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**DEVELOPMENT OF IMPROVED MOBILITY CONTROL  
AGENTS FOR SURFACTANT/POLYMER FLOODING**

**Final Report**

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## I. ABSTRACT

The goal of the laboratory work in this project was to develop mobility control agents that are more effective than the polymers currently used in surfactant/polymer flooding applications. This report summarizes the progress made during each phase of the project.

During the first year, the initial phase of the project included a literature survey of surfactant/polymer flooding, a summary of the current status of DOE-sponsored polymer and surfactant/polymer field projects, and a survey of oil industry personnel regarding difficulties encountered in the use of commercially available polymers. From these studies, the major problems in the use of partially hydrolyzed polyacrylamides were identified as: (1) mechanical degradation, (2) viscosity loss in brines, and (3) interactions with divalent ions; whereas the most serious deficiencies with xanthan gum polymers were: (1) high cost of the polymer, (2) potential for plugging of injection wells, (3) microbial degradation of the polymer, and (4) the requirement for filtration of the polymer solution. The purpose of Phase 1 of the project was to delineate clearly the strengths and weaknesses of the commercial polymers. The laboratory tests in the second phase then were designed to measure and compare the factors considered to be of greatest importance. All of this background work and much of the baseline laboratory testing was completed and reported in our first annual report.<sup>1</sup>

During the second year of the project, the Phase 2 baseline screening tests were completed, and Phase 3 work commenced on the synthesis, characterization, and preliminary screening of new or modified polymers. These results were presented in our second annual report.<sup>2</sup>

During the final year of the project, the preliminary screening tests were completed and polymers of interest were evaluated in more detail. This final report contains highlights of the significant accomplishments of the project and presents our conclusions regarding the development of improved mobility control agents. Our work has shown that moderate changes in the basic structure of acrylamide polymers can produce significant effects on performance in oil recovery applications. Better viscosity retention in brine can be obtained by stiffening the polymer chain of acrylamide-type materials. Enhanced shear stability can be attained by increasing the polymer hydrophilicity. Future research should be directed along these lines.

## II. HISTORY OF PROJECT

This project resulted from our response to a United States Department of Energy Request for Proposal. The project was jointly funded by DOE (Project Number DOE/BC/00047), and the New Mexico Energy and Minerals Department (Project Number 2-67-3321). The three-year program began on

September 29, 1978. A three month, no-cost extension was granted which extended the completion date to December 31, 1981.

### III. INTRODUCTION

Two principal types of polymers are currently used for polymer flooding: synthetic polymers called partially hydrolyzed polyacrylamides (HPAM) and a biologically-produced polysaccharide known as xanthan gum (XG). The generalized structures of these two polymers are shown in Figures 1 and 2, respectively. Although both types of materials have been successfully used in field applications, each suffers limitations that result in process inefficiencies or loss of cost effectiveness. Problems common to both polymer types include difficulties encountered with injection of polymers, especially where the reservoir permeability is low; interactions between surfactants and polymers; degradation caused by the presence of oxygen; and availability of bactericides which are compatible with the polymers. Problems specific to the use of XG include bacterial degradation, injection well impairment, and filtration requirements. Problems encountered primarily with HPAM include viscosity loss in brine, especially brines containing calcium and magnesium ions, and the necessity for special handling to prevent degradation by shearing. Although field tests are being conducted with both types of polymers, the majority of the field projects are using HPAM, probably because of economic considerations.

### IV. OBJECTIVES

The objective of this project was the laboratory development of mobility control agents that will function more effectively in surfactant/polymer flooding.

The purpose of Phase 1 of the project was to survey and assess application data in order to delineate problems encountered with currently available mobility control agents used in surfactant/polymer flooding processes.

Phase 2 of the project consisted of performing baseline laboratory screening tests on commercially available mobility control agents. Five different categories of tests were conducted: (1) basic viscosity and screen factor data, (2) Berea core testing, (3) temperature stability tests, (4) bacterial degradation, and (5) surfactant-polymer interactions. Much of this testing will not be new to those experienced in the use of polymers for mobility control. Frequently though, data in the open literature cannot be correlated because different test procedures have been employed. Thus the Phase 2 baseline data provided a convenient basis for comparison of different polymers at standardized sets of conditions.

These screening tests then served as a measure for judging new or modified polymers that were subsequently synthesized.

The third phase of the project consisted of polymer synthesis in order to determine the relationship between polymer structure and performance. Polymer structure-performance relationships were generated from a systematic structural modification of the presently available polymer types. These modified polymers were evaluated in tests similar to those used in the baseline screening; promising candidates were evaluated in more detail.

## V. SUMMARY OF PROGRESS

### A. PHASE 1: SURVEY AND ASSESSMENT OF APPLICATION DATA

The first phase of the project was an assessment of published information regarding problems encountered with polymers currently used for surfactant/polymer flooding. Based on a literature survey and input obtained from a questionnaire submitted to industry, academic, and government sources, inadequacies of the currently used mobility control materials were assessed. Details of this work were reported in our first annual report.<sup>1</sup>

Response from the questionnaire indicated that the most serious areas of concern with partially hydrolyzed polyacrylamides are: (1) shear degradation, (2) viscosity loss in brines, and (3) interaction with divalent ions. Of the deficiencies listed, the least serious was the requirement for filtration. The most serious deficiencies with xanthan gum polysaccharide are: (1) economics (high cost), (2) wellbore plugging, (3) microbial degradation, and (4) filtration requirements. The areas of least concern with xanthan gums are shear degradation and viscosity loss in brines.

### B. PHASE 2: BASELINE LABORATORY TESTS

Screening tests were designed using the information acquired in Phase 1. The areas of investigation included: (1) rheological properties, (2) temperature stability, (3) bacterial degradation, (4) surfactant-polymer interactions, and (5) flow tests in Berea sandstone cores. Tests were conducted on as many of the commercially available mobility control polymers as deemed necessary for this purpose. Results of these baseline tests are contained in our first two annual reports.<sup>1,2</sup>

## 1. Rheological Properties

A major feature of this project has been to test as many of the commercially available enhanced oil recovery (EOR) polymers as possible. These tests with uniform conditions for all the samples provide a basis for direct comparison of the various products and for evaluation of newly synthesized materials.

### a. Baseline Data

The tests have included measurements of solution viscosity and screen factors for 750 mg/L solutions in a series of standard brines. During the early stages of the project, solution viscosities were measured with a Brookfield viscometer, model LVT with a UL adaptor. For the remainder of the project, viscosities were determined with a Contraves LS-30 rheometer. Table 1 lists the commercial products tested. Several products that are not commercially available and many developmental polymers have also been tested. The standard brines are 0.01, 0.1, 0.3, 1.0 and 10.0% NaCl and 0.01, 0.1, 0.3, and 1.0% CaCl<sub>2</sub>. The pH of the brines was adjusted to 7.5 with NaOH prior to addition of polymer.

In addition, a great deal of rheological data has been collected on some of these polymers at varying polymer concentrations. A few have been tested in solutions of fixed ionic strength with varying amounts of NaCl and CaCl<sub>2</sub> or MgCl<sub>2</sub> (cf. section on the effect of divalent cations on solution viscosity), and some polymer solutions have been examined after being subjected to mechanical degradation. All of this amounts to a large volume of data.

In the interest of efficiently utilizing as much of this information as possible, a computerized storage and retrieval system has been established. Automated data handling provides easy access, allows automatic searches through the data base to facilitate comparisons, and is useful for other applications as well. Computer access makes it possible, for example, to find appropriate results for use in evaluating core flood experiments. The data may also be interpolated to approximate results at conditions other than those actually measured.

The information stored includes a complete description of the solution: identification of the polymer sample and its concentration, salts and their concentrations, and the temperature at which rheological properties were measured. Other data such as solution pH, solvent viscosity and solution age may have been included. The rheological data include the viscosity measurements at a series of shear rates between 0.01 and 128.5 sec<sup>-1</sup>, estimates of the zero-shear-rate viscosity and power-law parameters, and screen factors when measured.

In addition to the baseline testing, the intrinsic viscosities of several HPAM products have been obtained. One example of a commercial product studied in this project is Cyanatrol 950, an HPAM polymer in

emulsion form. Figure 3 shows the rheograms for concentrations of 150 to 2000 mg/L of the polymer on an "active polymer" basis in 3% NaCl. Zero-shear-rate viscosities were obtained from the measurements at lower shear rates where viscosity is not a function of shear rate, and these values were used in the intrinsic viscosity calculations. Plots of reduced viscosity and the ratio of the log of relative viscosity to concentration, each as a function of concentration, are shown in Figure 4. Extrapolation of the linear portions of both these lines gives estimates of the intrinsic viscosity of Cyanatrol 950 in 3% NaCl to be 32 dL/g. Using the Mark-Houwink constants published by Klein and Conrad,<sup>3</sup> an estimate of the viscosity average molecular weight is  $7.1 \times 10^6$ .

The principal contribution of this work is the direct comparison of commercially available polymers for a variety of salinity environments. Subsequent evaluation of interesting materials is then quickly accomplished. For example, the viscosities of a nonionic glucan polymer (trade name is JETCO Actigum CS-11-L) were found to be very high and almost insensitive to salinity increases. Scleroglucan is a polysaccharide produced from the fermentation of D-glucose by selected species of fungi known as *Sclerotium*.<sup>4</sup> The structure of this biopolymer is shown in Figure 5.<sup>5</sup> The viscosity results for a 2% NaCl solution, shown in Figure 6, are typical of rheograms at other salinities. In saline brines (>1% NaCl or CaCl<sub>2</sub>), the glucan polymer at the test condition of 750 mg/L generated the highest solution viscosities (Table 2) of any of the commercial polymers tested.<sup>1</sup> Thus, the glucan polymer was sufficiently interesting to be evaluated in subsequent core flooding experiments.

#### b. Effect of Divalent Cations on Viscosity of HPAM Solutions

This project has provided an empirical correlation<sup>6</sup> for HPAM solutions which allows prediction of solution viscosity from:

- the total ionic strength (I) of the solution
- the fraction contributed to the ionic strength by Ca<sup>2+</sup> or Mg<sup>2+</sup>
- the viscosity of the same concentration of polymer in an NaCl brine of the same ionic strength.

We investigated the relationship between the fraction of I due to Ca<sup>2+</sup> or Mg<sup>2+</sup> and the fraction of viscosity retained by the solution as compared to an equivalent NaCl brine. In the range of ionic strengths of usual interest and at 100 sec<sup>-1</sup>, we observed that this relationship was independent of the total ionic strength. Thus, a few measurements can be used to establish curves which predict viscosity for many intermediate values of ionic strength and concentration of divalent cations.

Viscosity measurements on another polymer, AMPS (sodium salt of 2-acrylamido-2-methylpropanesulfonic acid) homopolymer, have shown that the empirical correlation is not applicable with this material. The interaction between AMPS polymer and divalent cations appears to be more

complex than that observed for HPAM. The plots of viscosity retained (at  $95 \text{ sec}^{-1}$  and  $25^\circ\text{C}$ ) versus fraction of calcium ion show no definite trend with total ionic strength as shown in Figure 7. Other interpolation schemes will still allow some prediction of viscosities, but more measurements will be required than in the case of HPAM.

## 2. Thermal Stability

Long-term chemical stability at elevated temperatures is an extremely important consideration in evaluation of polymers for enhanced oil recovery. Processes are designed to operate over a period of years during which time the polymer solution will be required to withstand exposure to the reservoir temperature without substantial loss of solution viscosity. The purposes of this phase of the project have been to design a screening test which will predict the performance of polymers at elevated temperatures, to test representative samples of the currently available commercial polymers, and to test new products for comparison with those currently in use.

A number of factors have been considered in designing the long-term stability tests. These include temperature, dissolved oxygen, salinity, pH, and the effect of additives including formaldehyde and sodium dithionite (sodium hydrosulfite).

Initial tests conducted at  $25^\circ\text{C}$ ,  $43^\circ\text{C}$ ,  $66^\circ\text{C}$  and  $93^\circ\text{C}$  showed, predictably, that the rate of viscosity loss increased in a regular fashion with increasing temperature. Thus, the highest and lowest temperatures were chosen for comparison in the screening tests. The presence of oxygen accelerated the thermal degradation process at any of the elevated temperatures tested.<sup>1,2</sup>

## 3. Microbial Degradation

An important activity of many natural populations of bacteria is the degradation of organic polymeric compounds, a result of hydrolytic or phosphorolytic enzyme activity. Polymers used to increase viscosity of oilfield flood water, e.g., hydrolyzed polyacrylamides and xanthan gum polysaccharide, may be degraded by bacteria. Microbes may affect polymer solution viscosity either by direct enzymatic degradation and subsequent utilization of the monomeric units, indirect breakdown resulting from polymer-metabolic end products (e.g., organic acids and alcohols), or by co-metabolism, a process whereby recalcitrant molecules are altered by microbial enzyme activity, but not utilized by the microbes.

Many factors affect biodegradation, including the availability of oxygen or redox potential, pH, temperature, and inorganic nutrients (nitrogen, phosphorus, potassium, etc.). The conditions within an environment determine the types of bacteria which can occur and the way in which they function. Thus, bacterial degradation of polymers will be affected by the environment.

Two factors must be considered in the evaluation of stability of viscosity-building polymers in the field application -- the types of microorganisms capable of polymer degradation and the environmental parameters which affect the microbes.

The objective of the microbial degradation investigation of Phase 2 was to determine whether the polymers with potential use in oil recovery will remain biologically stable under field conditions.

#### a. Experimental Methods with Xanthan Gum

Details of the experimental work performed with xanthan gum are available in the second annual report.<sup>2</sup> Figure 8 shows typical results with XG solutions containing nutrient broth inoculated with B. megaterium and Ps. aeruginosa.

#### b. Results with Xanthan Gum

Following seven days of incubation under aerobic conditions, both microbes reduced the viscosity of the XG solution about 20%. In the absence of nutrient broth, the Ps. aeruginosa decreased viscosity 8.5% after 14 days incubation and the B. megaterium decreased the viscosity 24% (Table 3). No decrease was observed for the corresponding uninoculated control. The decrease of viscosity in the presence of these microbes and aerobic conditions was not unexpected.

Following seven days incubation, no decrease in viscosity occurred with the aerobic M. luteus and the anaerobic Desulfovibrio species (Table 3). Growth was noted by turbidity and sulfide production in the anaerobic culture of Desulfovibrio. The inability of Desulfovibrio to affect viscosity was anticipated, as these microbes require short-chain organic acids (e.g., lactic acid) for metabolism. It would be necessary for a different type of bacterium first to metabolize polymeric compounds to short chain organic acids and alcohols before the Desulfovibrio could grow.

#### c. Experimental Methods with Hydrolyzed Polyacrylamides

In this study, mixed-cultures, rather than "pure" mono-cultures, were used in order to simulate more closely field conditions in which many types of bacteria have potential for contamination of HPAM solutions. Lake water, used for preparation of viscous solutions at an oilfield site, or soil samples served as the mixed-culture inocula.

The microbes were grown in a medium containing: 2.5 g peptone, 50 mg calcium gluconate, 50 mg  $(\text{NH}_4)_2\text{SO}_4$ , 1.0 g NaCl, and 1 liter distilled water; initial pH was 7.0 to 7.5. Dow Pusher 700 was used at a concentration of 750 mg/L in the culture medium. Cultures were grown in 100 mL of this medium with constant shaking at 200 rpm for a period of 7 days at 25°C. Anaerobic cultures were incubated in "Gaspak" anaerobic systems.

The extent of microbial growth was determined by measurement of turbidity caused by the bacterial cells. A Klett-Summerson colorimeter was used with an optical filter of 420  $\mu\text{m}$  wavelength.

Thymol and formaldehyde were considered as inhibitors of microbial growth to provide control solutions. The extent of polymer degradation was determined by comparing viscosity of the control solution to viscosities of solutions with active microbial growth. Thymol was chosen for this study because it is possible for formaldehyde to cause cross-linking of acrylamide polymers in solution. A concentration of 0.004 g/dL thymol did not inhibit the development of the bacteria in the cultures. At 0.02 g/dL, thymol was an effective inhibitor of bacterial growth, so all subsequent control experiments were run using that concentration.

Viscosity was determined at 25°C by use of a variable shear-rate Contraves LS-30 rheometer. The viscosity values reported were obtained at a shear rate of 6  $\text{sec}^{-1}$ .

#### d. Results with Hydrolyzed Polyacrylamide

As shown in Table 4, the growth of the bacteria resulted in a substantial decrease in viscosity--from over 20  $\text{mPa}\cdot\text{s}$  for controls to between 6.0 and 7.2  $\text{mPa}\cdot\text{s}$ --a decrease of more than 60 percent. The growth of the bacteria also caused an increase in pH which may be due to the release of ammonia from the proteins (the peptone component) present in the medium. This is an ammonification process which is common to many types of soil and aquatic bacteria.

