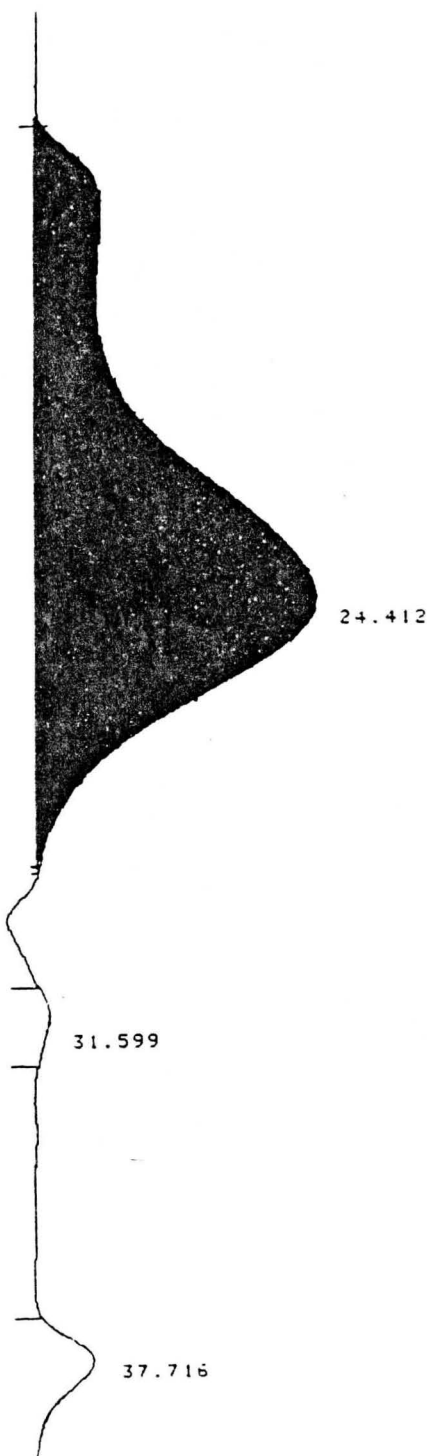


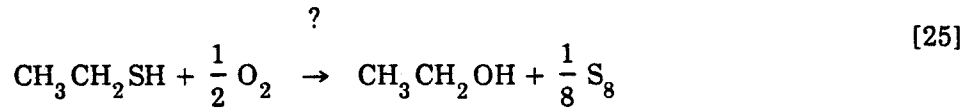
$$\text{where } k'_p < k_p$$

In this case, the reaction rate should decrease because propagation reactions on polymer chains stop to form a more stable radical with a lower propagation constant. A more stable radical could lead to an increase in the total radical concentration resulting in an increase in the termination rate. This could have an effect on the molecular weight by affecting the  $\tau$  and possibly  $\beta$  values in the molecular weight development.

Oxygen could slow the reaction as well. More importantly, oxygen may react with ethanol mercaptan as discussed in the inverse suspension section:

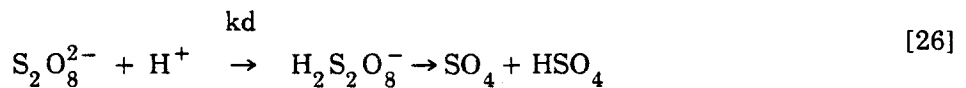
Figure II-13 Size Exclusion Chromatograph of R12





In fact R16, a run with a very high level of CTA gave a polymer with a visible yellow colour. There are several possible sources of oxygen. During storage of the CTA, frequent openings of the bottle could have led to dissolved oxygen and thus shelf aging. This source could be easily examined by employing fresh CTA in a reactor run and comparing results to runs already conducted. Inadequate sparging might result in CTA oxidation during the reaction. Dissolved oxygen would cause a lag time between when the initiator is added and when the reaction begins, but after this lag time has passed, the reaction would be expected to proceed normally. Oxygen content in the nitrogen sparge might explain the general decrease in reaction rates when compared to ampoule data. Even though there is little oxygen present in UHP nitrogen ( $< 2\text{ppm}$ ), a continuous sparge could result in substantial oxygen input to the reactor over the course of 2 hours. In fact, R16 in which nitrogen sparging was discontinued after initiator addition, and a vacuum was pulled, reaction rate seemed to be much faster than other runs resulting in an uncontrolled rise in temperature to 70 C. It is recommended that a continuous nitrogen sparge not be used in future runs because of the possibility of oxygen input to the reactor in the sparge stream.

Hruska (4) indicated that initiator decomposition may lead to oxygen formation, especially at lower pH:



But it thought that the small rates of initiator decomposition and moderate reaction pH levels would tend to make this effect very small in the reactions carried out in this research.

Moreover, ampoule data would reflect any effects initiator decomposition had on CTA performance.

As in the inverse suspension runs, molecular weight predictions based on ampoule data were found not to apply to reactor runs. Table II-7 lists the results of light scattering analysis on R9, R10, R11 and R16. It seems that higher levels of CTA did result in decreased molecular weights, but not to the extent expected from ampoule data. Again, oxidation of the CTA could be responsible. The bimodal distribution observed for R12 might be explained by a depletion of CTA as the reaction proceeded. Again, perhaps oxygen input through the nitrogen sparge led to this depletion. If in fact the CTA oxidizes, such a drift in molecular weight would be expected as the reaction proceeds.

Figures II-14 a,b & c show size exclusion chromatograms of the five standards produced, and compares them to currently available standards from Polysciences Co. . All the chromatograms were provided by Modchrom Inc., Mentor, Ohio. In terms of peak shape and dispersity, the standards produced compare well to those currently sold. Runs R2 and R11 produced slightly skewed peaks due possibly to a depletion of CTA, but to a lesser extent than that in R12. Poor temperature control likely also played a part in the fairly long low molecular weight tail seen for R2.