Some growth of the microbes occurred when the organic component (peptone) of the nutrient medium was omitted (Table 5). Under these conditions, the microorganisms must be able to use HPAM or some organic compounds found in the Pusher 700 solution to support their growth. Although the most active growth of the bacterial population resulted in a decrease of the solution viscosity to 6.2  $\text{mPa}\cdot\text{s}$ , a small population, growing at the expense of either HPAM or an associated organic compound, also resulted in a significant decrease in viscosity to 9.4  $\text{mPa}\cdot\text{s}$ . In very dilute nutrient conditions, microbial activity may decrease the viscosity of HPAM solutions. However, the greatest impact is from actively growing bacterial populations.

Anaerobic conditions limit the extent of microbial effect on viscosity (Table 6). This suggests that the viscosity of the HPAM

solution will be most subject to change upon preparation and storage in aerobic conditions, but it will be more stable after injection into an anaerobic reservoir. However, the microbial inoculum used may not have contained types of anaerobic bacteria capable of functioning in the reducing environment.

Microbial populations capable of decreasing the viscosity of HPAM solutions appear to be ubiquitous. They are found not only in water samples but in diverse soil samples as well (Table 7). These microbes are also common contaminants of the research laboratory environment, since microbial growth and reduction of solution viscosity will occur in culture flasks which have not been inoculated and do not contain thymol (Tables 4 and 7). The populations will vary with sources as noted in house plant soil. In this case, the pH of the inoculated medium decreased, as well as the solution viscosity. From the soils of a house plant, lawn, and an open lot, there was a decrease of viscosity in the culture medium containing thymol and presumably no bacterial activity. This suggests that the decrease in viscosity may be due in part to presence of metabolic by-products.

Mixed-cultures and two bacterial isolates were grown in the medium without HPAM. The cells were separated from the medium by centrifugation and the supernatant combined with HPAM in order to test the hypothesis that end-products of bacterial growth decrease viscosity of the HPAM solution. The results (Table 8) indicate that end-products of bacterial growth are not totally responsible for the decrease in viscosity. Only the products of one culture (mixed-culture 5) caused such a decline. Although the growing mixed-culture (3) decreased the viscosity by approximately 48 percent, the products of the growth of this culture had little influence on viscosity. It seems the active growth and metabolism of bacterial cultures is necessary to cause a decrease in viscosity of the HPAM solution.

It is apparent that there is a potential for microbial contamination of HPAM solutions resulting in a decrease in viscosity. The conditions which facilitate it are those which enhance microbial growth, e.g., aerobic environments and supply of nutrients. However, the microbes can grow at the expense of either HPAM or other compounds found in Dow Pusher 700 with a resultant loss in solution viscosity. The present study has not defined the mechanism by which microbial populations cause a decline in viscosity, but it appears that the process requires active growth and metabolism of a bacterial culture.

#### 4. Surfactant-Polymer Interaction

In a tertiary process in which a surfactant slug is followed by a polymer solution, either mixing or rapid propagation of polymer due to "inaccessible pore volume" or both may result in polymer invasion of the surfactant. The polymer can cause changes in the surfactant phase

behavior which may adversely affect the overall performance of the process.

Results of Pope et al<sup>8</sup> and preliminary tests in this laboratory<sup>2</sup> have indicated that this phenomenon exhibits very little polymer specificity. It did not seem appropriate, therefore, to conduct an extensive series of tests on the whole spectrum of polymer products of interest. Further investigation of the interaction between polymers and surfactants should be conducted both at a basic level and in the context of design of specific floods, but it was not considered appropriate to the aims of this project to pursue the subject further.

## 5. Flow Tests in Berea Sandstone Cores

Rheological tests on polymer solutions can provide a great deal of useful information, but there are important features of polymer flooding which can be measured only by flowing the solutions through rock samples. Phenomena such as plugging tendencies, changes in permeability to water after polymer injection, polymer retention in the reservoir, and polymer degradation during flow through a porous medium are measured in this project using cores of Berea sandstone. Details of the test procedures have been provided in previous reports.<sup>1,2</sup> A summary of the resistance factor and retention data obtained with the commercial products is given in Table 9.

Because of the favorable rheological behavior of Scleroglucan, flow tests were conducted with this polymer (Actigum CS-11-L). Results are also presented in Table 9. One area of concern regarding the use of this nonionic polymer is the extremely high level of polymer retention in the Berea core. Figures 9 and 10 compare the polymer concentrations in the core effluent for glucan to similar tests previously conducted with xanthan gum. The aqueous medium in both cases was 2% NaCl. The greater amount of retention for the glucan polymer is apparent. Similar trends were observed when the aqueous medium for the comparison was 0.1% NaCl. A high level of adsorption for the glucan polymer has been reported in the literature.<sup>9</sup>

Results from the core testing were also used as a basis to compare some of the newly synthesized polymers that will be discussed in the following section of this report.

## C. PHASE 3: POLYMER SYNTHESIS AND PRELIMINARY SCREENING

### 1. Objectives of Phase 3

The objectives of this phase of the laboratory work were two-fold. Our initial task was to obtain structure-utility correlations which would be helpful in designing and making mobility control agents that are more effective than the polymers currently used in surfactant/polymer flooding. Our second priority was to concentrate further synthesis and characterization efforts on polymers which, based on our preliminary screening data, appeared to be superior to present commercial materials.

### 2. Approach

The approach to meeting these objectives was to synthesize, characterize, and test polymers similar to poly(acrylamide-co-sodium acrylate), but with specific structural alterations. These polymers were tested under a uniform set of conditions in order to obtain systematic correlations of polymer performance with polymer structure. The areas of structural alteration investigated were:

-- substitution of alkyl or hydroxyalkyl groups for one of the amide hydrogen atoms on acrylamide residues

-- incorporation of groups expected to stiffen the polymer chain or investigation of polymer types with more rigid and/or hydrophobic backbones

-- variation of the relative amount of residues containing amide and carboxylate anion, thereby altering the charge-to-mass ratio of the polyanion, i.e., the degree of hydrolysis

-- preparation of similar materials by different synthetic methods to investigate the effects of sequencing of ionic charges

-- preliminary investigation into the effects of polymer association using cationic polymers and several commercial anionic materials.

#### a. Synthesis Approach

To attain these structural objectives, synthetic work was conducted in the following areas during the term of the project:

-- Copolymers of acrylamide and sodium acrylate with carboxyl contents significantly lower or higher than those of commercial copolymers were synthesized by free-radical copolymerization.

-- A series of partially hydrolyzed polyacrylamides were prepared with a range of carboxyl contents extending from far below to well beyond those of commercial HPAM polymers. These materials were synthesized from a common source homopolymer by identical procedures.

-- A-B-A block copolymers of acrylic acid and acrylamide were prepared.

-- Poly(methacrylamide-co-sodium methacrylates) with reduced viscosities high enough to be of interest were prepared both by copolymerization and by alkaline hydrolysis of the amide homopolymer.

-- Water-soluble, N-alkyl-substituted acrylamides and methacrylamides, and their respective copolymers with sodium acrylate and methacrylate were prepared by free-radical polymerization.

-- A number of N-hydroxyalkyl-substituted acrylamides and methacrylamides were prepared. Several of these polymers were subjected to alkaline hydrolysis.

-- Partially imidized polyacrylamides and polymethacrylamides were prepared by acid-catalyzed imidization and were solubilized by partial alkaline hydrolysis. Their performance in the preliminary testing merited a more exhaustive effort in further synthesis and characterization. Other polymers of this type containing maleimide, N-substituted maleimide, maleic anhydride, dimethacrylamide, and methacrylic anhydride were also synthesized.

-- Several quaternary ammonium salts based on DMAPMA (dimethylamino-propylmethacrylamide) were prepared and copolymerized with acrylamide. These materials were blended in various proportions with HPAM and poly(acrylamide-co-sodium AMPS) to test the viscosity-building effects of polymer association.

#### b. Test Procedures for Preliminary Screening

At the beginning of the project, it was apparent that the hundreds of polymer samples we wished to test could not be subjected to extensive rheological or core tests. Consequently, we designed and tested a simple procedure that would permit the rapid evaluation of a large number of samples. This procedure provided a data base with known polymer structures to permit the evaluation of new or modified structures. Results of these tests were used to correlate the performance of the polymer to its composition. These structure-utility correlations could then be used to design improved polymers for EOR applications. Naturally, the preferred mobility control polymer should increase the viscosity of water at low polymer concentrations. Phase I of the project documented

that the primary drawbacks with the widely used HPAM polymers are the loss of viscosity-building properties as a result of mechanical degradation of the polymer or an increase in salinity of the aqueous solution. Therefore, the preliminary screening test centered on these two very important characteristics -- viscosity retention in brine and irreversible shear degradation.

The various polymers were dissolved in 0.01% and 2% NaCl solutions and capillary flow times were measured at 25°C using a Cannon-Ubbelohde dilution-type capillary viscometer. This simple screening procedure<sup>10</sup> provided data on the viscosity loss in brine by comparing the ratios of the reduced viscosity in 2% NaCl to that in 0.01% NaCl. Shear degradation was estimated by comparing reduced viscosity in each brine before and after passage through a screen-shear apparatus.<sup>10</sup> Results of extensive testing obtained with this screening procedure are discussed elsewhere.<sup>1,2,10</sup>

For carboxyl-containing polymers, the charge-to-mass ratio or degree of hydrolysis was determined by procedures we have previously discussed.<sup>2,11</sup> In addition, a procedure was developed for direct analyses of the percentages of amide and imide groups in the imidized polymers.<sup>12</sup>

### 3. Screening of Various Structures and Commercial Polymers

The preliminary screening results for several polymer structures are given in Table 10. These results agree with known behavior: linear polymers like polyethylene oxide are very sensitive to mechanical degradation whereas the cellulosic polymers are not. Solutions of nonionic polymers exhibit little or no sensitivity to NaCl concentration, but many solutions of ionic polymers lose more than 90% of their specific viscosity when NaCl concentration is increased from 0.01% to 2%. Since the xanthan gum polymer used in mobility control does have a low ionic charge, some loss in solution viscosity occurs as the salinity is increased from 0.01% NaCl to 2% NaCl, but the loss is not nearly as severe as with HPAM. The generally accepted rod-like structure for xanthan gum could also account for some of these observed effects.

Results obtained from similar tests performed with many of the commercially available HPAM polymers are shown in Table 11, and Figures 11 and 12. If the reduced viscosity in 2% NaCl is assumed to be some measure of the polymer molecular weight, the results show that the extent of mechanical degradation increases as molecular weight increases (Table 11 and Figure 11). Additionally, as the anionic charge increases for polymers of similar molecular weights, increased sensitivity to brine is observed (Table 11). Both of these observations are well known and merely lend credibility to the preliminary test procedure. For polymers of similar ionic charge, the molecular weight of the polymer seems to have little effect on the viscosity retained when salinity is increased (Figure 12). When comparing HPAM polymers of similar molecular weights and degree

of ionic charge, the polymers made by copolymerization seem to be slightly less sensitive to salinity increase as shown in Table 11--this difference will be addressed later in the report.

Because of the differences in manufacturing methods employed with the commercial HPAM products and the somewhat limited range of hydrolysis for such materials, the bulk of the structure-activity correlations were obtained with polymers that were synthesized or modified in our laboratory. Much of the work involved acrylamide-type or modified acrylamide polymers.

#### 4. Structure-Utility Relationships

##### a. Molecular Weight

Molecular weight and molecular weight distribution affect performance of mobility control polymers -- especially shear degradation. The use of size separation to characterize the molecular weight distribution of HPAM or other high molecular weight products for EOR still presents problems. Commercially packed columns do not have large enough pores to separate the polymers of interest. In addition, some of the commercial GPC columns develop voids when HPAM solutions are passed through them.

The most promising approach seems to be the system developed by Omorodion et al<sup>13</sup> for nonionic polyacrylamides. This involves separation on columns of controlled-porosity glass using a mobile phase containing a surfactant. Tables 12 and 13 contain specifics of the system used in our study. The problem of adsorption of polymer on the column packing can be solved by repeated injections of the HPAM solutions. Other problems remain, however.

Two of these are illustrated in Figure 13. This figure shows two superimposed chromatograms, plotted as differential refractive index detector response versus retention volume for runs at 1 and 3 mL/min flow rates. The sample in both cases is a 1500 mg/L solution of Dow Pusher 700 dissolved in the mobile phase (Table 13). The peaks to the right of the diagram are totally permeating pulses because the polymer is ionic and its exclusion from some of the pore space causes mobile ions to migrate into these pores to maintain a balance of charges. No similar totally permeating peak is observed in the chromatograms of unhydrolyzed polyacrylamide. The fact that the two totally permeating peaks coincide means that the flow rates and times used to calculate retention volumes are accurate. The polymer peaks which elute from 125 to 250 mL are quite different in these two runs. The 3 mL/min peak elutes later and thus must consist of smaller molecules which are able to penetrate a larger volume of the pore space. Since the only difference in run conditions was the flow rate, it appears that the larger molecules are degraded to smaller sizes at the higher flow rate. Hence, the molecular weight distribution may depend on the conditions of the test. We cannot yet be certain that

the integrity of the sample is maintained at 1 mL/min. Further decrease in flow rate would not be expected to produce significant changes in the chromatogram because the bulk of the sample is already excluded from all of the pore space and elutes at the total exclusion volume as indicated by the steep rise at about 150 mL. This brings up a second problem: even the 3000 Å controlled-porosity glass does not have large enough pores to affect a separation.

Addition of a non-solvent, methanol, should decrease the polymer size. Figure 14 shows the results obtained with varying amounts of methanol. Addition of 5 and 10% by volume produced small, but possibly significant, changes in the chromatogram; addition of 20% methanol resulted in more drastic changes, but reproducibility was adversely affected.

Loss of column efficiency and inadequate reproducibility remain serious difficulties. The present system requires lengthy run times which may have an adverse effect on reproducibility and limits the number of samples which can be processed. Finally, a reliable standard will be required before more than qualitative results can be obtained.

Lack of a suitable means to determine rapidly the molecular weights of large macromolecules limits the ability to assess the effect of this variable. Thus, we are forced to rely on a more indirect measure and regard the reduced viscosity in brine, such as 2% or 3% NaCl, as some index of the viscosity-average molecular weight. Screen factors, when measured, can be used as an indication of the presence of high molecular weight fractions for similar HPAM-type polymers.<sup>14</sup>

#### b. Charge-to-Mass Ratio of Polyanion

For many of the polymer types studied, the copolymer composition has been varied in order to obtain copolymers whose anions have varying charge-to-mass ratios or degrees of hydrolysis. This structural variation is very important when considering viscosity loss in brine.

In order to secure HPAM polymers of varying carboxyl contents which had been prepared from a single source polymer, several portions of 5-6 million molecular weight polyacrylamide from Polysciences, Inc. were partially hydrolyzed with NaOH under controlled conditions. The technique of Meister et al<sup>15</sup> was employed. These polymers permitted the investigation of the effects of carboxyl content on viscosity retention in brine and shear stability without the added variable of molecular weight.

These results (Table 14) clearly show that increasing the degree of hydrolysis makes the polymer more sensitive to the increase in salinity but decreases the susceptibility to mechanical degradation. Both effects appear to reach a plateau at about 30% sodium acrylate content.

### c. Effects of Sequencing of the Ionic Charges

To study the effect of the sequencing of ionic charges on the polymer backbone, several block copolymers were synthesized. Block copolymers are macromolecules composed of chemically dissimilar, terminally-connected segments whose sequential arrangements can vary from A-B to A-B-A to multiblock  $-(A-B)_n-$  systems. In this study, block copolymers of acrylamide and acrylic acid were prepared by aqueous solution polymerization using a polyfunctional azoamidino compound as initiator.<sup>16</sup> Synthesis details are given in Table 15. Acrylamide and polyfunctional azoamidino catalyst were dissolved in distilled, deaerated water. The mixture was heated at 60° for 5 minutes under a stream of nitrogen with constant stirring. The polymerization reaction was allowed to proceed at room temperature for 1-7 days to obtain a viscous solution of acrylamide homopolymer with reactive end groups. Block polymers then were made using the following procedures.

Procedure 1: Acrylic acid was added into the viscous solution obtained in the first step. The mixture was heated at 60°C for 5 min., and the reaction was terminated after keeping the mixture at room temperature for 1-7 days. The copolymer was then precipitated in a methanol-acetone mixed solvent.

Procedure 2: The acrylamide homopolymer obtained as described above was isolated by precipitation with methanol, dried and powdered. This polymer was redissolved in water to give a homogeneous solution. To this solution, acrylic acid was added. The mixture was heated at 60°C for 5 min. and the reaction was allowed to proceed at room temperature for various times (Table 15). The block copolymer was isolated by precipitation with a methanol-acetone mixed solvent.

Solutions of the acrylamide-acrylic acid block polymers show better brine resistance than solutions of random copolymers prepared from these monomers (Table 16). When the carboxyl content is increased, these block copolymers are not as adversely affected by the salinity increase as are comparable HPAM polymers prepared by post-hydrolysis or by copolymerization (Figure 15). Because the number of block copolymers with high molecular weights were somewhat limited, the effect of sequencing on shear stability is not definitive (Figure 16).

### d. Strength of Acid Moieties

There is no obvious correlation between a copolymer's  $pK_a$  at 100% neutralization and the viscosity retained when salinity is increased from 0.01% to 2% NaCl. This indicates that productive results would not be expected from varying the acid strength of comonomer residues in order to improve viscosity retention in NaCl brines. In brines containing hardness ions, however, the more acidic comonomer residues may show improved viscosity retention.

### e. N-Alkyl Substitution

Two possible approaches to improve HPAM-type polymers are: (a) substituting alkyl groups for one or both of the hydrogens on the amide nitrogen, and (b) stiffening the polymer backbone. The second method will be discussed in a later section of this report.

Hester, et al<sup>17</sup> have synthesized N,N-dimethyl and N,N-diethyl-acrylamide polymers for EOR evaluation, but surprisingly there is not much work reported in the literature on the synthesis and testing of N-mono-substituted acrylamide polymers for this application. Our investigation consisted of the synthesis and evaluation of two homopolymers and four copolymers for possible use in EOR. The polymers studied were the following:

- Poly(N-methylacrylamide)
- Poly(N-isopropylacrylamide)
- Poly(N-methylacrylamide-co-sodium acrylate)
- Poly(N-isopropylacrylamide-co-sodium acrylate)
- Poly(N-n-butylacrylamide-co-sodium acrylate)
- Poly(N-t-butylacrylamide-co-sodium acrylate)

### (1) Experimental Procedure

The homopolymers and copolymers were prepared by aqueous solution polymerization, using potassium persulfate ( $K_2S_2O_8$ )/sodium metabisulfite ( $Na_2S_2O_5$ ) as initiator/activator. Commercial monomers were purified either by distillation under reduced pressure or by recrystallization. The reactions were carried out in a nitrogen atmosphere and the water used as the polymerization solvent was deaerated. Polymeric products were isolated and purified by reprecipitation and washing.

#### (a) Synthesis of Homopolymers

The experimental procedure followed to prepare these polymers was a simple one. A weighed amount of monomer was dissolved in an appropriate amount of distilled, deaerated water in a 50 mL serum bottle. The bottle was flushed and sealed under a nitrogen stream, and the initiator solution was then introduced into the bottle by use of a syringe. As the reaction progressed, the solution became more and more viscous. At the appropriate stage, the reaction was terminated by pouring the viscous solution into a constantly stirred non-solvent. When copolymers were made, the polymerization reactions were terminated at conversions of 30% or less, so that the copolymers isolated would be relatively uniform in composition.

In our homopolymer synthesis work, we found that lower reaction temperatures, lower percentages of initiator and higher concentrations of monomer in the aqueous solutions helped produce polymers of higher viscosity. In general, high purity monomers were necessary to obtain high molecular weight polymers. Use of an activator did catalyze the

polymerization reaction effectively but yielded lower viscosity polymers. The polymers usually were precipitated in methanol, ethanol or acetone. However, the precipitation of poly(N-isopropylacrylamide) presented problems. Methanol, ethanol, dioxane, tetrahydrofuran, dimethylsulfoxide and acetone were tried; all were either ineffective or very poor precipitants. The poly(N-isopropylacrylamide) was precipitated successfully by warming the aqueous solution to 80°C, or by removing the water azeotropically with toluene.

#### (b) Synthesis of Copolymers

Copolymers were prepared from N-substituted acrylamides and sodium acrylate or acrylic acid. Efforts were made to establish optimum reaction conditions by varying the proportions of monomer:initiator:activator (MIA) and by varying the aqueous solution concentration, pH, and temperature.

The reactions of poly(N-methylacrylamide-co-sodium acrylate) were first conducted at "high" MIA proportions of 100:40:4 and then were progressively changed to a ratio of 100:0.1:0.05. It was observed that very high and very low MIA proportions yielded only low viscosity copolymers. MIA proportions of 100:0.5:0 (no activator) yielded the highest viscosity copolymers. For copolymers of nearly the same acid content, increases in the MIA proportions caused marginal decreases in the reduced viscosity of the copolymers in 0.01% NaCl brine. The optimum temperature range for copolymerization reactions was 15-25°C. For the N-methylacrylamide copolymer system, MIA proportions representing initiator fractions lower than 100:0.5:0 generated low viscosity polymers. However, for the N-isopropylacrylamide copolymer system, MIA proportions representing lower initiator fractions led to copolymers displaying higher values of reduced viscosity.

Only a few copolymers of N-n-butylacrylamide or N-t-butylacrylamide with sodium acrylate were prepared since these butyl-substituted monomers are insoluble in water. In the preparation of poly(N-n-butylacrylamide-co-sodium acrylate), sodium dodecyl sulfate (lauryl sulfate) was added to the reaction mixture as an emulsifier. The optimum MIA proportions were 100:0.1:0.05. In two emulsion copolymerizations with N-n-butylacrylamide, the amounts of sodium acrylate added to the monomer feed solution were the equivalent of 50 and 60% acrylic acid. However, the copolymers isolated at low conversions contained over 75% acrylic acid.

N-t-butylacrylamide was found to be soluble in dimethylformamide-water. Therefore, N-t-butylacrylamide was copolymerized in that mixed solvent system by following the usual redox recipe.

Seven samples of poly(N-methylacrylamide-co-sodium acrylate) were prepared by hydrolysis of homopolymers in basic aqueous solutions and were precipitated using the methods discussed above. The sodium salt form of the resulting copolymers contained weight percents of sodium acrylate residues ranging from 8.4% to 41.5%. For hydrolysis of poly(N-methylacrylamide), drastic conditions such as high temperature,

excess sodium hydroxide and extended heating periods were necessary to achieve the desired degree of hydrolysis (Table 17). In contrast, hydrolyzed polyacrylamide could be prepared by using the stoichiometric amount of sodium hydroxide needed to hydrolyze the desired fraction of amide units. The sodium hydroxide was added to an aqueous one percent solution of polyacrylamide and the solution was maintained at 60°C for 2 hours.<sup>15</sup>

## (2) Discussion

### (a) Effect of N-Substitution

Although the differences involving N-methyl substituted versus unsubstituted copolymers are small, poly(N-methylacrylamide-co-sodium acrylates) tend to retain a slightly larger fraction of their specific viscosity in 2% NaCl than do the unsubstituted analogs. However, the N-methyl substitution seems to make the copolymers more sensitive to shear degradation (Tables 18 and 19). When compared with analogous unsubstituted copolymers, poly(N-isopropylacrylamide-co-sodium acrylate) samples have exhibited slight improvements in resistance to both NaCl and shear (Tables 19 and 20).

### (b) Charge-to-Mass Ratio

The relationship between degree of hydrolysis and viscosity loss in brine for the N-substituted analogs follows the general trend commonly observed with HPAM-type polymers (Tables 18-20).

### (c) Effects of Possible Sequence Variation

Variations in the structural details of copolymer chains may result when different synthetic methods are used in the preparation of the copolymers. Most of the N-alkyl substituted copolymers were synthesized by copolymerization, i.e., using two monomers, but some poly(N-methylacrylamide-co-sodium acrylate) samples were synthesized by partial hydrolysis of poly(N-methylacrylamide) (Table 17). Although both synthetic methods should produce essentially random copolymers, those synthesized by one method may have an increased number of like-monomer sequences (more nearly like block copolymers), and those prepared by the other method may be more nearly like alternating copolymers. As with HPAM, poly(N-methylacrylamides) synthesized by partial hydrolysis tend to lose a somewhat larger fraction of their viscosity when subjected to increased NaCl than do samples of the same polymer type synthesized by copolymerization (Table 18).

Poly(N-alkylacrylamide-co-sodium acrylate) samples with the alkyl substituent being either a methyl or isopropyl group have shown a small improvement in viscosity retention in 2% NaCl when compared with

poly(acrylamide-co-sodium acrylate) samples. This improvement may be the result of the alkyl substitution or a variation in the sequencing of the ionic changes on the polymer chain.

Poly(N-n-butylacrylamide-co-sodium acrylate) samples of sufficiently high viscosity may exhibit a small improvement in viscosity retention in NaCl brine, compared with what would be expected from other copolymers having similar weight percent sodium acrylate residues, but a direct comparison is not possible for two reasons. Because of the water insolubility of N-n-butylacrylamide, these samples were synthesized by an emulsion polymerization method, rather than the solution polymerization method used for other polymer types. Also, all of these poly(N-n-butylacrylamide-co-sodium acrylate) samples have higher percentages of sodium acrylate residues than most of the other samples being compared.

#### (d) Berea Core Tests

A few flow tests in Berea core were conducted to compare the effect of N-alkyl substitution on adsorption (or retention) of acrylamide polymers. These tests showed some interesting results. In the initial tests, homopolymers of acrylamide and N-methylacrylamide of nearly equal viscosity were utilized (Table 21 and Figure 17). The data from these tests indicate that the N-methyl substitution of acrylamide polymers reduces the amount of polymer retention in the Berea core sample. This suggests either that the poly(N-methylacrylamide) is adsorbed less on the rock surfaces than is polyacrylamide or that there is less mechanical entrapment of the N-substituted polymer.

Similar tests (Table 21 and Figure 18) were also performed on the following copolymers:

- Poly(N-methylacrylamide-co-sodium acrylate)
- Poly(N-isopropylacrylamide-co-sodium acrylate)
- Poly(acrylamide-co-sodium acrylate)

Several tentative hypotheses can explain the behavior observed. First, consider the data of Figure 17, which compares acrylamide and N-methylacrylamide homopolymers. Because of the presence of a methyl group on the amide nitrogen, the poly(N-methylacrylamide) polymer molecules may be slightly more basic than the analogous unsubstituted polymer molecules. As a result, rock surfaces which are generally basic in nature, may attract the N-substituted polymer molecules less than the unsubstituted polymer molecules. This attraction might involve the hydrogens of the amide groups acting as hydrogen-bond donors to the chemically combined oxygens at the rock surface. If so, the decreased number of amide hydrogens and the steric bulk of the methyl groups of the N-substituted polymer might also play a role in the reduced attraction. It is likely that the polyacrylamide polymer chains in solution extend more than poly(N-methylacrylamide) chains, due to better solvation by

water of the more polar polyacrylamide. This chain extension increases the hydrodynamic size of the unsubstituted polymer molecules, which may cause more mechanical entrapment of the polyacrylamide during flow.

Secondly, the decreased retention of poly(N-methylacrylamide-co-sodium acrylate) compared to poly(acrylamide-co-sodium acrylate) shown in Figure 18 can be explained by the phenomena discussed above. However, the increased retention of poly(N-isopropylacrylamide-co-sodium acrylate) indicates that another factor besides those mentioned previously becomes important when the size of the N-alkyl substituent is larger than methyl.

Acrylamide, N-methylacrylamide, N-ethylacrylamide, N-isopropylacrylamide and their homopolymers and copolymers with acrylic acid are soluble in cold water whereas the homopolymers of N-n-butylacrylamide and N-t-butylacrylamide are not. Since poly(N-isopropylacrylamide) is insoluble in hot water, it appears that the isopropyl substituent is the limiting size of alkyl group for solubility of N-substituted acrylamide homopolymers in cold water. Thus, the decreased hydrophilicity of poly(N-isopropylacrylamide-co-sodium acrylate) may be a very important factor in its behavior in the core tests. The poly(N-isopropylacrylamide-co-sodium acrylate) molecules would have a strong tendency to adsorb on the rock surfaces owing simply to their poor solvation by water. This factor then would dominate and cause the poly(N-isopropylacrylamide-co-sodium acrylate) to adsorb more on the Berea core than poly(N-methylacrylamide-co-sodium acrylate) or poly(acrylamide-co-sodium acrylate).

#### f. Chain Stiffening

One possible approach to improving HPAM polymers is to stiffen the more flexible carbon backbone of acrylamide-type polymers. Theoretically, a polymer chain stiffened by steric hindrance and/or internal rigidity should increase the hydrodynamic size of randomly coiled macromolecules. As a consequence, a rigid molecule should, when compared with an otherwise similar non-stiffened molecule, generate a greater viscosity in brines and hard waters. Chain stiffening, however, might have an adverse effect on polymer solubility.

#### (1) Methacrylamide Polymers

Interest in the methacrylamide polymer system was initially confined to its structural relationship to polyacrylamide. The presence of a methyl-stiffened backbone with its concomitant increase in polymer hydrophobicity and chain inflexibility made polymethacrylamide an obvious choice for comparative studies leading to structure/behavior correlations. Similar chemistries made possible the preparation of parallel series of N-substituted acrylamide and methacrylamide monomers. The recognized propensity of methacrylamide polymers to form stable intramolecular imide rings also made it an attractive subject for study.<sup>18-20</sup> Unfortunately, the high degree of chain transfer to the methacrylamide monomer (which is

about two orders of magnitude higher than that of acrylamide at 60°C with persulfate initiation)<sup>21</sup> severely limited the molecular weight of any homopolymer which could easily be prepared.

#### (a) Experimental Methods

The methods generally used to produce high molecular weight polyacrylamides yielded polymethacrylamides which developed very little viscosity in aqueous solution in comparison with 5 to 6 million nominal molecular weight polyacrylamide purchased from Polysciences, Inc. (Cat. #2806). Attempts to improve molecular weight by reducing initiator and activator concentrations resulted in water-insoluble polymers. When these materials were hydrolyzed, they generated solution viscosities which were very low compared with commercial HPAM. Using no activator and systematically decreasing initiator concentration and temperature raised viscosities of the hydrolyzed products in 0.01% NaCl to only about 20 percent of the desired reduced viscosity level of 80 dL/g. The cross-linking agent, N,N'-methylenebisacrylamide (MBA) was added to several low initiator, room temperature polymerizations. After hydrolysis, the best of these materials demonstrated viscosities comparable to those of commercial HPAM. Table 22 details the preparative procedures for several of the methacrylamide homopolymers.

#### (b) Discussion

These polymethacrylamides were found to be soluble in strong acids and saturated, aqueous solutions of  $ZnCl_2$  and  $FeCl_3$  at room temperature. All but the samples made with high MBA levels also dissolved in 5 M urea, ethylene and triethylene glycol, glycerol, and 200 and 400 mw poly(ethylene glycol). In some cases, 2 to 4 days of stirring at 80°C were necessary for complete dissolution.

Either 5 M aqueous urea or ethylene glycol were utilized as effective solvents for a direct comparison of these polymethacrylamides with 5 to 6 million molecular weight polyacrylamide. Table 23 contains the viscosity data as measured in ethylene glycol and Table 24 lists the 5 M urea results. Assuming there are no drastic differences in the conformations of the two polymer types in ethylene glycol or aqueous urea, these observations demonstrate the large contribution of chain extension to the viscosity of the partially hydrolyzed polymethacrylamides arising from the presence of the backbone-stiffening methyl groups.

Viscosities in the range of commercial HPAM were achieved, and the point of diminishing returns with respect to viscosity enhancement via MBA was established. Therefore, no further attempts utilizing other reagents or different procedures were made to increase polymethacrylamide molecular weights. Our investigation then concentrated on hydrolysis of these materials for comparison with HPAM.

In dilute base at room temperature, about 30 percent of the amide

residues of polymethacrylamide are rapidly hydrolyzed. Boiling the polymer in a strong caustic solution failed to raise the degree of hydrolysis above 68 weight percent sodium methacrylate. This agrees with the observations of such early investigators of the methacrylamide system as Arcus,<sup>22</sup> Pinner,<sup>23</sup> and Moens and Smets<sup>19</sup> concerning the incompleteness of the alkaline hydrolysis of polymethacrylamide. It is assumed that this phenomenon is due to electrostatic repulsion of carboxylate groups which increase with continued hydrolysis. Table 25 contains screening data for a number of these polymers. In Table 26, the behavior of several of these samples is compared with that of similar HPAM polymers.

Poly(methacrylamide-co-sodium methacrylates) were also prepared via aqueous, persulfate-initiated copolymerizations of methacrylamide with both methacrylic acid and sodium methacrylate. Samples of the former were insoluble in distilled water, but dissolved slowly if the pH was increased above 9. Some of the measured carboxyl content was doubtless the result of alkaline hydrolysis of amide groups. The viscosities of all copolymers were significantly lower than those of the hydrolyzed samples. Viscosity retentions in 2 percent NaCl, however, were about twice as large. This is consistent with behavior previously observed with HPAM and poly(acrylamide-co-sodium acrylates) prepared via copolymerization. Copolymerization data are contained in Table 27, and these materials are compared with similar poly(acrylamide-co-sodium acrylates) in Table 28.

These data show that poly(methacrylamide-co-sodium methacrylates), regardless of the source of their sodium methacrylate groups, are marginally inferior to the majority of the commercial HPAM mobility control agents tested in terms of both brine and shear stability. In view of the sterically-induced greater polymer-chain extension and the probable decreased solvation in solution, the slightly increased sensitivity to shear is not surprising. The salt sensitivity in brine indicates that the polymer-chain stiffening due to methyl groups is insufficient to overcome the hydrophobicity which results from the same groups. Since the viscosity data in ethylene glycol and urea indicate that the unhydrolyzed polymers are of low molecular weight, poly(methacrylamide-co-sodium methacrylate) appears to be a much more efficient viscosity builder, mer-unit for mer-unit, than HPAM in solutions of low ionic strength.