Table II-8 lists molecular weights as calculated by three independent sources and compares them to those calculated in this research. As can be seen, there is substantial disagreement in these values, particularly for R10 and R11. Part of this deviation may be explained by the analysis method used by Modchrom. SEC calibration was carried out with the Polysciences standards such that the peak elution times were assigned the weight average molecular weights of the samples, even though the standards are broad. This leads to an error because the shapes of the analysed standards differs from the shape of the Polysciences standards. It seems that R9, which has a fairly normal shape, has good

Table II- 7 Light Scattering Analysis of Solution  
Polymers

	<u>Repetitions</u>	<u>Average</u>
	116 700	
R9 -	108 300	108 200
	99 600	
	601 300	
R10 -	520 300	612 700
	716 400	
	837 900	
R11 -	1 087 000	902 100
	781 500	
	14 600	
R16 -	11 720*	13 100
	12 900*	

\* water content not accounted for

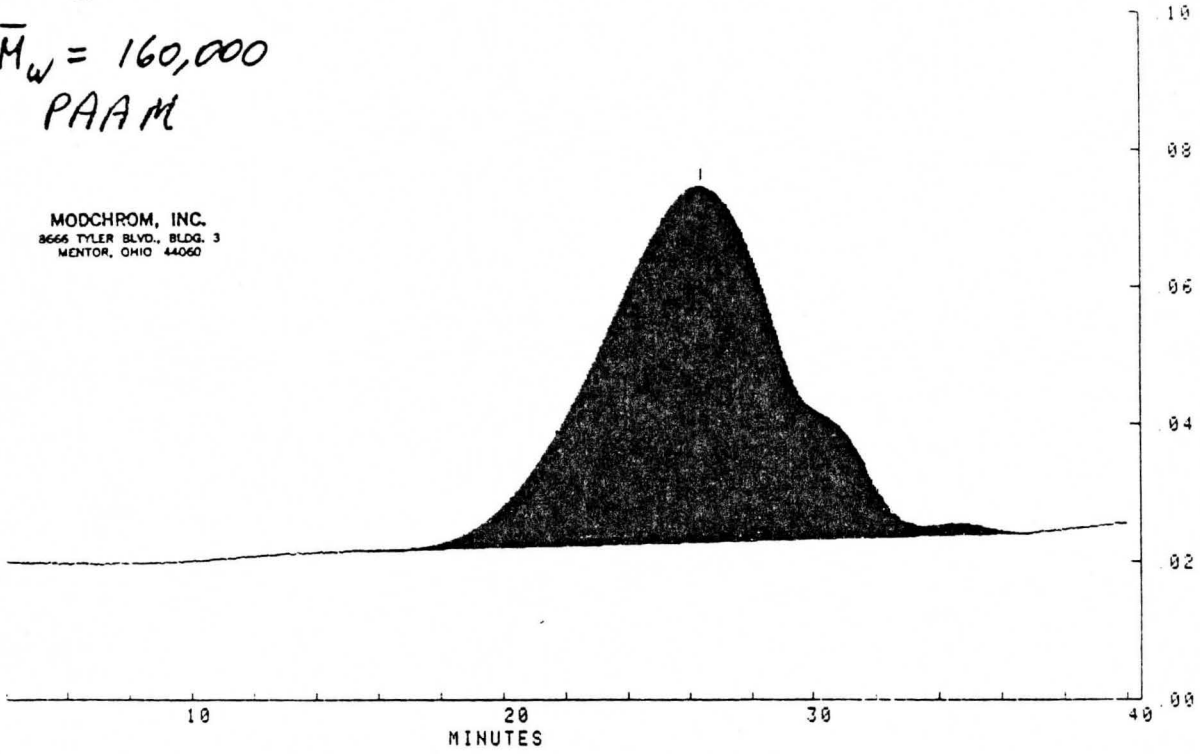


Figure II- 14 a,b,c Comparison. to Polysciences Standards

Page 1

$\bar{M}_w = 160,000$   
PAA M

MODCHROM, INC.  
8666 TYLER BLVD., BLDG. 3  
MENTOR, OHIO 44060



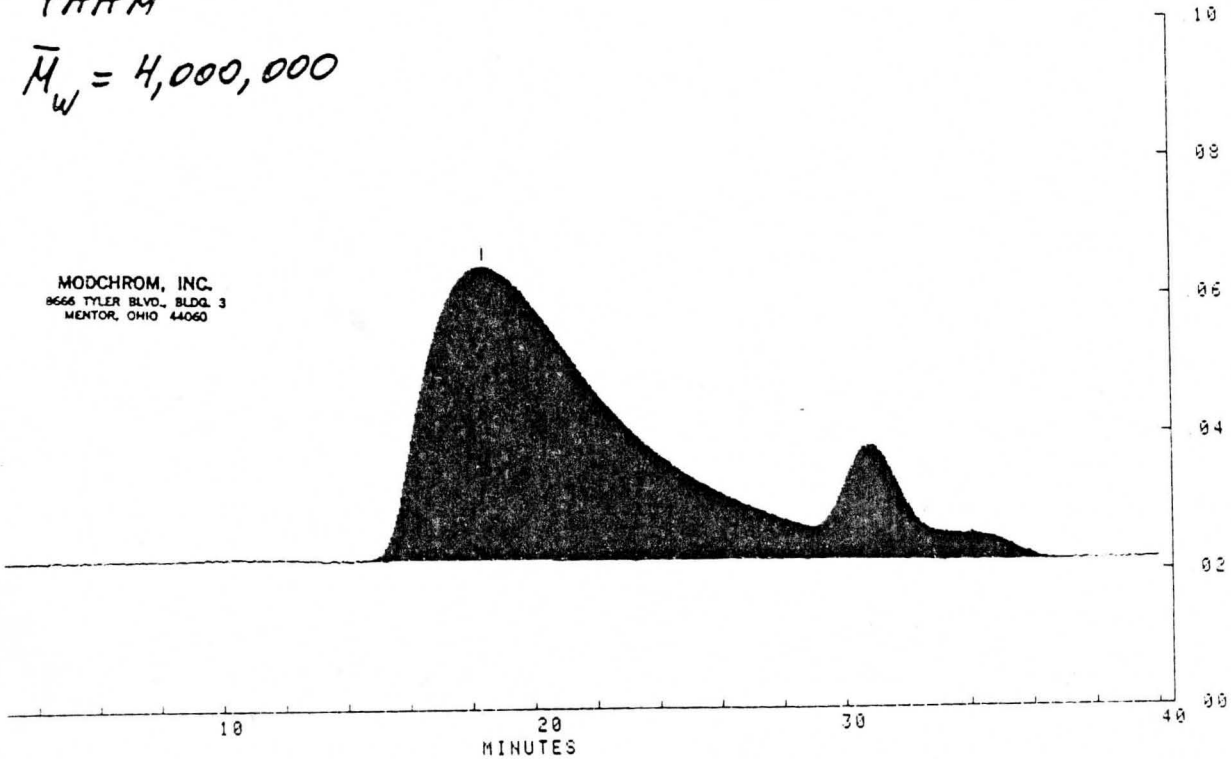
01-FEB-84 11:10

POLYMERIZATION

PAA M  
 $\bar{M}_w = 4,000,000$

18-383 PAA M 4000K

MODCHROM, INC.  
8666 TYLER BLVD., BLDG. 3  
MENTOR, OHIO 44060



Page 1

01-FEB-84 10:05

POLYMERIZATION

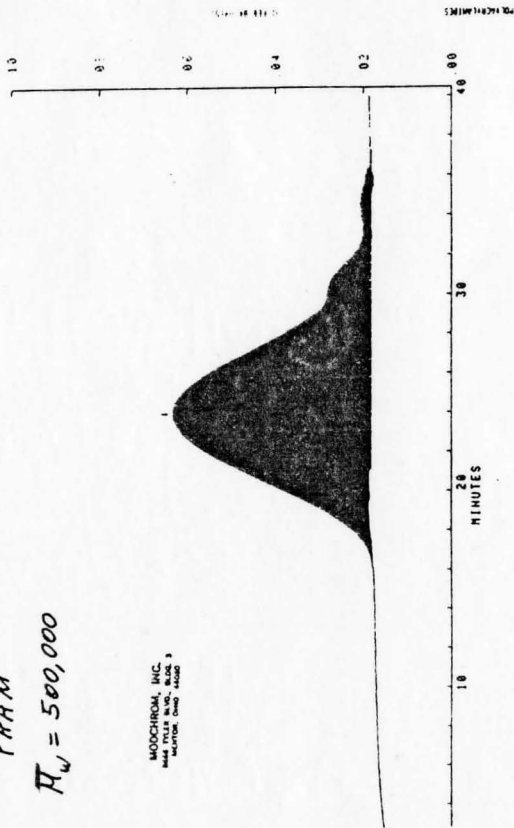
b. (BRACKETED NUMBERS REPRESENT MODCHROM ANALYSIS RESULTS FOR  $\bar{M}_w$ )

PAAM

$\bar{M}_w = 500,000$

MOOCHROM, INC.  
 MADE IN U.S.A. MODEL 3  
 TAPES, CHD 14000

22.917 PAAM 300

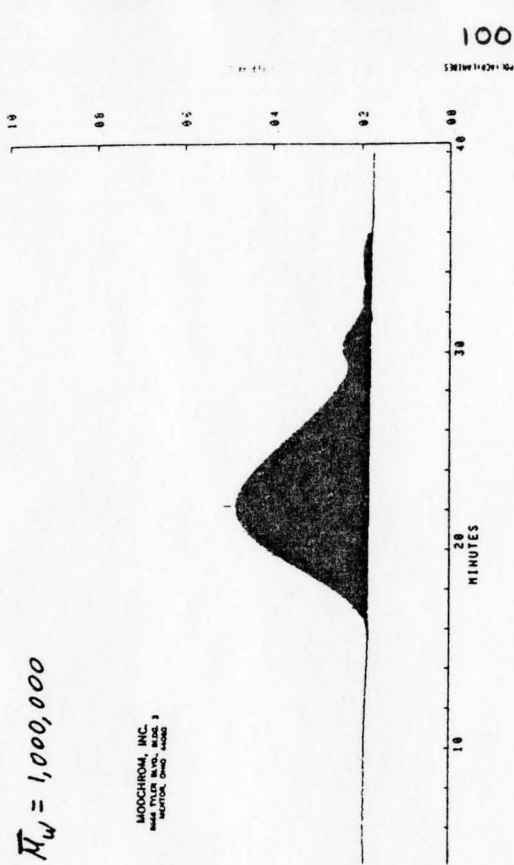


PAAM

$\bar{M}_w = 1,000,000$

MOOCHROM, INC.  
 MADE IN U.S.A. MODEL 3  
 TAPES, CHD 14000

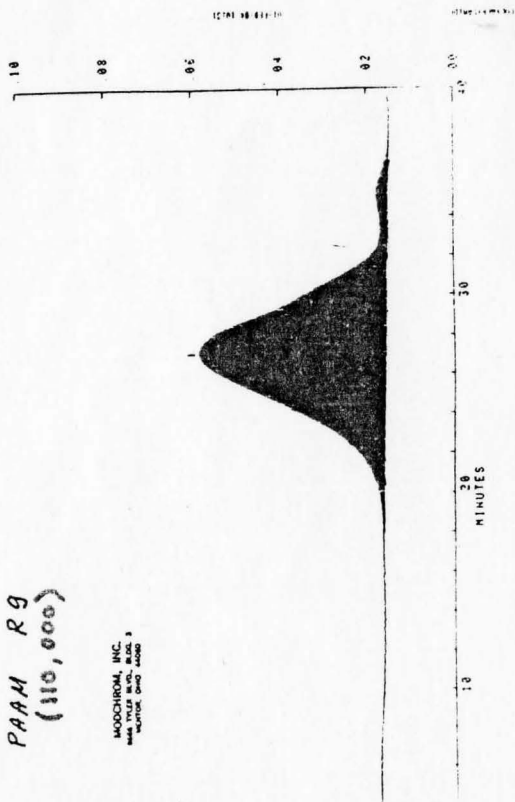
22.917 PAAM 300



PAAM R9  
 (110,000)

MOOCHROM, INC.  
 MADE IN U.S.A. MODEL 3  
 TAPES, CHD 14000

27.017 PAAM 30

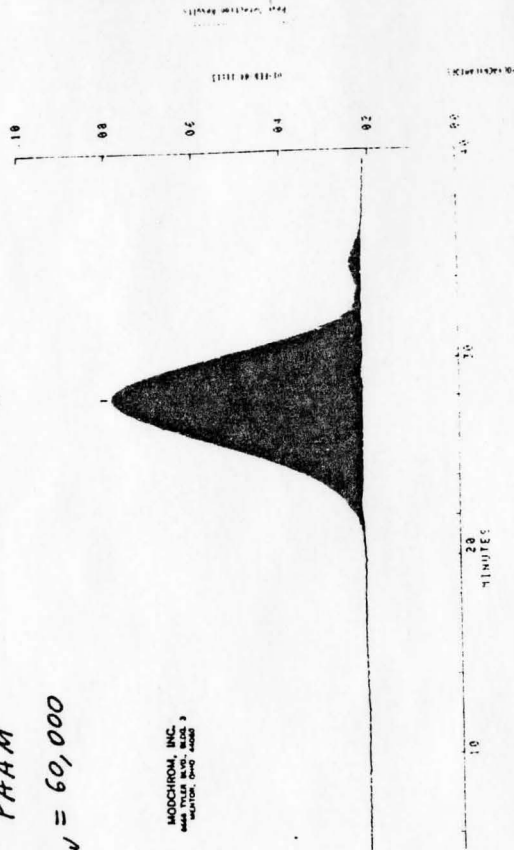


PAAM

$\bar{M}_w = 60,000$

MOOCHROM, INC.  
 MADE IN U.S.A. MODEL 3  
 TAPES, CHD 14000

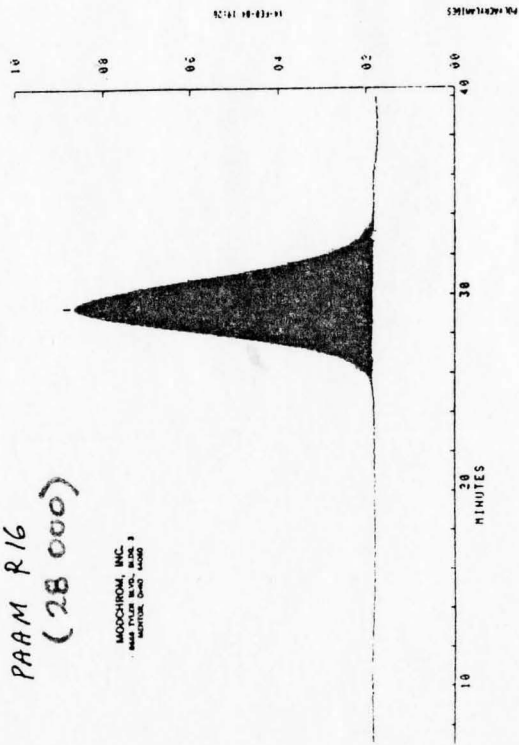
28.017 PAAM 30



C.

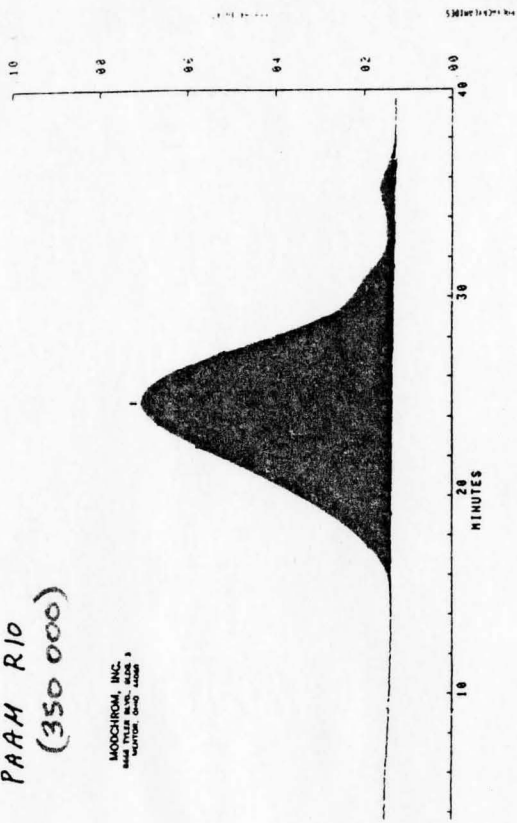
PAAM R16  
(28 000)