Several N-substituted methacrylamide polymers and copolymers were prepared. They served as a check against similar acrylamides and provided an opportunity to investigate whether pendant hydrophobic or hydrophilic groups could modify the steric and hydrophobic effects of the methylated backbone.

### (c) Effects of Hydrophobic Substitution

Structures of N-methyl and N-ethylmethacrylamide (purchased from Polysciences and Pfaltz and Bauer, respectively) are depicted in Figure 19. These monomers were polymerized in aqueous media under a dry nitrogen atmosphere with persulfate catalyst and without a cross-linking agent. No attempts were made to proceed further with this series of aliphatic

substituents since the N-ethyl monomer exhibited sufficient water immiscibility to necessitate the addition of methanol to the polymerization mixtures. The molecular weights of these homopolymers were apparently quite low. Poly(N-methylmethacrylamide) was water-soluble; but whether this is due to low molecular weight or a lessening of the overall hydrophobicity is unknown. All the N-ethyl homopolymers were insoluble in water.

As expected, alkaline hydrolysis of these polymers was quite slow, and drastic conditions were necessary to achieve 35 weight percent carboxyl contents with the N-methyl materials. Several attempts failed to produce more than 20 percent hydrolysis in the N-ethyl polymers. Reduced viscosities were low, but retentions in brine were quite good, giving some confirmation to our previous findings with N-methyl and N-isopropylacrylamide/sodium acrylate copolymers. The screening data for these samples are contained in Table 29.

Work with partially hydrolyzed polymethacrylamides has demonstrated the large degree of molecular extension which can arise from steric chain stiffening due to the presence of backbone methyl groups. The brine stability of these polymers is quite poor, however, probably due to increased hydrophobicity rather than increased extension of the molecule.

## (2) Effects of Hydrophilic Side Chains

Polyvinylcarboxamides containing additional hydrophilic groups were investigated to determine whether increased hydration would act as a protective sheath against shear stress and impart some degree of rigidity against collapse in brine.

Monomers were prepared by the condensation of the appropriate amino alcohol and unsaturated acid chloride in acetonitrile. The synthesis was a modification of the method of Jedlinski and Paprotny.<sup>24</sup> Cross-linked poly(4-vinylpyridine) was used to advantage as the HCl-acceptor. Liquid products were isolated via solvent evaporation. Solids were recrystallized from acetonitrile. Structures are contained in Figures 20 through 22.

All homo- and copolymers of this series appeared to be highly cross-linked, since they swelled but were insoluble in cold water. The acrylamide polymers dissolved upon prolonged boiling in distilled water. The methacrylamides polymers swelled somewhat on boiling, but alkaline hydrolysis was necessary to solubilize them. Polymerization conditions are described in Tables 30 and 31.

Although the screening data is somewhat limited (Tables 32 and 33), it appears that pendant hydrophilic moieties may improve the brine stability and shear resistance. Additional work with hydrolyzed versions of some of these polymers is planned.

### (3) Ring-Containing Polymers

To increase the level and vary the source of chain rigidity, closed rings were introduced into the backbones of water-soluble polymers. Due to their relative ease of generation, five- and six-membered anhydrides and imides were chosen as the cyclic groups to be used in exploring the effects of this structural modification.

Our studies involving cyclic anhydrides can be described rather briefly. For the most part, the anhydride groups were extremely susceptible to hydrolysis.

Attempts to generate acrylamide-type polymers containing five-membered anhydride rings by copolymerizing maleic anhydride with acrylamide and acrylic acid (as represented in Figure 23) failed to produce polymers with useful viscosities. Several maleic anhydride/styrene copolymers (Figure 24) were then prepared. Although viscosities were somewhat improved and the polymers were water-soluble in the presence of dilute ammonia, the anhydride rings of these samples appeared to be rapidly hydrolyzed during the course of dissolution. There was no improvement in brine stability above that seen with HPAM polymers.

The copolymerization of methacrylic anhydride with methacrylic acid (as represented in Figure 25) was utilized to prepare polymers containing six-membered anhydride rings. The acrylamide analog was not prepared due to the expected hydrolysis of the anhydride ring.

The poly(methacrylic anhydride-co-sodium methacrylates) were water-soluble, low viscosity materials which, as can be seen in Table 34, did demonstrate somewhat better viscosity retention in brine than comparable partially hydrolyzed polymethacrylamides. The addition of even small amounts of base to the anhydride polymers resulted in ring-opening hydrolysis. As a result, the enhanced viscosity in 2% NaCl was lost even though the initial viscosity in 0.01% NaCl was slightly higher.

Although the behavior of the methacrylic anhydride polymers seemed to offer some confirmation of our hypothesis, the overall results using anhydrides to stiffen polymer backbones were disappointing. Viscosities and probable molecular weights were uniformly low, which limited the validity of most comparisons with other polymer types. The anhydride group also proved to be extremely labile in aqueous solution.

The next attempt to produce a more stable ring structure consisted of the copolymerization of maleimide with acrylamide and acrylic acid (Figure 26) to produce polymers containing five-membered imide rings. Unfortunately, these imides also proved susceptible to ring-opening hydrolysis in the presence of the alkali which was needed to solubilize the polymers. In order to further stabilize the maleimide group, N-methyl and N-phenyl maleimide monomers were prepared and similarly copolymerized. The N-methyl substitution failed to retard hydrolysis of the imide rings to an appreciable extent. N-phenyl maleimide appeared to resist alkaline hydrolysis quite well but copolymerized poorly with unsaturated amides and

acids. None of the polymers containing maleimide or its derivatives displayed any increased viscosity retention in brine after hydrolysis.

The most successful method found for the introduction of imide rings into the chains of water-soluble polymers was acid-catalyzed imidization (Figure 27). The formation of six-membered imide rings by polyvinylcarboxamides in the presence of mineral acids has been widely reported.<sup>18-20</sup> The procedure is considerably simpler than the attempted copolymerizations and better control is possible. It also has the attractive feature of using previously prepared homopolymers for which solution viscosity behavior before and after hydrolysis has already been investigated. Since this reaction has been looked upon as a curiosity or a nuisance, several aspects of acid-catalyzed imidization remain poorly defined. Little has been done on quantifying the amount of imidization resulting from various reaction conditions or on ascertaining the incidence of intra- versus intermolecular imidization which might occur. Nor have the stabilities of these imides been examined previously.

The acrylamide homopolymer used in these studies was 5 to 6 million (nominal) molecular weight material purchased from Polysciences, Inc. The polymethacrylamides were prepared in our laboratory by procedures which have already been described. It should be noted, however, that to produce the highest molecular weight methacrylamide homopolymers, the cross-linking agent N,N'-methylenebisacrylamide was utilized. The imidization medium of choice was reagent grade hydrochloric acid, diluted to 6 N. Less concentrated HCl and several other acids were also used, and all appeared to induce imidization.

Both polymers proved soluble in 6 N HCl, although the solutions were somewhat cloudy. With 2 to 4 percent solids in the reaction mixtures, 36 to 60 hours were generally necessary for complete dissolution of the polymers. Several additional days of stirring were always allowed after dissolution was complete. Appreciable amounts of imide were detected in samples removed from the acidified mixtures 96 to 240 hours after the addition of the polymer.

In addition to the dissolution and stirring phases, usual practice entailed heating the samples at near boiling for periods of up to one week. Data which show imide formation versus time of heating for the initial portion of this period are in Figure 28. The imidized polymers always precipitated from the acid medium within 8 days. Infrared and analytical studies showed that, up to a point, this increase in temperature resulted in further imidization. Prolonged heating, however, induced the loss of imide structures, the resolubilization of the polymer in the imidization medium, and almost complete acid-catalyzed hydrolysis. Figure 29 contains the carbonyl region infrared spectra of a polymethacrylamide sample at several stages of the imidization procedure.

Acid-catalyzed hydrolysis in place of imidization was the main result of all attempts to imidize partially hydrolyzed polymers by the same methods used for homopolymers. If the homopolymers were not in contact with the acid mixture for at least 96 hours prior to heating, acid-catalyzed hydrolysis also occurred.

Dissolving these materials without destroying most of the imide content presented difficulty. The imidization procedure radically alters the solubility characteristics of the homopolymers, especially polyacrylamide. The following results were noted:

- Neither polymer type swells in water, even after prolonged heating.
- Weak alkaline conditions, even combined with the application of heat, also fail to have much effect on solubility.
- Neither polymer can be resolubilized in concentrated HCl.
- Stirring in excess base at room temperature for a week to 10 days, or for shorter periods with heating, dissolves both polymer types, but much imide character is lost, especially by polyacrylamide.
- All but the most highly imidized samples dissolve in ethylene glycol at 90°C. They cannot be diluted from this solvent system into water, but can be hydrolyzed to a water-soluble state by the addition of sodium hydroxide in ethylene glycol.

Our best results were obtained by stirring the imidized samples with sufficient equivalents of sodium hydroxide or sodium carbonate to produce a degree of hydrolysis of about 30 to 40 weight percent of the sodium salt form of the acid. At room temperature, this process takes from 5 to 10 days. Heating can reduce this time to several hours, but problems with imide stability arise especially for the polyacrylamide samples if the conditions are too severe. Small particle size and thorough stirring are critical with the small-scale apparatus used. It is important that hydrolysis be as rapid as possible and evenly distributed to ensure total dissolution with minimal ring-opening. Attempts at in situ neutralization and hydrolysis of imidization mixtures, before the polymers have precipitated, need further investigation.

Once a reliable way of putting the imidized samples into solution had been found, it was possible to compare their viscosity-building characteristics, viscosity retention in brine, and shear stability with those of the large number of polymers which we had already tested. The results showed that imidization greatly improved the viscosity characteristics of the polymers. The screening data for a number of the partially imidized, partially hydrolyzed polyacrylamides in Table 35 can be compared to screening data for several commercial HPAM polymers previously presented in Table 11. Tables 36 and 37 contain similar comparative data for the methacrylyl system.

It is apparent that the effects of imidization on viscosity enhancement and retention in brine are much greater for the methacrylamides than for the acrylamides. It is likely that part of the

reason for this phenomenon is that much more methacrylyl imide survived the hydrolysis (and solubilization) process than does acrylyl imide.

The results of the initial screening tests on the imidized polymers were sufficiently encouraging to warrant further investigation of these materials. Core testing is in progress. Other tests have shown:

- Imidized polyacrylamides are more sensitive to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  than comparable HPAM. The difference between imidized polymethacrylamides and partially hydrolyzed polymethacrylamides is less obvious, since both demonstrate a sensitivity to hard waters.
- Partially hydrolyzed, partially imidized polyacrylamides subjected to stability tests showed a 16 percent loss of initial viscosity at 77°F (25°C) over 80 days and a 21 percent loss in initial viscosity at 140°F (60°C) over 10 days. These tests are being carried out in 0.01 percent NaCl. Oxygen was not excluded and no stabilizers were present.

In order to verify that the improved performances observed with the acid-catalyzed imides were not just the results of imide cross-linking or some unforeseen artifact of the acid treatment, terpolymers containing methacrylamide, sodium methacrylate, and dimethacrylamide (Figure 30) were prepared and screened. The free-radical cyclopolymerization of dimethacrylamide has been reported to yield a polyimide in which six-membered rings predominate and interchain cross-links are rare.<sup>25-27</sup>

Dimethacrylamide was prepared by the room temperature reaction of equimolar quantities of methacrylamide with methacrylyl chloride in dry acetonitrile. Cross-linked poly(4-vinylpyridine) served advantageously as the HCl-acceptor. The product was isolated by evaporation from the mother liquor, and then redissolved and recrystallized from dry acetone. The monomer was water-soluble and was copolymerized with sodium methacrylate in a persulfate-initiated reaction (Figure 30). Although the viscosities of these materials were somewhat lower than those of the acid-treated homopolymers, viscosity retentions in brine were significantly higher than those of partially hydrolyzed polymethacrylamides. These results confirm that indeed the enhanced performance of the imidized polymers is due to the presence of imide rings and not due to imide cross-linking or some other phenomena.

## 5. Conclusions

### N-Alkyl Substitution

- (1) Several of the aqueous solutions of poly(N-alkylacrylamide-

co-sodium acrylate) polymers show somewhat better retention of viscosity in salt solution than do analogous unsubstituted polymers; however, the reason for this improvement appears to be the result of method of synthesis rather than the N-alkyl substitution.

(2) On the other hand, N-methyl substitution makes the polymers more shear sensitive in low salt solutions.

(3) The N-methyl substitution of acrylamide polymers reduces the amount of polymer retention in Berea core, but N-isopropyl substitution increases retention.

#### Methacrylamide System

(1) The backbone methyl groups increase substantially the solution viscosities of ionized polymethacrylamides in 0.01% NaCl.

(2) The viscosity retentions in brine of partially hydrolyzed polymethacrylamides (HPMAM) are significantly poorer than those of comparable HPAM polymers.

(3) N-methyl substitution of methacrylamide-sodium methacrylate copolymers does improve the viscosity retention in brine.

(4) The presence of either hydrophobic or hydrophilic N-substitution does not appear to alter significantly the hydrophobic effects of the backbone methyl groups of polymethacrylamide. Both types of substitution may improve viscosity retention in brine.

#### Charge-to-Mass Ratio

(1) For the variety of polymers studied, increased sensitivity to brine was observed when the anionic charge was increased.

(2) For HPAM, shear stability improves with increasing charge-to-mass ratio. The effect appears to reach a plateau at about 30 weight percent sodium acrylate.

#### Sequencing

(1) Non-regular alternation of carboxyl and amide groups appears to increase brine tolerance in both HPAM and HPMAM.

(2) Acrylamide-acrylic acid block copolymers show better viscosity retention in brine than equivalent materials made by copolymerization.

### Hydroxyalkyl N-Substitution

(1) Small amounts of pendant, trihydroxy substitution increases the shear resistance of unhydrolyzed acrylamide polymers.

(2) High levels of these trihydroxy substituents adversely affect the viscosity retention in brine.

### Imide System

(1) Both polyacrylamide and polymethacrylamide form imide rings readily in 6 N HCl. The reaction also appears to proceed in less concentrated HCl and several other acids.

(2) The maximum amount of imidization, with 2 to 4 percent polymer solids in 6 N HCl, occurs after 120 to 168 hours of dissolution and mixing, followed by 10 to 24 hours at 80 to 90°C.

(3) Partial imidization, followed by partial alkaline hydrolysis of both polyacrylamide and polymethacrylamide, yields polymers with viscosities in 0.01 percent NaCl at least as good as most commercial HPAM polymers, and with viscosity retentions in 2 percent NaCl which are significantly superior at low polymer concentrations. These imidized polymers are, however, more sensitive to hardness ions.

(4) The positive effects of imidization on polymethacrylamide appear to be greater than those on polyacrylamide.

(5) Imide rings generated in polymethacrylamide are much more stable to alkaline hydrolysis than those in polyacrylamide.

(6) Acid-catalyzed hydrolysis seems to occur simultaneously with imidization and becomes the dominant reaction after extended heating.

(7) Attempts to imidize partially hydrolyzed polyacrylamide or partially hydrolyzed polymethacrylamide by the same procedures used for the homopolymers result in further hydrolysis and little or no imidization in the end product.

(8) Infrared studies of carbonyl frequencies demonstrate that six-membered rings predominate in acid-catalyzed imidization of polyacrylamide and polymethacrylamide.

### Recommendations for Future Research

This work has demonstrated that the shear stability and viscosity retention in brine of acrylamide-type polymers can be enhanced by certain structural modifications as summarized above. Based on this study, future research should be directed toward (1) refining the use of chain stiffening by imide rings, and (2) optimizing N-hydroxyalkyl-substitution.