MOCHROM, INC.  
MAYFIELD BLVD., SUITE 3  
MAYFIELD, OHIO 44130



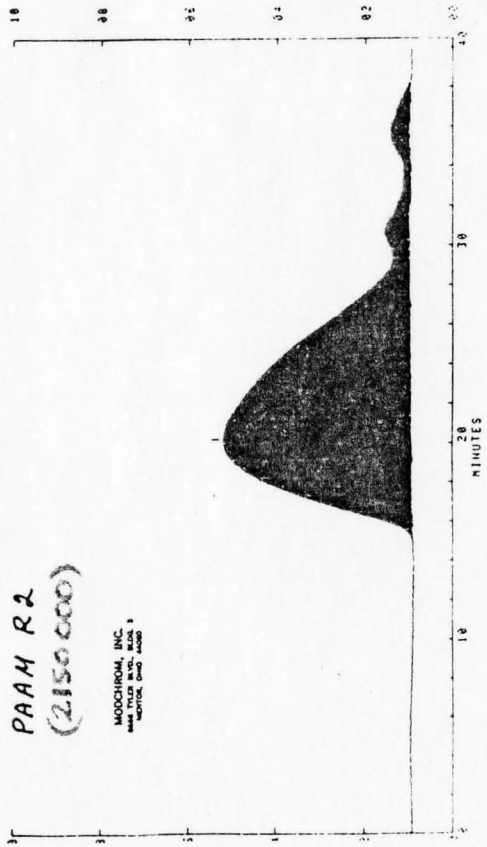
PAAM R10  
(350 000)

MOCHROM, INC.  
MAYFIELD BLVD., SUITE 3  
MAYFIELD, OHIO 44130



PAAM R2  
(2150 000)

MOCHROM, INC.  
MAYFIELD BLVD., SUITE 3  
MAYFIELD, OHIO 44130



PAAM R11  
(550 000)

MOCHROM, INC.  
MAYFIELD BLVD., SUITE 3  
MAYFIELD, OHIO 44130

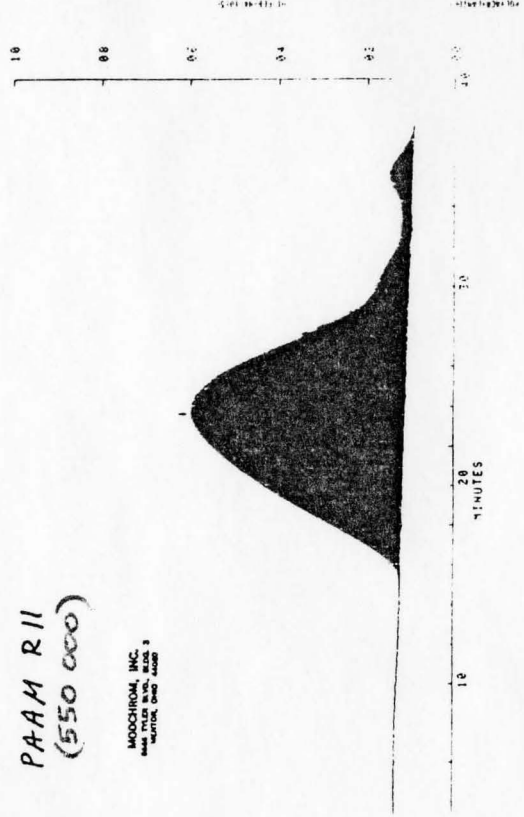


Table II- 8 A Comparison of Different Analysis Methods on Polyacrylamide Standards

<u>Sample</u>	<u>LALLS</u> <u><math>\bar{M}_w</math> avg</u>	<u>Viscometry</u> <u><math>\bar{M}_w</math> *</u>	<u>Modchrom</u> <u><math>\bar{M}_w</math></u>	<u>Nalco</u>	
R16	13 100	15 800	28 000		
R9	108 200	123 000	110 000	$\bar{M}_w$	115 000
				$\bar{M}_n$	40 000
R10	612 700	492 000	350 000	$\bar{M}_w$	430 000
				$\bar{M}_n$	175 000
R11	902 100	749 000	550 000	$\bar{M}_w$	665 000
				$\bar{M}_n$	280 000
R2	1 811 000	1 870 000	2 150 000	$\bar{M}_w$	1 050 000
				$\bar{M}_n$	480 000

\* Viscometry results courtesy of Mr. Vlado Hruska, McMaster Institute of Polymer Production Technology.

agreement between molecular weights, while R11, which is skewed towards higher molecular weights, has very poor agreement. A more accurate analysis involves calibrating the SEC by the broad calibration method discussed in the theory section.

Nevertheless, the disagreements between the different sources are disconcerting. Perhaps they attest to the inaccuracy of the characterization methods used. Certainly, further analysis of standards R10, R11 and R16 is required before they can be used suitably as standards.

As well as the four solution runs which resulted in acceptable standards, there were four runs which did not produce usable standards. Because R12 resulted in a bimodal polymer, its usefulness as a standard is limited. It is possible to mix together different molecular weight polymers to produce a very broadly dispersed standard out of R12, which would be useful as a standard, but this was not attempted. In R13, 2mg of  $\text{FeCl}_3$  was used as a CTA; that amount having been calculated from a  $k_{tc}/k_p$  given in a verbal communication (3), and a desired molecular weight of 30 000. Though this quantity seems very small for a 1 gallon reactor, the given transfer constant was much larger than that for ethanol mercaptan. The run, however, ran away because of high viscosity. This indicated a polymer with a molecular weight of over 2 000 000. It is possible that oxygen diminished the CTA's effectiveness, or that the given value of the transfer ratio was incorrect.

Propionamide was used as a CTA in R14 (100 mg). The batch polymerized during reactor warm up prior to initiator input, resulting in a high viscosity solution. The reason for this is unknown. A second run was conducted with a larger quantity of propionamide (8.0g). Judging by the viscosity of the polymer produced, the molecular weight was in the 700 000 - 1.5 million range, whereas a very low molecular weight polymer was expected. This polymer was saved, but not processed because that molecular weight range is already well covered by other standards.