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TABLE 1

## Commercial Products Tested

<u>Partially Hydrolyzed Poly(acrylamides)</u>	<u>Polysaccharides</u>
Allied Colloids Alcoflood 800	Abbott Xanthan Broth
" " " 900	Henkle Galactosol
" " " 900L	Hercules Natrosol 250 HHR
" " " 1100	Jetco Actigum CS-11-L
" " " 1100L	Kelco Xanflood
" " " 1200	Pfizer Biopolymer 1035
" " " 1200L	Stauffer Colloid XHO
Amoco Sweepaid 103	" " XHX
Betz Hi Vis	" " XH1
Calgon Polymer 340	" " XH2
" " 454	" " XH3
" " 815	
" " 825	
" " 835	
Cort N-Hance 315	
" " 330	
" " 335	
Cyanamid Cyanatrol 920	
" " 930	
" " 940	
" " 950	
" " 960S	
Dow Pusher 500	
" " 700	
" " 1000	
Nalco Nal-flo	

TABLE 2

Effect of Salinity on Rheology of Glucan Solutions

Jetco Actigum CS-11-L

750 mg/L Polymer, 25°C

<u>Percent Salt</u>	<u>K</u>	<u>n</u>	<u>Screen Factor</u>
0.01% NaCl	142.5	0.337	3.0
0.1% NaCl	142.5	0.337	2.8
1.0% NaCl	140.0	0.334	3.1
10.0% NaCl	159.0	0.349	-
0.01% CaCl <sub>2</sub>	120.0	0.356	2.9
0.1% CaCl <sub>2</sub>	130.5	0.333	3.7
1.0% CaCl <sub>2</sub>	145.0	0.331	3.6
2.0% CaCl <sub>2</sub>	145.0	0.359	-

$$\text{Power Law Model: } \mu = K(\dot{\gamma})^{n-1}$$

$\mu$  = viscosity, mPa·s (cp)

K = Consistency Index, mPa·s<sup>n</sup>

$\dot{\gamma}$  = shear rate, s<sup>-1</sup>

n = flow behavior index, dimensionless

Viscosities measured with a Contraves LS-30 Rheometer

TABLE 3

## Microbial Degradation of Xanthan Gum (750 mg/L)\*

<u>Aerobic Cultures</u>	<u>Fraction of Original Viscosity @ 6 sec<sup>-1</sup></u>
<u>Nutrient Broth Medium</u>	<u>After 7 days</u>
Control	0.97
Bacillus megaterium	0.79
Pseudomonas aeruginosa	0.81
Micrococcus luteus	0.99
<u>Salt Broth Medium</u>	<u>After 14 days</u>
Control	1.04
Bacillus megaterium	0.72
Pseudomonas aeruginosa	0.90
Micrococcus luteus	0.96
<u>Anaerobic Cultures</u>	<u>Fraction of Original Viscosity @ 6 sec<sup>-1</sup></u>
<u>Postgate's Medium E</u>	<u>After 7 days</u>
Desulfovibrio with 2% NaCl	1.02
Desulfovibrio without Organics	0.97

\* Viscosities were measured at 25°C with a Contraves LS-30 rheometer

TABLE 4

Inhibition of Microbial Growth  
100 mL Solution of Pusher 700 in Culture Medium

<u>Mixed Culture Inoculum mL</u>	<u>Thymol Solution* mL</u>	<u>Turbidity Klett units</u>	<u>Final pH</u>	<u>Viscosity @ 6 s<sup>-1</sup> mPa·s</u>
0.0	0.1	0	7.5	20.2
1.0	0.1	153	8.0	6.0
0.0	0.5	0	7.6	20.9
1.0	0.5	0	7.6	21.1
0.0	1.0	0	7.5	23.0
1.0	1.0	0	7.4	22.2
0.0	-	102	7.8	7.2
1.0	-	100	7.6	7.0

\* This solution consisted of 4 grams thymol in 100 mL ethanol

Viscosities were measured at 25°C with a Contraves LS-30 rheometer

TABLE 5

## Effect of Nutrients

<u>Conditions</u>	<u>Inhibitor*</u>	<u>Turbidity Klett units</u>	<u>pH</u>	<u>Viscosity @ 6 s<sup>-1</sup> mPa·s</u>
mineral-salts	-	2	7.9	9.4
peptone	-	147	8.8	6.2
peptone	+	0	8.1	21.4

TABLE 6

## Effect of Anaerobiosis

<u>Conditions</u>	<u>Inhibitor*</u>	<u>Turbidity Klett units</u>	<u>pH</u>	<u>Viscosity @ 6 s<sup>-1</sup> mPa·s</u>
aerobic	-	100	7.6	7.0
aerobic	+	0	7.6	21.1
anaerobic	-	26	7.4	15.0
anaerobic	+	0	7.2	19.5

\* - means inhibitor not added

+ means inhibitor was added

Viscosities were measured at 25°C with a Contraves LS-30 rheometer

TABLE 7

## Soil Samples

<u>Soil Sample</u>	<u>Inhibitor*</u>	<u>Final pH</u>	<u>Viscosity @ 6 s<sup>-1</sup> mPa·s</u>
none	-	8.5	8.1
none	+	8.3	22.9
house plant	-	6.9	5.6
house plant	+	8.1	11.4
lawn	-	8.5	5.5
lawn	+	8.1	13.2
desert	-	8.7	8.2
desert	+	8.4	20.4
lot	-	8.7	8.3
lot	+	8.4	18.7

\* See Table 5

Viscosities were measured at 25°C with a Contraves LS-30 rheometer

TABLE 8

## Effect of Microbial Products

<u>Culture</u>	<u>Inhibitor*</u>	<u>Turbidity Klett units</u>	<u>pH</u>	<u>Viscosity @ 6 s<sup>-1</sup> mPa·s</u>
mixed (3)	-	146	8.7	12.1
mixed (3)	+	0	9.0	22.6
mixed (5)	+	0	8.8	16.1
isolate (5)	+	0	7.9	24.4
mixed (2)	+	0	8.7	21.4
isolate (2F)	+	0	8.6	25.7

\* See Table 5

Viscosities were measured at 25°C with a Contraves LS-30 rheometer

TABLE 9

## Resistance Factors and Polymer Retention in Berea Sandstone

750 mg/L, Room Temperature, 1 ft/day

Polymer	Supplier	Polymer Resistance Factor		Residual Resistance Factor		Polymer Retention, lbs/ac.ft.	
		0.1% NaCl	2% NaCl	0.1% NaCl	2% NaCl	0.1% NaCl	2% NaCl
Sweepaid 103	Amoco	19.0	3.5	2.6	1.1	99	147
Hi Vis	Betz	19.5	3.9	2.1	1.3	68	130
Cyanatrol 960S	Cyanamid	40.6	10.8	14.8	3.9	103	155
Pusher 500	Dow	12.5	3.4	2.7	1.4	65	125
Pusher 700	Dow	14.2	7.1	3.3	1.1	70	135
Pusher 1000	Dow	34.1	6.4	4.2	1.5	107	160
Na1-flo	Nalco	24.4	6.1	2.2	3.2	95	149
Xanthan Broth	Abbott	19.5	20.5	1.2	1.2	36	77
Xanflood	Kelco	13.5	11.6	5.3	6.7	48	75
Biopolymer 1035	Pfizer	14.6	13.6	3.2	2.3	41	46
Colloid XHO	Stauffer	6.1	3.4	1.9	1.3	33	200
Actigum CS-11-L	Jetco	51.5	19.4	21.2	4.2	532	666

Initial permeability to water for Berea cores: 350-550 md.

TABLE 10

Comparative Preliminary Screening Data  
Representative Samples of Various Polymer Types

Informal Polymer Name	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention	
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)	Shear* (%)	Brine** (%)
Polyacrylamide	0.0653	0	14.0	12.5	56.2	86.9
Hydrolyzed Polyacrylamide	0.0139	41.7	120.4	13.0	90.1	10.7
Poly AMPS	0.0138	100	50.7	10.4	67.8	20.5
Polyethylene Oxide	0.0783	0	21.2	20.1	62.9	94.5
Hydroxyethyl Cellulose	0.0799	0	18.3	18.0	97.7	98.2
Xanthan Gum	0.0114	Low	44.6	23.2	96.4	52.1
Glucan	0.0167	0	24.2	23.8	90.3	98.5
Carboxymethyl Cellulose	0.0164	Low	51.8	11.6	94.5	22.5

$$* \text{ Shear Effect} = \frac{[(\eta_{sp})_{.01}]_s}{[(\eta_{sp})_{.01}]_u} \times 100$$

$$** \text{ Brine Effect} = \frac{(\eta_{sp})_2}{(\eta_{sp})_{.01}} \times 100$$

Viscosities were determined in a Cannon-Ubbelohde Dilution-Type viscometer at 25°C and pH of 9.5

$(\eta_{sp})_2$  = Specific Viscosity in 2% NaCl

$(\eta_{sp})_{.01}$  = Specific Viscosity in 0.01% NaCl

$[(\eta_{sp})]_s$  = Specific Viscosity of Sheared Polymer Solution

$[(\eta_{sp})]_u$  = Specific Viscosity of Unsheared Polymer Solution

TABLE 11

## Comparative Screening Data: Commercial Samples

Sample Number	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention*	
			0.01% NaCl (dL/g)	2.0% NaCl	Shear (%)	Brine (%)
Poly(acrylamide-co-sodium acrylate) made by Hydrolysis						
203	0.0156	17.5	90.7	12.5	87.2	13.8
204	0.0160	18.5	74.1	9.0	88.8	12.1
34	0.0101	29.1	115.6	12.6	84.4	10.9
25	0.0116	31.1	164.8	18.3	66.2	11.1
132	0.0173	41.7	115.6	10.5	92.4	9.0
32	0.0143	41.9	209.4	18.5	67.1	8.8
Poly(acrylamide-co-sodium acrylate) made by Copolymerization						
294	0.0169	9.4	45.5	8.3	90.2	18.3
326	0.0190	24.4	109.8	27.6	74.5	25.1
295	0.0160	27.8	140.1	23.8	77.6	17.0
296	0.0163	34.9	124.5	17.3	85.8	13.9
298	0.0170	37.8	104.3	14.8	91.6	14.2
299	0.0178	39.2	122.1	16.9	93.9	13.8
300	0.0175	41.4	137.0	20.7	92.6	15.1
301	0.0193	40.6	182.1	21.4	74.2	11.8
302	0.0184	44.9	182.3	31.0	67.9	17.0
303	0.0173	38.7	160.7	29.2	79.3	18.1
Poly(acrylamide-co-ammonium acrylate) made by Copolymerization						
278	0.0163	33.4	118.0	11.5	97.3	9.7
290	0.0168	34.7	127.7	13.8	89.9	10.8
280	0.0172	36.3	204.3	22.5	94.2	11.0
285	0.0162	37.6	202.8	30.7	86.3	15.1
284	0.0160	39.2	175.8	25.9	87.7	14.7
291	0.0165	43.2	187.0	22.1	89.2	11.8
293	0.0167	45.7	284.4	31.7	70.5	11.1

\* see Table 10 for definitions

TABLE 12

## Characteristics of GPC Columns

<u>Column Number</u>	<u>Packing</u>	<u>Mesh Size</u>	<u>Mean Pore Diameter (Å)</u>
1	CPG03000	120/200	2734
2	"	"	"
3	"	"	"
4	CPG02000	200/400	1902
5	"	"	"
6	CPG01000	"	1038

TABLE 13

Analysis Conditions  
Room Temperature

Mobile Phase: 0.02 M Sodium Sulfate (pH 3.5)  
1% Methanol  
60 mg/L Tergitol NP-10

Detector: Water Differential Refractive Index at 28

TABLE 14

Screening Data for HPAM Prepared from 5 to 6 Million MW Poly(acrylamide)

Sample Number	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention*	
		0.01% NaCl (dL/g)	2.0% NaCl (dL/g)	Shear (%)	Brine (%)
319**	<1***	10.0	8.3	67.8	83.7
306	5.6	23.6	9.2	82.8	38.8
307	8.0	63.6	16.9	78.9	26.6
308	13.5	85.7	12.7	84.6	14.9
309	16.1	106.2	14.8	91.4	13.9
310	28.8	122.7	12.7	94.1	10.4
325	38.6	118.0	13.0	93.2	11.0
312	40.5	120.7	13.7	95.5	11.4

\* see Table 10 for definitions

\*\* starting material was acrylamide homopolymer -- Polyscience Lot 3-1590

\*\*\* the carboxyl content observed was within the experimental error of the determination

TABLE 15

## Synthesis Details of Block Copolymers from Acrylamide and Acrylic Acid

Polymer Number	Acrylamide	Acrylic Acid	Solvent H <sub>2</sub> O	Azoamidino Catalyst	Reaction Time at 60°C	Reaction Time at 26°C	Yield	Reduced Viscosity*** in 2% NaCl
247*	5.0 g	5.0 g	100 mL	0.1100 g	50 min,	0	5.4 g	4.3 dL/g
248*	5.0	2.5	100	0.1100	50 "	5 days	4.0	3.1
249*	5.0	5.0	75	0.1100	60 "	0	4.0	4.2
259*	5.0	5.0	100	0.1000	50 "	0	5.0	4.8
250*	5.0	5.0	100	0.1000	5 "	1 day	4.6	9.1
251*	5.0	5.0	100	0.1000	4 "	2 "	6.0	9.1
276*	5.0	5.0	100	0.0250	4 "	1 "	4.6	10.3
266*	5.0	5.0	100	0.0125	4 "	2 "	1.0	11.3
267*	5.0	5.0	100	0.0170	4 "	1 "	3.7	14.0
268**	5.0	5.0	100	0.0120	5 "	1 "	3.0	18.6
269**	5.0	5.0	100	0.0250	5 "	16 hrs	6.4	11.6
270**	5.0	5.0	100	0.0125	5 "	24 "	4.2	12.4
271**	5.0	5.0	100	0.0125	5 "	45 min	3.2	19.4
274**	5.0	0.5	100	0.0125	5 "	24 hrs	3.6	12.0

\* Block Copolymers Synthesized by Procedure #2

\*\* Block Copolymers Synthesized by Procedure #1

\*\*\* Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer (size 75) at 25°C

TABLE 16

## Comparative Screening Data: Block and Random HPAM Copolymers

Sample Number	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention	
			0.01% NaCl (dL/g)	2.0% NaCl	Shear* (%)	Brine** (%)
Block HPAM Copolymers						
267	0.0151	5.7	26.5	14.0	32.7	52.9
274	0.0144	13.3	55.1	12.0	84.0	21.8
270	0.0146	17.0	27.2	12.4	72.4	45.4
269	0.0154	30.4	56.6	11.6	78.4	20.6
268	0.0156	49.0	111.6	18.6	87.4	16.7
271	0.0171	53.4	148.4	19.4	89.8	13.1
Random HPAM Copolymers						
85	0.0133	6.0	14.8	4.9	96.3	32.9
183	0.0142	25.5	116.1	19.1	88.6	16.5
223	0.0146	28.9	121.7	15.3	87.9	12.6
297	0.0160	31.0	95.7	13.3	90.7	13.9
131	0.0173	41.7	138.6	14.0	86.7	10.1
24	0.0120	42.1	117.1	11.5	86.2	9.8
219	0.0153	54.4	102.0	11.5	86.4	11.3

$$* \text{ Shear Effect} = \frac{[(\eta_{sp})_{.01}]_s}{[(\eta_{sp})_{.01}]_u} \times 100$$

$$** \text{ Brine Effect} = \frac{(\eta_{sp})_2}{(\eta_{sp})_{.01}} \times 100$$

Viscosities measured with a Cannon-Ubbelohde Dilution-Type viscometer (size 75) at 25°C

$(\eta_{sp})_2$  = Specific Viscosity in 2% NaCl

$(\eta_{sp})_{.01}$  = Specific Viscosity in 0.01% NaCl

$[\eta_{sp}]_s$  = Specific Viscosity of Sheared Polymer Solution

$[\eta_{sp}]_u$  = Specific Viscosity of Unsheared Polymer Solution

TABLE 17

## Hydrolysis of Homopoly(N-methylacrylamide)

Sample Number	Poly(N-methyl-acrylamide) (gms)	Sodium Hydroxide 1 N solution (ml)	Temperature (°C)	Time (hr)	Degree of Hydrolysis*
147	2.00	7.4	60	2	11.1
160	0.500	2.10	60	24	8.4
164	1.8	8.10	96	48	22.3
167	1.17	7.2	98	95	24.3
169	1.30	12.0	98	88	30.6
179	0.6	10.0	98	140	41.5
166	0.75	5.0	96	24	20.5

\* As measured by the weight percent of sodium acrylate residues found by acid titration of the isolated polymer.