#### 5.4 THE SECOND VIRIAL COEFFICIENT AND ITS RELATIONSHIP TO $\bar{M}_w$

Figure II-15 is a logarithmic plot of  $A_2$  vs  $\bar{M}_w$ . Included in this plot are data from sources other than this research. The best fit line, as shown, gives the following relationship:

$$A_2 = \theta_1 \bar{M}_w^{\theta_2}$$

$$\theta_1 = 0.01636 \pm 0.0076$$

$$\theta_2 = -0.211 \pm 0.037$$

95% C.I.

There is considerable scatter in the data in Figure II-15, reflecting by the uncertainties of the parameters in the relationship between  $A_2$  and  $\bar{M}_w$ . There is also a lack of data in the lower molecular weight range which casts some doubt on the validity of the relationship at this extreme.

Nevertheless, such a relationship can prove helpful in future light scattering analysis. Accuracy can be improved and analysis time can be minimized by forcing a line with a known slope of  $2A_2$  through a set of points for which  $A_2$  has been given by the  $A_2$  vs  $\bar{M}_w$  relationship. Since  $\bar{M}_w$  is unknown for a set of points until an intercept has been calculated, a trial and error or similar approach is required. It is likely that, because  $A_2$  is based on a larger data set, the accuracy of the calculated molecular weight will be greater.

Alternatively, if there is doubt in the accuracy of the  $A_2$  vs.  $\bar{M}_w$  relationship, a weighting could be applied in regression analysis so that there is a sum of squares penalty as the slope of a  $KC/R_\theta$  plot deviates from that given by the relationship. This approach would give weighting to previous data, but not to the extreme where previous data is assumed correct. As more data becomes available, the weighting factor could be increased to account for the greater accuracy of the relationship.



Random errors associated with the light scattering instrument would be reduced with either of these approaches. Also non random errors such as those involved with concentration and high end filtration would likely be reduced.

## 5.5 RECOMMENDATIONS

Further confirmation of the molecular weights of standards R10, R11 and R16 is needed before they can be used with accuracy. This initially would involve repetitions of light scattering analysis on R16. Then the simplest way of confirming the molecular weights of R10 and R11 would be SEC analysis with a calibration curve defined by R16 and R2. Of course the adsorption problems encountered would have to be eliminated before this is attempted. The resulting analysis should give a good indication of the true molecular weights of R10 and R11.

The matter of the ineffectiveness of ethanol mercaptan in the inverse suspension polymerizations should be investigated further through research on the solubility of this CTA in oil. Also, investigating the possibilities of both shelf aging and oxidation might prove helpful in explaining the high amounts of CTA needed in solution runs when compared to ampoule data. Perhaps a reactor run should be attempted with a fresh bottle of CTA. The addition of CTA before heating but after sparging might also prove interesting. In this case, lessening the amount of Versenex 80 would prevent any polymerization before the CTA is added.

On the matter of the relationship between  $A_2$  and  $\bar{M}_w$ , more data are required in the low molecular weight range. The planned preparation of a standard with a molecular weight of about 50 000, and the continuing analysis of R16 should help alleviate this situation.



## 6. CONCLUSIONS

Five polyacrylamide standards with acceptable molecular weight distributions were prepared. Further analysis must be conducted before the molecular weights of three of these standards are known with enough certainty to calibrate an SEC.

Ampoule kinetic data with 100ppm of ethanol mercaptan compared fairly well to data from Kim (6) with no CTA present, however, it seemed as though the rate of polymerization in the 1 gallon pilot plant reactor was generally slower than that in ampoules. The presence of larger amounts of CTA and/or inadequate deoxygenation may have contributed to this difference.

Ethanol mercaptan was not an effective transfer agent in inverse suspension polymerizations conducted in the batch reactor. Oil solubility may have led to partitioning and/or an oxidation or aging process may have resulted in CTA depletion. All of these factors could have contributed to the ineffectiveness. It was also found that CTA levels required in solution polymerization to give a desired molecular weight were larger than those implied by ampoule data. Again, oxidation or aging of the CTA may have played roles.

A relationship between  $A_2$  and  $\bar{M}_w$  was presented. Though the uncertainty in the relationship is fairly large, the relationship presented represents a first step in making light scattering analysis of polyacrylamides simpler and more accurate. Further additions to the data set presented should improve the accuracy of the relationship.

## 7. REFERENCES

- (1) Brandrup, J. and Immergut, E.H., eds., Polymer Handbook, John Wiley and Sons, N.Y. (1975).
- (2) Chiantore, O. and Hamielec, A.E., *J. Liq. Chromat.*, 7, 1753 (1984).
- (3) Hamielec, A.E., Verbal Communication, (1984).
- (4) Hruska, V., M. Eng Thesis, McMaster University, (1985).
- (5) Hunkeler, D., Unpublished data, McMaster University, (1985).
- (6) Kim, C.J., Ph.D. Thesis, McMaster University, (1983).
- (7) Kim, C.J., et. al., *J. Liq. Chromat.*, 5(7), 1277-1294 (1982).
- (8) Kulicke, W.M., et. al., *Prog. Polym. Sci.*, Vol 8, 373-468 (1982).
- (9) Modchrom, Inc., (supplied SEC data), Mentor, Ohio, (1985).
- (10) McMaster University, "Determination of Mw", (a guide to light scattering analysis - author unknown).
- (11) Molyneux, P., "Water Soluble Synthetic Polymers: Properties and Behavior", Vol. 1, CRC Press, Boca Raton, Florida, (1982).
- (12) Molyneux, P., "Water Soluble Synthetic Polymers: Properties and Behavior", Vol. 2, CRC Press, Boca Raton, Florida, (1982).
- (13) Nalco Chemical Co., (supplied molecular weight data), Naperville, Illinois, (1985).
- (14) Shawki, S., PhD Thesis, McMaster University, (1978).
- (15) Weast, R.C., ed., "Handbook of Chemistry and Physics", CRC Press, Cleveland, Ohio, (1974).