TABLE 18

Comparative Screening Data: Poly(N-methylacrylamide-co-sodium acrylate)

Sample Number	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention	
			0.01% NaCl (dL/g)	2.0% NaCl (dL/g)	Shear*	Brine**
Polymers made by Copolymerization						
79	0.0151	9.5	35.69	12.97	80.7	36.3
78	0.0151	16.1	74.94	13.17	75.1	17.6
122	0.0160	24.3	63.46	10.00	89.8	15.8
76	0.0147	28.4	76.66	10.11	89.1	13.2
124	0.0169	31.8	24.96	4.30	92.6	17.2
74	0.0141	36.2	81.20	9.89	91.0	12.2
75	0.0149	36.4	102.73	13.00	80.4	12.7
121	0.0157	36.8	36.49	5.38	83.4	14.8
46	0.0151	42.7	103.85	13.04	80.0	12.6
45	0.0152	46.6	113.12	14.79	73.3	13.1
Polymers made by Hydrolysis						
166	0.0117	20.5	85.90	10.36	96.8	12.1
164	0.0129	22.3	40.58	3.66	99.5	9.0
167	0.0132	24.7	85.65	10.02	97.2	11.7
169	0.0127	30.6	94.81	10.72	98.4	11.3
179	0.0125	41.5	87.05	9.10	97.2	10.4

$$* \text{ Shear Effect} = \frac{[(\eta_{sp})_{.01}]_s}{[(\eta_{sp})_{.01}]_u} \times 100$$

$$** \text{ Brine Effect} = \frac{(\eta_{sp})_2}{(\eta_{sp})_{.01}} \times 100$$

Viscosities measured with a Cannon-Ubbelohde Dilution-Type viscometer (size 75) at 25°C

$(\eta_{sp})_2$  = Specific Viscosity in 2% NaCl

$(\eta_{sp})_{.01}$  = Specific Viscosity in 0.01% NaCl

$[\eta_{sp}]_s$  = Specific Viscosity of Sheared Polymer Solution

$[\eta_{sp}]_u$  = Specific Viscosity of Unsheared Polymer Solution

TABLE 19

## Screening Data for Poly(acrylamide-co-sodium acrylate)

Sample Number	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention	
			0.01% NaCl (dL/g)	2.0% NaCl	Shear*	Brine**
309	0.0170	16.1	106.19	14.76	91.4	13.9
184	0.0187	18.8	11.72	0.86	94.4	7.4
185	0.0152	14.2	14.43	1.34	98.6	9.3
6	0.0608	19.6	103.92	9.07	94.5	8.7
310	0.0179	28.8	122.71	12.72	94.1	10.4
181	0.0207	31.5	15.16	1.25	98.7	8.2
132	0.0173	41.7	115.57	10.46	92.4	9.0
178	0.0146	41.7	103.71	11.11	95.9	10.7
16	0.0069	43.0	151.33	16.41	96.0	10.8
7	0.0086	50.8	143.86	13.66	90.3	9.5
40	0.0126	52.9	64.02	4.93	94.3	7.7

$$* \text{ Shear Effect} = \left[ (\eta_{sp})_{.01} \right]_s / \left[ (\eta_{sp})_{.01} \right]_u \times 100$$

$$** \text{ Brine Effect} = \left[ (\eta_{sp})_2 / (\eta_{sp})_{.01} \right]_u \times 100$$

Viscosities measured with a Cannon-Ubbelohde Dilution-Type viscometer (size 75) at 25°C

$(\eta_{sp})_2$  = Specific Viscosity in 2% NaCl

$(\eta_{sp})_{.01}$  = Specific Viscosity in 0.01% NaCl

$[\eta_{sp}]_s$  = Specific Viscosity of Sheared Polymer Solution

$[\eta_{sp}]_u$  = Specific Viscosity of Unsheared Polymer Solution

TABLE 20

Screening Data for Poly(N-isopropylacrylamide-co-sodium acrylate)

Sample Number	Polymer Conc. (g/dL)	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity		Viscosity Retention	
			0.01% NaCl (dL/g)	2.0% NaCl	Shear* (%)	Brine** (%)
69	0.0151	17.6	16.13	2.27	97.6	14.1
58	0.0169	28.9	71.64	12.25	89.0	17.10
43	0.0125	31.5	40.58	4.81	89.5	11.9
57	0.0153	33.0	48.83	6.19	95.5	12.7
56	0.0152	45.3	85.96	11.64	92.0	13.5
61	0.0154	46.8	88.83	11.27	88.1	12.7
13	0.0081	51.3	85.54	12.38	85.5	14.5

$$* \text{ Shear Effect} = \left[ (\eta_{sp})_{.01} \right]_s / \left[ (\eta_{sp})_{.01} \right]_u \times 100$$

$$** \text{ Brine Effect} = \left[ (\eta_{sp})_2 / (\eta_{sp})_{.01} \right]_u \times 100$$

Viscosities measured with a Cannon-Ubbelohde Dilution-Type viscometer (size 75) at 25°C

$(\eta_{sp})_2$  = Specific Viscosity in 2% NaCl

$(\eta_{sp})_{.01}$  = Specific Viscosity in 0.01% NaCl

$[\eta_{sp}]_s$  = Specific Viscosity of Sheared Polymer Solution

$[\eta_{sp}]_u$  = Specific Viscosity of Unsheared Polymer Solution

TABLE 21

## Berea Core Tests

Sample Number	Polymer Type	Wt. of Acid: Sodium Salt (%)	Reduced Viscosity 0.01% NaCl (dL/g)
38	Poly(N-methylacrylamide)	0	4.77
9	Poly(acrylamide)	0	6.12
46	Poly(N-methylacrylamide- co-sodium acrylate)	42.7	103.12
61	Poly(N-isopropylacrylamide- co-sodium acrylate)	46.8	88.83
17	Poly(acrylamide-co-sodium acrylate)	40.7	117.70

Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer (size 75) at 25°C

TABLE 22

## Preparation of Methacrylamide Homopolymers

<u>Sample Number</u>	<u>MAAM*</u>	<u>MBA**</u>	<u>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub></u>
M2	30.03 g	0 g	0.3076 g
M3	30.05	0	0.1584
M4	29.63	0	0.1253
M5	30.22	0.0003	0.1076
M6	30.05	0.0004	0.1072
M7	30.01	0.0006	0.1072
M8	30.00	0.0009	0.1072
M9	30.08	0.0018	0.1071
M10	29.98	0.0027	0.1071
M11	30.10	0.0045	0.1071
M9A	30.04	0.0018	0.1070
M9B	30.00	0.0018	0.0603
M9C	29.98	0.0018	0.0300
M9D	30.01	0.0018	0.0151

5% solids  
22 - 26°C  
168 hours

\* MAAM: methacrylamide

\*\* MBA: N,N'-methylenebisacrylamide

TABLE 23

Reduced Viscosities of Poly(methacrylamides) in Ethylene Glycol  
as Compared with  $5-6 \times 10^6$  MW Poly(acrylamide)

Sample Number	Absolute * Viscosity (mPa·s)	Specific Viscosity	Reduced Viscosity (dL/g)	Intrinsic Viscosity (dL/g)
M3	17.67	0.04	0.21	0.13
M4	19.41	0.14	0.72	-
M5	20.68	0.21	1.03	0.88
M6	25.73	0.51	2.47	1.21
M7	21.27	0.25	1.24	1.15
M8	23.16	0.36	1.82	1.43
M9	26.69	0.57	2.74	1.98
M10	24.84	0.46	2.52	1.75
PAAM	48.79	1.87	9.95	8.93
M9A	27.04	0.61	2.69	2.00
M9B	28.46	0.75	2.98	2.56
M9C	30.12	0.89	3.10	2.67
M9D	30.31	0.93	3.19	2.70

$$T = 25^{\circ}\text{C}$$

$$\eta_s = 17.03 \text{ mPa}\cdot\text{s}$$

$$\dot{\gamma} = 6 \text{ sec}^{-1}$$

$$c = 0.18 \text{ to } 0.21 \text{ g/dL}$$

\* viscosities measured with a Contraves LS-30 Rheometer

TABLE 24

Reduced Viscosities of Poly(methacrylamides) in 5 M Urea  
as Compared with  $5-6 \times 10^6$  MW Poly(acrylamide)

Sample Number	Absolute * Viscosity (mPa·s)	Specific Viscosity	Reduced Viscosity (dL/g)
M3	1.24	0.06	0.38
M4	1.36	0.16	1.06
M5	1.49	0.27	1.65
M6	1.64	0.40	2.52
M7	1.50	0.28	1.68
M8	1.54	0.32	2.09
M9	1.66	0.42	3.08
PAAM	8.14	5.96	33.75
M9B	1.85	0.59	3.73
M9C	1.99	0.70	4.09

$$T = 25^{\circ}\text{C}$$

$$\dot{\gamma} = 6 \text{ sec}^{-1}$$

$$\eta_s = 1.17 \text{ mPa}\cdot\text{s}$$

$$c = 0.16 \text{ to } 0.17 \text{ g/dL}$$

\* viscosities measured with a Contraves LS-30 Rheometer

TABLE 25

Screening Data: Poly(methacrylamides)  
After Alkaline Hydrolysis

Sample Number	Carboxyl* Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
M1	24.1	12.81	0.93	94.3	7.3
M2	32.3	18.42	1.42	91.6	7.7
M3	22.3	16.90	1.45	97.8	8.6
M4	20.4	22.34	2.30	92.8	10.3
M5	23.0	28.46	2.07	93.3	7.3
M6	27.3	27.36	2.09	99.9	7.6
M7	31.0	29.28	2.35	99.9	8.0
M8	27.9	60.25	5.67	97.3	9.4
M9	38.0	122.05	6.72	71.7	5.5
M10	40.7	95.03	5.30	78.5	5.6
M11	31.4	78.95	6.16	87.5	7.8
M9A	28.1	114.06	7.11	73.5	6.2
M9B	38.3	138.11	8.11	70.2	5.9
M9C	40.1	140.22	8.24	69.8	5.9
M9D	40.3	140.11	8.19	70.4	5.9

\* weight percent sodium methacrylate

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type  
Viscometer (size 75) at 25°C

TABLE 26

Comparative Screening Data: Partially Hydrolyzed  
Poly(methacrylamides) versus Partially Hydrolyzed Poly(acrylamides)

Sample Number	Carboxyl* Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
Partially Hydrolyzed Poly(acrylamide)					
204	18.5	74.14	8.96	88.8	12.1
180	25.0	107.85	14.35	91.2	13.3
19	31.3	123.25	13.28	96.0	10.8
18	34.6	118.49	15.88	90.2	13.4
133	41.7	100.26	11.81	95.8	10.7
Partially Hydrolyzed Poly(methacrylamide)					
189	20.6	41.18	3.82	92.6	9.3
190	27.9	60.25	5.67	92.3	9.4
193	31.4	78.95	6.16	87.5	7.8
191	38.0	122.05	6.72	71.7	5.5
192	40.7	95.03	5.30	78.5	5.6

\* weight percent sodium salt of free acid

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type  
Viscometer (size 75) at 25°C

TABLE 27

Copolymerization Conditions:  
Poly(methacrylamide-co-sodium methacrylates)

<u>Sample Number</u>	<u>MAAM</u> *	<u>MAAC</u> **	<u>NaOH</u>	<u>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub></u>
96	10.09 g	10.62 g	5.00 g	0.1326 g
97	15.33	5.31	2.50	0.1321
98	19.26	1.06	0.50	0.1331
170	4.81	16.57	10.50	0.1364
-	16.93	3.67	2.00	0.1330
-	8.15	12.25	7.75	0.1318

9 to 10% solids  
25°C  
24 hours

\* methacrylamide

\*\* methacrylic acid

TABLE 28

Comparative Screening Data: Copolymerized Poly(methacrylamide-co-sodium methacrylates) versus Similar Poly(acrylamide-co-sodium acrylates)

Sample Number	Carboxyl* Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
Poly(methacrylamide-co-sodium methacrylates)					
98	5.7	15.4	3.4	89.8	22.4
-	17.9	24.4	4.1	90.2	16.6
97	22.6	25.2	3.7	92.9	14.8
96	51.9	45.7	4.0	94.5	8.8
-	61.0	40.8	4.1	83.8	10.1
170	76.1	41.9	4.9	89.1	11.7
Poly(acrylamide-co-sodium acrylates)					
-	6.0	14.8	4.9	96.3	32.9
-	19.2	14.4	1.3	98.6	9.3
-	23.6	83.9	9.8	94.5	11.7
-	52.9	64.0	4.9	94.3	7.7
-	54.4	102.0	11.5	86.4	11.3

\* weight percent sodium salt of free acid

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type  
Viscometer (size 75) at 25°C

TABLE 29

Screening Data: N-Substituted Methacrylamides, Hydrophobic Groups

Sample Number	Carboxyl* Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
Poly(N-methylmethacrylamide-co-sodium methacrylate)					
175	11.8	29.69	4.06	93.0	13.7
176	31.3	24.69	5.01	93.2	20.3
177	41.0	26.19	5.45	92.1	20.8
221	48.9	41.96	3.57	98.0	8.5
220	60.7	21.83	1.54	98.6	7.0
Poly(N-ethylmethacrylamide-co-sodium methacrylate)					
-	4.1	25.44	17.88	99.7	70.3
-	8.2	24.37	9.42	96.7	38.7
-	12.9	25.48	7.39	99.7	29.0
-	21.4	29.16	6.59	95.4	22.6

\* weight percent sodium salt of free acid

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type  
Viscometer (size 75) at 25°C

TABLE 30

Preparation of Poly(N-(tris(hydroxymethyl)aminomethane)acrylamides)

<u>Sample Number</u>	<u><math>\eta_{sp}/c</math></u>	<u>N-tris-acrylamide</u>	<u>Acrylamide</u>	<u>Initiator (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub></u>	<u>Water</u>
194	10.98 dL/g	3.00 g	3.00 g	0.0116 g	100 mL
195	14.23	4.00	2.00	"	"
197	9.81	2.00	4.00	"	"
198	10.51	1.20	4.60	0.0121	95
199	17.51	0.60	5.40	"	100

6% solids  
 22 - 24°C  
 18 hours

TABLE 31

## Preparation of Poly(N-(hydroxyalkyl)methacrylamides)

<u>Sample Number</u>	<u><math>\eta_{sp}/c</math></u>	<u>Hydroxyalkyl monomer</u>	<u>Meth-acrylamide</u>	<u>Water</u>	<u>Initiator <math>K_2S_2O_8</math></u>	<u>Time</u>
N-ethanolamine derivative						
-	47.83 dL/g	5.00 g	3.00 g	100 mL	0.0080 g	120 hrs
-	53.68	4.00	4.00	"	"	"
-	46.70	3.00	5.00	"	"	"
N-diethanolamine derivative						
-	38.76	5.00	3.00	"	"	"
-	59.68	4.00	4.00	"	0.0079	"
-	56.42	3.00	5.00	"	0.0080	"
N-tris(hydroxymethyl)amino methane derivative						
-	49.86	6.00	4.00	190	0.0100	24
-	40.01	5.00	5.00	"	"	"
-	44.80	4.00	6.00	"	"	"
-	66.12	4.00	6.00	"	"	"

8 - 10% solids  
25°C

TABLE 32

Screening Data Comparing Poly(N-(tris(hydroxymethyl)aminomethane)acrylamide-co-acrylamide) to Poly(acrylamide)

Sample Number	N-(tris(hydroxymethyl)-* aminomethane)acrylamide (%)	Reduced Viscosity**		Viscosity Retention Shear Brine (%)
		0.01% NaCl (dL/g)	2.0% NaCl (dL/g)	
199	10.0	16.4	14.2	85.4 86.8
198	20.7	10.5	9.5	83.1 90.3
197	33.3	9.8	7.6	84.9 77.7
194	50.0	10.8	7.7	82.8 71.3
195	66.7	14.2	6.0	77.4 42.0
21 (PAM)***	0	32.2	33.6	45.0 100
20 (PAM)***	0	15.3	16.3	66.7 100
4 (PAM)****	0	14.0	12.5	56.2 86.9
320 (PAM)****	0	13.4	11.4	69.2 85.6
265 (PAM)***	0	10.7	11.1	65.7 100
319 (PAM)****	0	10.0	8.3	67.8 83.7

\* weight percent in monomer feed

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type viscometer (size 75) at 25°C

\*\*\* acrylamide homopolymer synthesized by our group

\*\*\*\* acrylamide homopolymer purchased from Polysciences, Inc.

TABLE 33

Screening Data: N-Substituted Methacrylamides, Hydrophilic Groups

Nominal Carboxyl Content (wt. %)	Amide* (wt. %)	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
Monohydroxy Derivative					
25	28	47.8	8.9	90.4	18.6
25	32	53.7	7.5	88.3	14.0
25	46	46.7	6.7	87.6	14.3
Dihydroxy Derivative					
30	21	38.8	5.4	90.9	13.9
30	34	59.7	10.2	92.4	17.1
30	51	56.4	5.9	83.9	10.5
Trihydroxy Derivative					
30	18	49.9	5.5	88.8	11.0
30	28	40.0	4.8	91.6	12.0
30	33	44.8	6.2	88.7	13.8
40	30	66.1	7.9	73.5	12.0

\* weight percent methacrylamide

\*\* viscosities measured with a Cannon-Ubbelohde Dilution-Type  
Viscometer (size 75) at 25°C

TABLE 34

Poly(methacrylic anhydride-co-sodium methacrylates)  
versus Partially Hydrolyzed Poly(methacrylamides)

Sample Number	Carboxyl Content (wt. %)*	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
Anhydrides					
-	15.3	16.9	5.8	94.4	34.4
-	22.1	18.8	4.2	89.6	22.3
-	25.8	20.4	4.4	86.6	21.6
-	36.0	29.5	5.6	93.5	18.8
-	40.9	28.6	4.3	91.0	15.1
HPMAM					
154	20.4	22.3	2.3	92.8	10.3
186	23.0	28.5	2.1	93.3	7.3
-	24.1	12.8	0.9	94.3	7.3
187	27.3	27.4	2.1	99.9	7.6
87	32.3	18.4	1.4	91.6	7.7
192	40.7	95.0	5.3	78.5	5.6

\* Wt. % sodium methacrylate

\*\* Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer  
(size 75) at 25°C

TABLE 35

Screening Data: Partially Hydrolyzed,  
Partially Imidized Poly(acrylamides)

Sample Number	Carboxyl Content (wt. %)*	Imide Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
			0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
272	14.2	-	88.5	17.3	88.1	19.5
273	19.2	18	109.2	29.9	91.5	27.4
253	35.7	12	64.4	10.3	80.5	15.9
252	37.7	10	155.1	19.6	77.4	12.7
216	42.8	20	132.1	26.6	94.5	20.2
215	51.0	-	115.6	22.3	97.2	19.2
246	58.4	5	80.8	9.2	91.4	11.4
240	81.2	3	109.9	7.3	95.4	6.7

\* Wt. % sodium acrylate

\*\* Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer  
(size 75) at 25°C

TABLE 36

Screening Data: Partially Hydrolyzed,  
Partially Imidized Poly(methacrylamides)