APPENDIX A

APPENDIX A : SEC Calibration Using Broad Standards - A Worked Example

For PEO the Apple computer gives a calibration curve based on narrow standards :

$$\begin{aligned}\log M &= 9.63816 + 0.047757v - 0.020008v^2 + 3.9004 \times 10^{-4}v^3 \\ &= \phi_1(v) * \end{aligned}$$

Consider 2 hypothetical polyacrylamides which have been analysed by light scattering or some other method to give weight average molecular weights :

STANDARD 1	$\bar{M}_w = 715\ 000$
STANDARD 2	$\bar{M}_w = 181\ 000$

The first step involves analysing standard 2 using  $\phi_1(v)$

Results :  $\bar{M}_w = 107\ 726$  - Too low  
 $\log \bar{M}_w = 5.03232$

(These results are obtained by analysing the chromatograph of standard 2. This is done by sending the stored data from the Varian Vista data station to the Apple computer for processing. )

$$\phi_1(v) = c_1 + c_2v + c_3v^2 + c_4v^3$$

$\log \bar{M}_w = 5.03232$  from analysis using  $\phi_1(v)$

the contribution to this value from the  $c_2, c_3$  and  $c_4$  terms is :

$$5.03232 - 9.63816 \text{ from } * \quad ( = -4.60584 )^{**}$$

The correct molecular weight of standard 2 is 181 000.

$$\log 181\ 000 = 5.25768$$

Because the correct molecular weight is higher than that predicted, the calibration curve must be shifted up. This involves increasing the  $c_1$  term in \* by an amount that can be calculated using the  $c_2+c_3+c_4$  contribution value calculated above,

$$\begin{aligned}c_{1\text{new}} &= 5.25768 + 4.60584 \\ &= 9.86352 \end{aligned}$$

$$\begin{aligned}\text{Thus, } \phi_{1\text{new}}(v) &= 9.86352 + 0.047757v - 0.020008v^2 \\ &\quad + 3.9004 \times 10^{-4}v^3 \end{aligned}$$

This calibration curve gives the correct molecular weight

for standard 2. In Figure II-1, it is represented by the dotted line. When standard 1 is analysed using this calibration curve :

Results :  $\bar{M}_w = 583\ 952$  - Too low

Now, a trial and error approach is needed to shift the slope of the calibration curve up without changing the shape defined by the PEO calibration curve.

$$\text{Let } \log \bar{M}_w = \phi + \epsilon c_2 v + \epsilon c_3 v^2 + \epsilon c_4 v^3$$

Where  $\epsilon$  is a factor to increase the slope of the curve, and  $\phi$  is a value such that the new curve correctly predicts the molecular weight of standard 2.

Try  $\epsilon = 1.10$  thus,

$$\phi_{\text{trial}} = \phi + 0.052533v - 0.022009v^2 + 4.29044 \times 10^{-4} v^3$$

To force the curve to correctly predict the molecular weight of standard 2 :

$$\begin{aligned} &= \log 181\ 000 - 1.1(c_2 v_{x_2} + c_3 v_{x_2}^2 + c_4 v_{x_2}^3) \\ &\text{where } v_{x_2} \text{ is the elution volume of the weight average} \\ &\text{molecular weight of standard 2.} \end{aligned}$$

$$\begin{aligned} \text{From **}, \quad 4.60584 &= 0.047757 v_{x_2} - 0.020008 v_{x_2}^2 + 3.9004 \times 10^{-4} v_{x_2}^3 \\ v_{x_2} &= 22.475 \end{aligned}$$

$$\begin{aligned} \text{Therefore } \phi &= \log 181\ 000 - (-5.06573) \\ &= 10.32341 \end{aligned}$$

$$\text{Thus } \phi_{\text{trial}} = 10.32341 + 0.052533v - 0.022009v^2 + 4.29044 \times 10^{-4} v^3$$

Analysing standard 1 again :

Results :  $\bar{M}_w = 655\ 351$  - Too low

Try  $\epsilon = 1.20$

$$\phi_{\text{trial}} = \phi + 0.057308v - 0.0240096v^2 + 4.68048 \times 10^{-4} v^3$$

$$\begin{aligned} \phi &= -1.2(c_2 v_{x_2} + c_3 v_{x_2}^2 + c_4 v_{x_2}^3) + \log 181\ 000 \\ &= 5.257679 + 5.406515 \\ &= 10.66419 \end{aligned}$$

Analysing standard 1 with the new calibration curve :

Results :  $\bar{M}_w = 737\ 000$  - Too high

After two more values of  $\phi$ , try  $\phi = 1.174$

$$\begin{aligned} &= \log 181\,000 - 1.174(c_2v_{x_2} + c_3v_{x_2}^2 + c_4v_{x_2}^3) \\ &= 5.257679 + 5.406515 \\ &= 10.66419 \end{aligned}$$

$$\begin{aligned} \text{Therefore } \phi_{\text{trial}} &= 10.66419 + 0.056067v - 0.0234894v^2 \\ &\quad + 4.57907 \times 10^{-4}v^3 \end{aligned}$$

Analysing standard 1 :

$$\text{Results : } \quad \bar{M}_w = 715\,000$$

Analysing standard 2 :

$$\text{Results : } \quad \bar{M}_w = 182\,000$$

Further calculations can be done if more accuracy is required, but this calibration curve gives adequate results. It may be tested by analysing a third standard with a molecular weight between those of standards 1 and 2.

Note that this worked example is hypothetical, and thus calibration curve calculated does not apply to polyacrylamide SEC analysis. Problems with adsorption and the lack of very accurate molecular weight data for the polyacrylamide standards at the time of analysis prevent the presentation of the actual calculations of the calibration curve.

APPENDIX B

REDUCED SPECIFIC VISCOSITY DETERMINATION OF NALCO 677A. Equipment

1. Three 100 ml beakers.
2. Balance capable of weighing to  $\pm .02g$  (Mettler P1200 or equivalent).
3. pH meter capable of reading to  $\pm .01$  pH units (Beckman Zerometric or equivalent).
4. Three magnetic stirring bars that can fit into 100 ml beakers.
5. Assorted volumetric pipettes.
6. Volumetric flasks, three 100 ml  
   one 500 ml  
   two 1 liter
7. Water bath (18" deep) capable of maintaining a constant temperature of  $30.00 \pm .02^{\circ} C$ .
8. Three size 75 Cannon Ubbelohde semi-micro dilution viscometers.
9. A source of vacuum with a trap.
10. Three electric stopwatches reading to  $\pm 0.1$  second (Fisher Scientific #14-653). Mechanical stopwatches could be substituted here.

B. Reagents

1. 2M  $NaNO_3$

Dissolve 170 g. of Bakers reagent grade  $NaNO_3$  in about 800 ml D.I. water and dilute to 1 liter.

2. 1M  $NaNO_3$

Using volumetric flasks, dilute 500 ml of the 2M  $NaNO_3$  to 1 liter.

3. 1%  $Na_2CO_3$

Dissolve 10g of Bakers reagent grade  $Na_2CO_3$  in 500 ml D.I. water and dilute to 1 liter.

4. D.L. NaOH ( $\sim .017N$ )

Dilute 1 ml of Bakers reagent grade 50% NaOH to 1 liter with D.I. water.

5. D.L. HCL ( $\sim .012N$  HCL)

Dilute 1 ml of Bakers reagent grade HCL to 1 liter with D.I. water.



6. This is to be called the stock solution, is 1% product, and should be used within 4 hours for further work.

REDUCED SPECIFIC VISCOSITY (RSV) - (to be done in triplicate)

C. Working Solution Preparation (Prepare in triplicate)

1. Weigh out ( $x \pm .05g$ ) of the 1% (as product) stock solution into a 100 ml beaker.

$$x = \frac{491.8}{\% \text{ polymer in product}}$$

% polymer should be obtained by following the procedure for determination of polymer solids.

2. To this beaker add 50 ml 2M  $\text{NaNO}_3$ , 1 ml of 1%  $\text{Na}_2\text{CO}_3$ , and a magnetic stirring bar.
3. Stir for 15 minutes on a magnetic stirrer at a rate that will produce a  $\frac{1}{4}$ " vortex. The pH of this solution should be 9 to 9.5. If not, adjustment to this range with dilute NaOH or dilute HCL will be necessary.
4. Quantitatively transfer the contents of the 100 ml beaker into a 100 ml volumetric flask and dilute to the mark with D.I. water. Invert a number of times to mix.

D. PROCEDURE

1. Pipette at least 2 ml of 1M  $\text{NaNO}_3$  into three clean and dry size 75 Ubbelohde Viscometers in a constant temperature bath adjusted to  $30 \pm .02^\circ\text{C}$ .
2. Allow about five minutes for temperature equilibration.
3. Determine the efflux time of the solvent in these viscometers to the nearest 0.1 second, using an electric timer. To do this, draw up the solvent with vacuum to over the upper red line. Let the viscometer drain under gravity and determine the time it takes the meniscus to move between the red lines. Repeat two or three times. Average the efflux times in each viscometer and record this as  $t_0$ . With some practice these viscometers can be run simultaneously, by slightly staggering the starting times.

4. Clean each viscometer with the aid of a vacuum, by removing the solvent, rinsing three times with water, then three times with acetone, and then drying. During each rinsing step make sure that the entire internal volume of the viscometer is thoroughly rinsed, and then completely evacuated before refilling.
5. Add at least 2.0 ml of working solution (Part A, Step 4) into each dry viscometer. The working solution should be reasonably clear or the fine capillary of the viscometer could become plugged. If the sample has much particulate matter, this should be allowed to settle and the supernatant portion used as sample. If settling is too slow, filtration through a medium or coarse pad with vacuum may be necessary. Most of the dilute sample solutions will be clear enough to use as prepared in Part C.
6. Allow about five minutes to equilibrate and determine the efflux time twice in each viscometer. Duplicate results should agree within  $\pm 0.2$  seconds. If not, repeat until this is obtained. Record the average  $t$  in each viscometer.
7. The run has now been completed and the viscometer can be readied for another run by following the instructions in Step 4.
8. All the efflux times,  $t$ , should be between about  $1.15 t_0$  and about  $2.0 t_0$ . If this is not the case, then repeat from Part A<sub>0</sub> using an appropriate weight of stock solution in Step 1.
9. The solvent time  $t_0$  need be run only occasionally, once or twice a week, or when a new batch of solvent is prepared.

#### E. CALCULATIONS

1. The weight  $x$  of sample needed was calculated in such a way as to always give a working solution (Part A, Step 4) concentration of .045g/100cc. The other information necessary is the sample and solvent efflux times,  $t$  and  $t_0$  respectively.
2. The calculation for each of the triplicate runs is:

$$RSV = \frac{1}{.045} \left( \frac{\text{avg } t}{\text{avg } t_0} - 1 \right)$$

3. Average the three values of the RSV and report this to the nearest unit as the final value of the RSV.
4. If any of the individual RSV's differs from either of the others by  $> 2$  units, discard it, and report the average of the remaining two numbers. If all three RSV's differ from each other by  $> 2$  units, repeat the whole RSV determination from the start.