Sample Number	Carboxyl Content (wt. %)*	Imide Content (wt. %)	Reduced Viscosities**		Viscosity Retained	
			0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
212	28.0	-	196.7	43.2	74.2	22.0
256	29.2	16	159.6	23.8	90.5	14.9
257	30.3	22	183.9	38.2	75.3	20.7
213	30.4	24	136.8	31.7	88.4	23.2
210	31.2	21	155.9	34.8	85.4	22.3
-	31.3	15	158.5	23.6	90.5	14.9
209	31.3	27	140.9	39.8	93.0	28.3
211	34.8	25	170.1	41.4	79.5	24.3
255	45.9	15	123.7	16.8	89.0	13.6
-	58.4	6	130.2	13.5	88.4	10.4
-	64.8	-	129.6	14.4	86.7	11.1
214	75.1	9	142.7	19.1	76.4	13.4

\* Wt. % sodium methacrylate

\*\* Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer  
(size 75) at 25°C

TABLE 37

Screening Data: Poly(methacrylamides)  
After Alkaline Hydrolysis

Sample Number	Carboxyl Content (wt. %)*	Reduced Viscosities**		Viscosity Retained	
		0.01% NaCl (dL/g)	2.00% NaCl (dL/g)	Shear (%)	Brine (%)
5	24.1	12.81	0.93	94.3	7.3
8	32.3	18.42	1.42	91.6	7.7
9	22.3	16.90	1.45	97.8	8.6
12	20.4	22.34	2.30	92.8	10.3
13	23.0	28.46	2.07	93.3	7.3
14	27.3	27.36	2.09	99.9	7.6
15	31.0	29.28	2.35	99.9	8.0
16	27.9	60.25	5.67	97.3	9.4
17	38.0	122.05	6.72	71.7	5.5
18	40.7	95.03	5.30	78.5	5.6
19	31.4	78.95	6.16	87.5	7.8

\* Wt. % sodium methacrylate

\*\* Viscosities measured with a Cannon-Ubbelohde Dilution-Type Viscometer (size 75) at 25°C

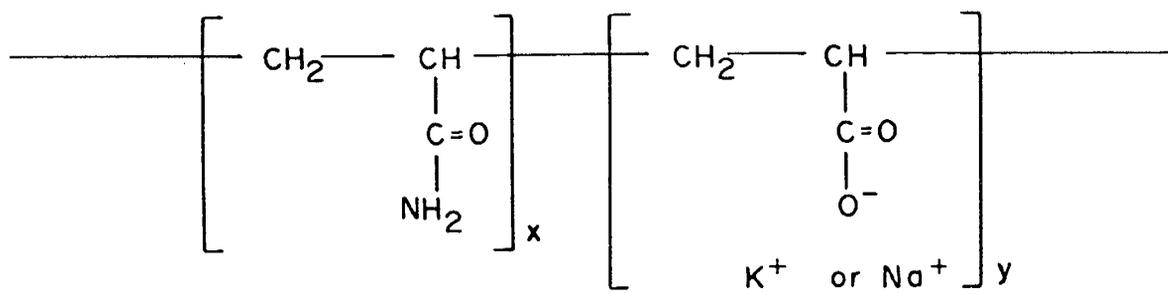


FIGURE 1

Molecular Structure of Partially Hydrolyzed Polyacrylamides

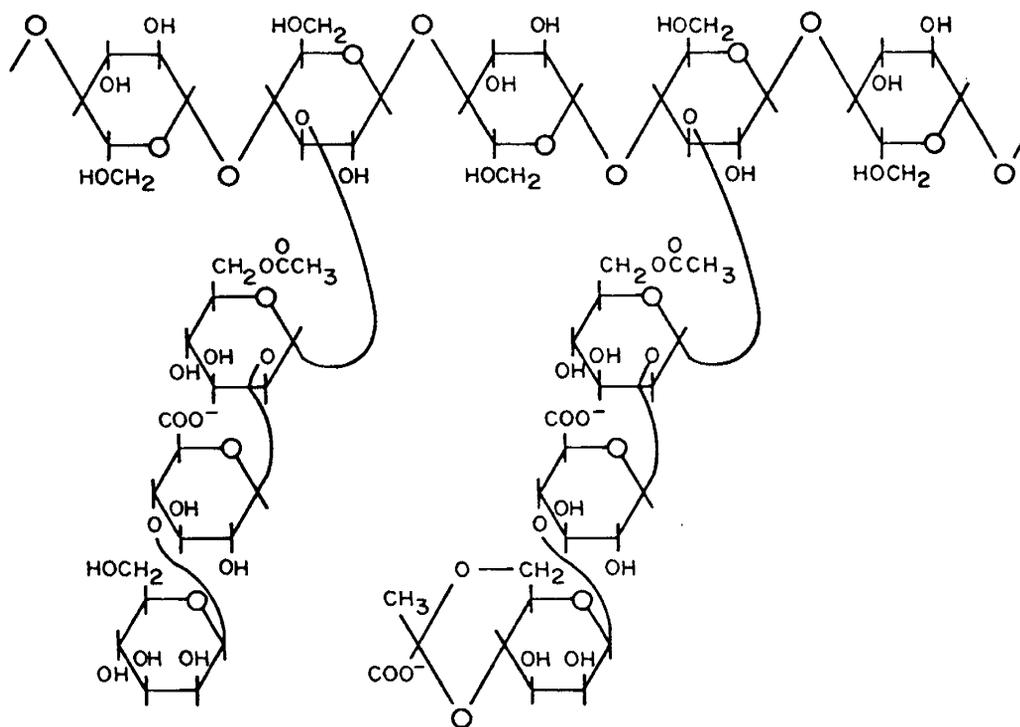


FIGURE 2

Structure of Extracellular Polysaccharide of *Xanthomonas campestris*, According to Jansson et al. (1975).<sup>28</sup>

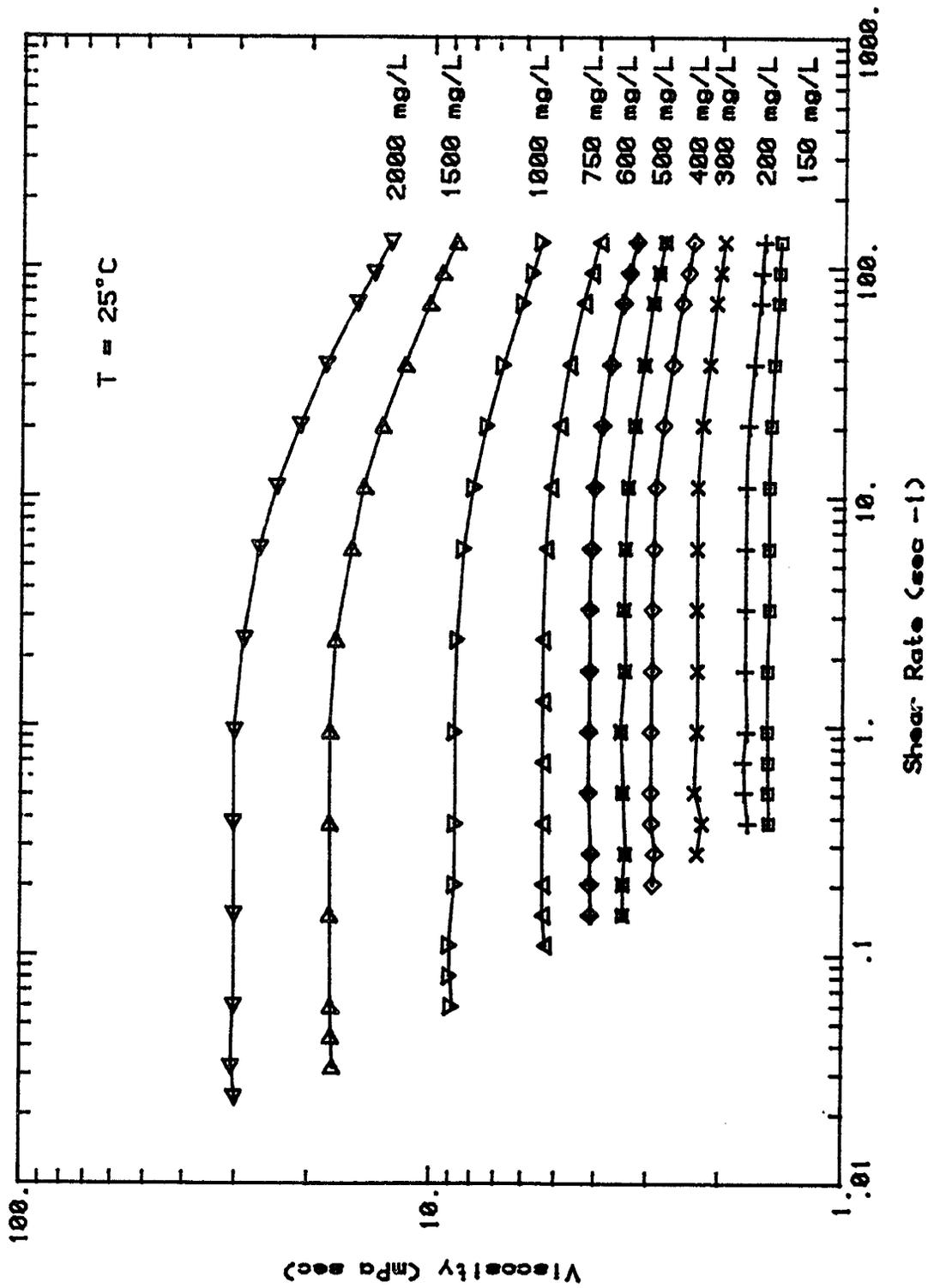


Figure 3. Viscosity of Cyanatrol 950 in 3% NaCl

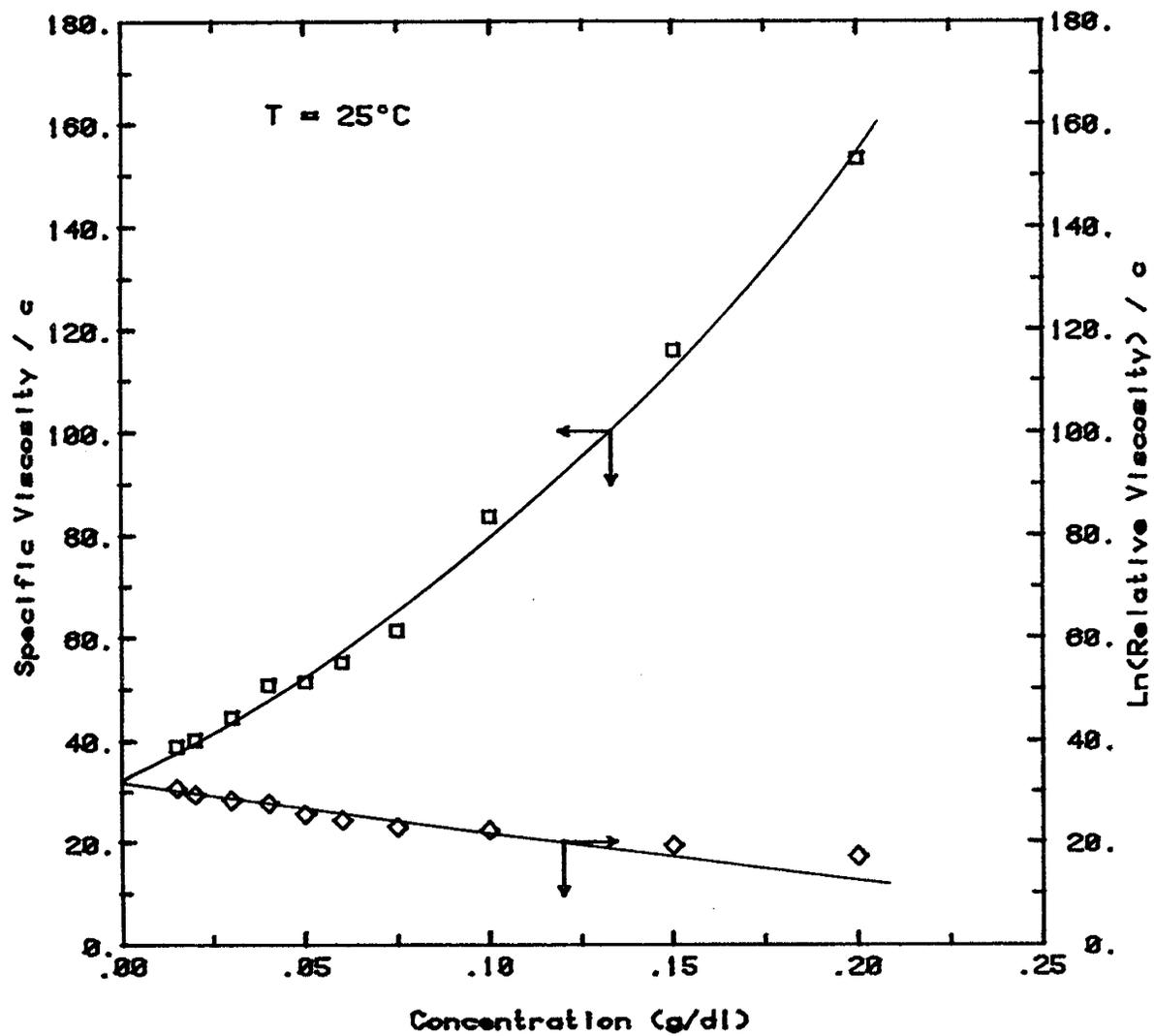
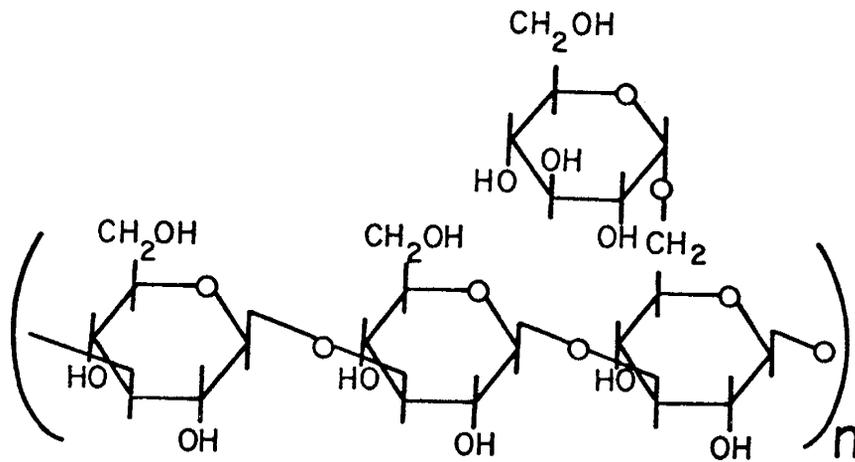


Figure 4. Intrinsic Viscosity of Cyanatrol 950 In 3% NaCl



STRUCTURE OF SCLEROGLUCAN

FIGURE 5

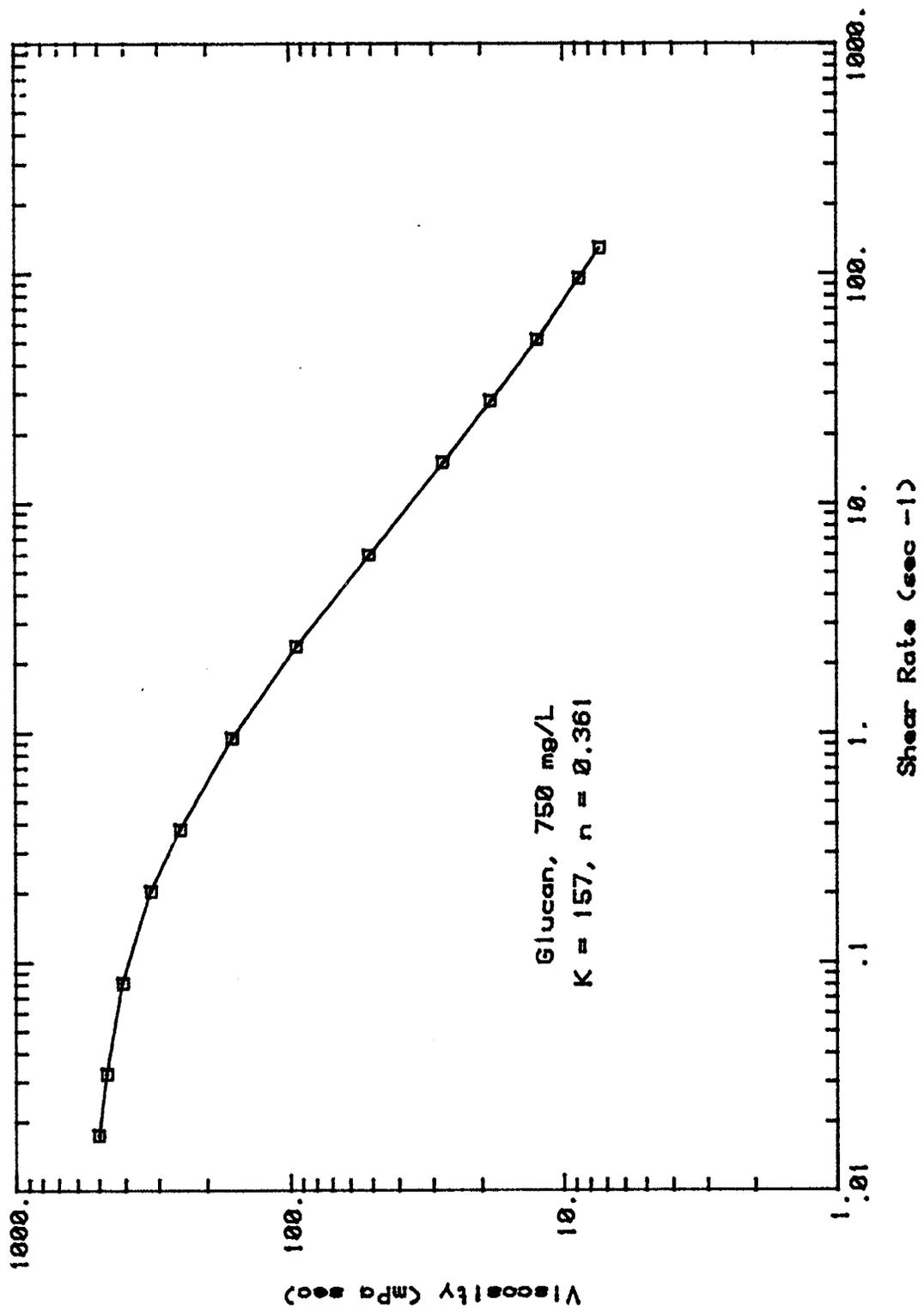


Figure 6. Rheogram of Glucan Polymer in 2% NaCl

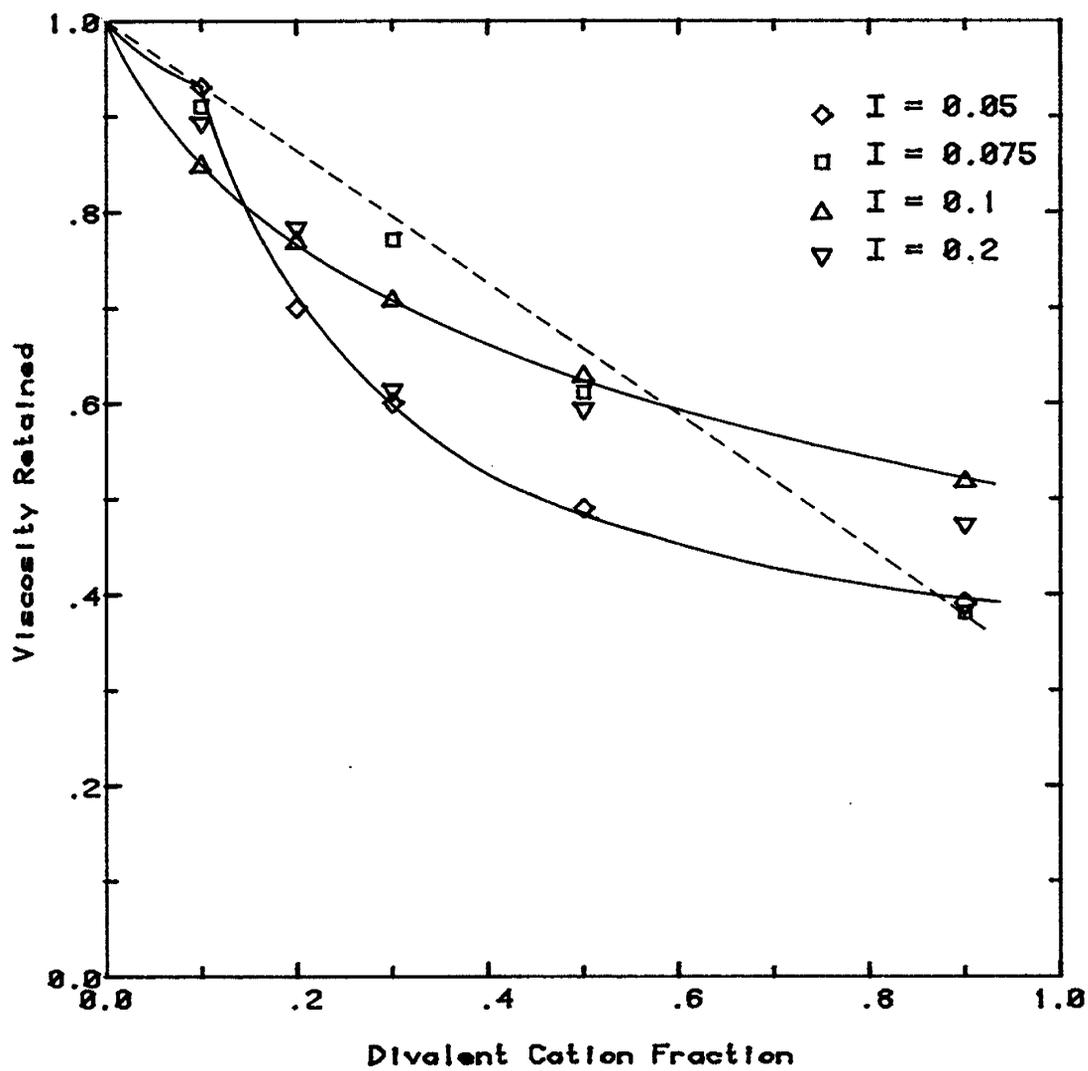


Figure 7. Effect of Calcium Ion on AMPS Homopolymer

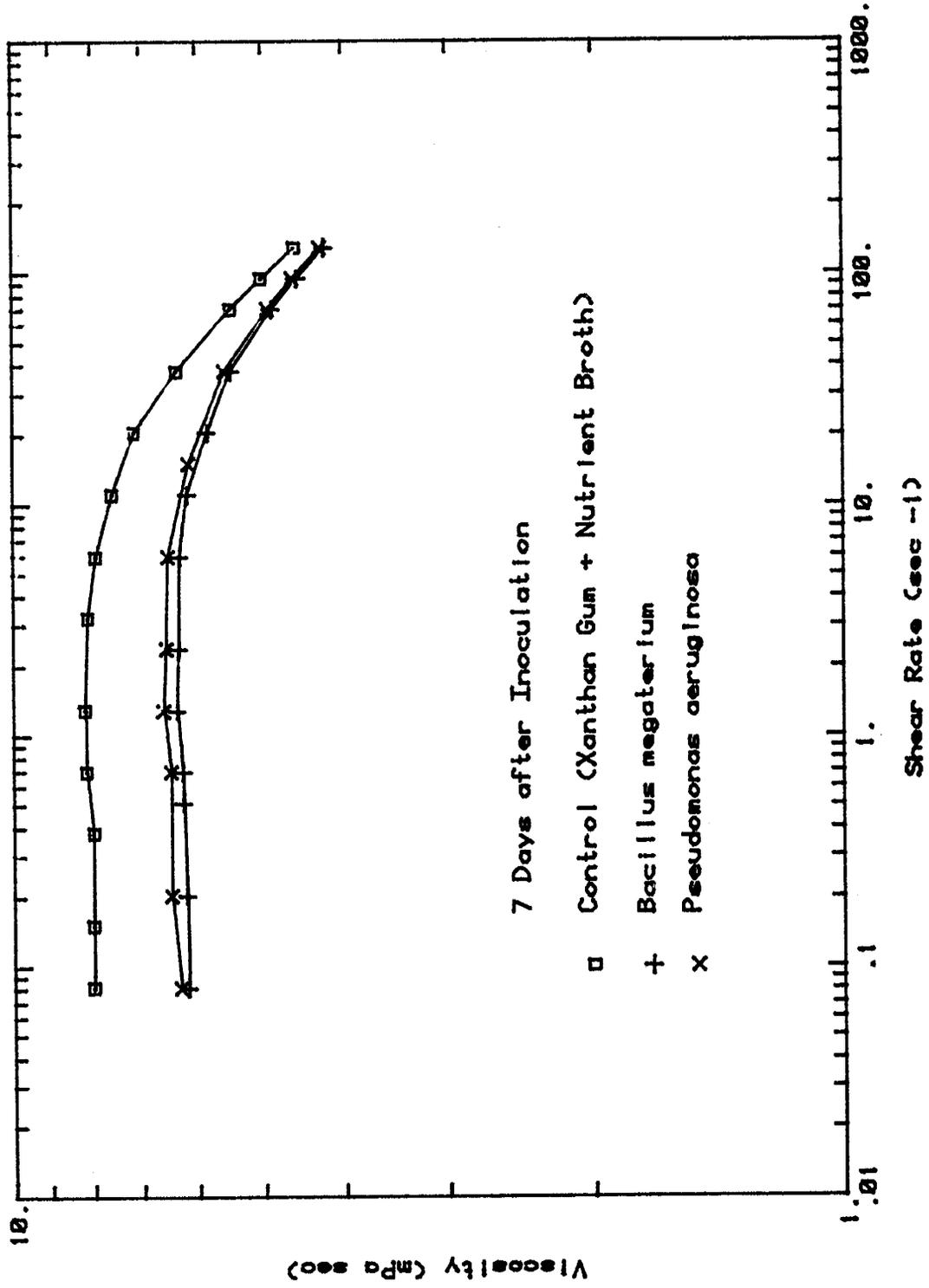


Figure 8. Effect of Some Aerobic Microbes on Viscosity of Xanthan Gum Solutions

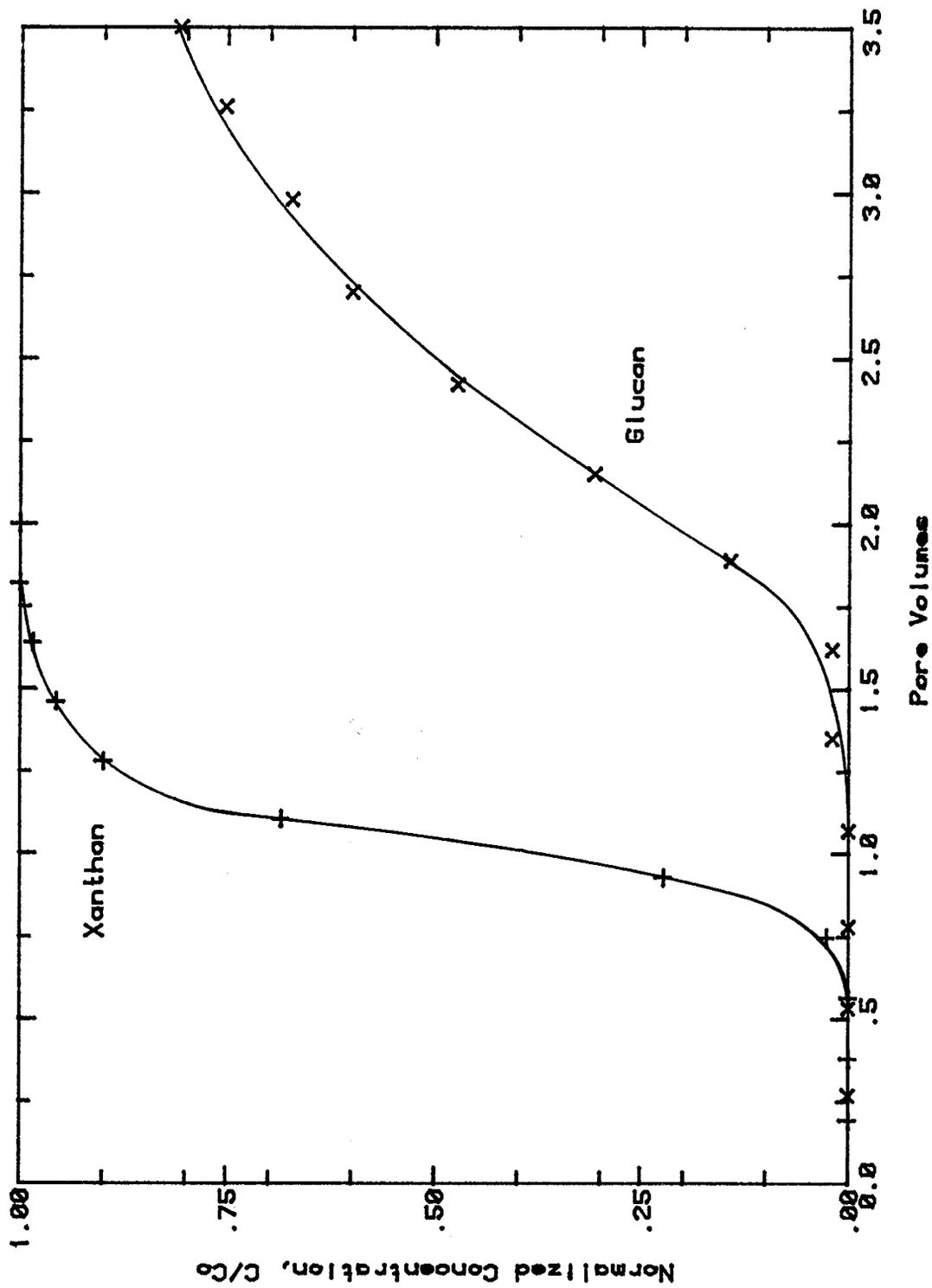


Figure 9. Comparison of Polymer Breakthrough Curves for Xanthan Gum and Scleroglucan

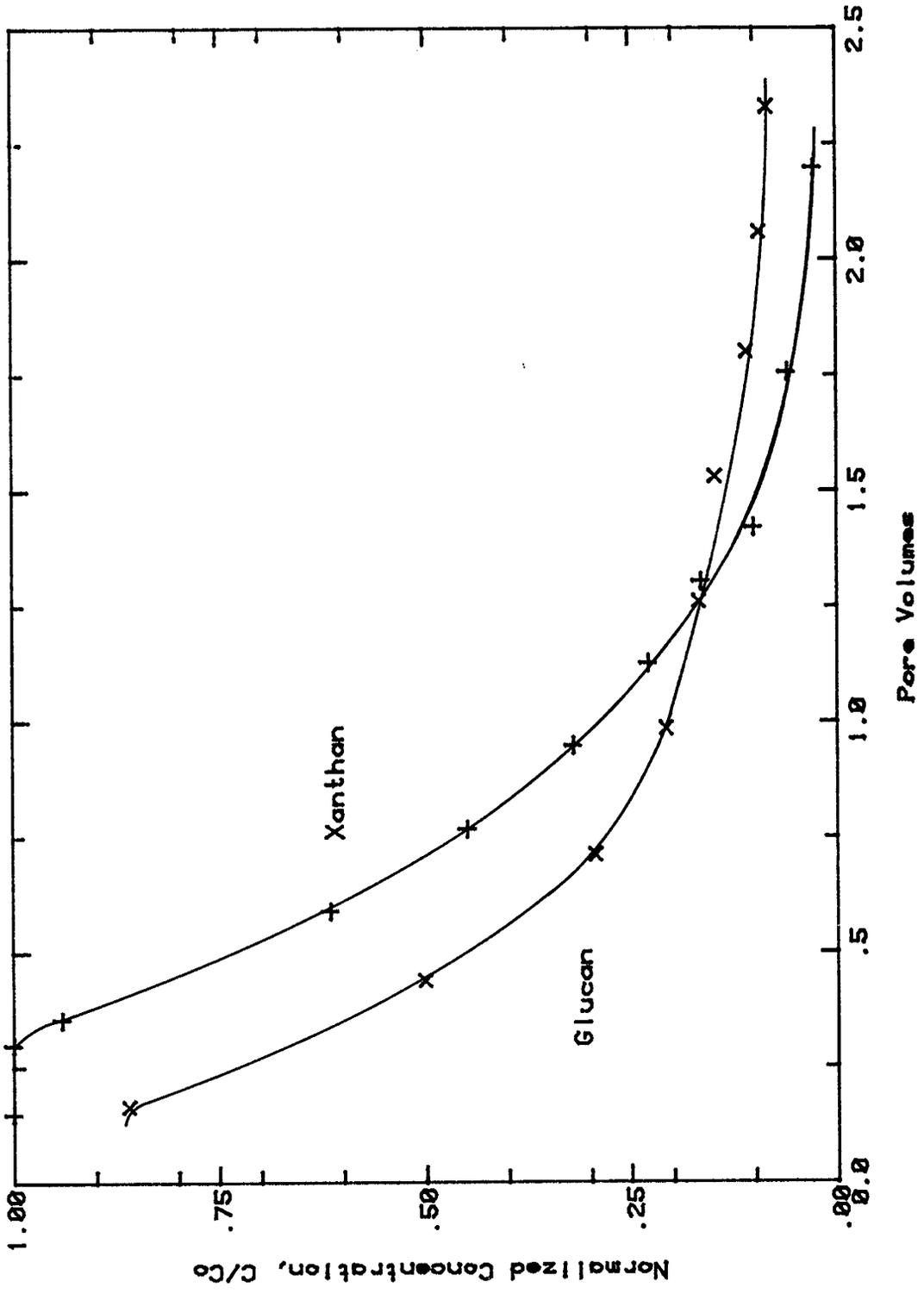


Figure 10. Brine Displacement of Xanthan Gum and Scleroglucan

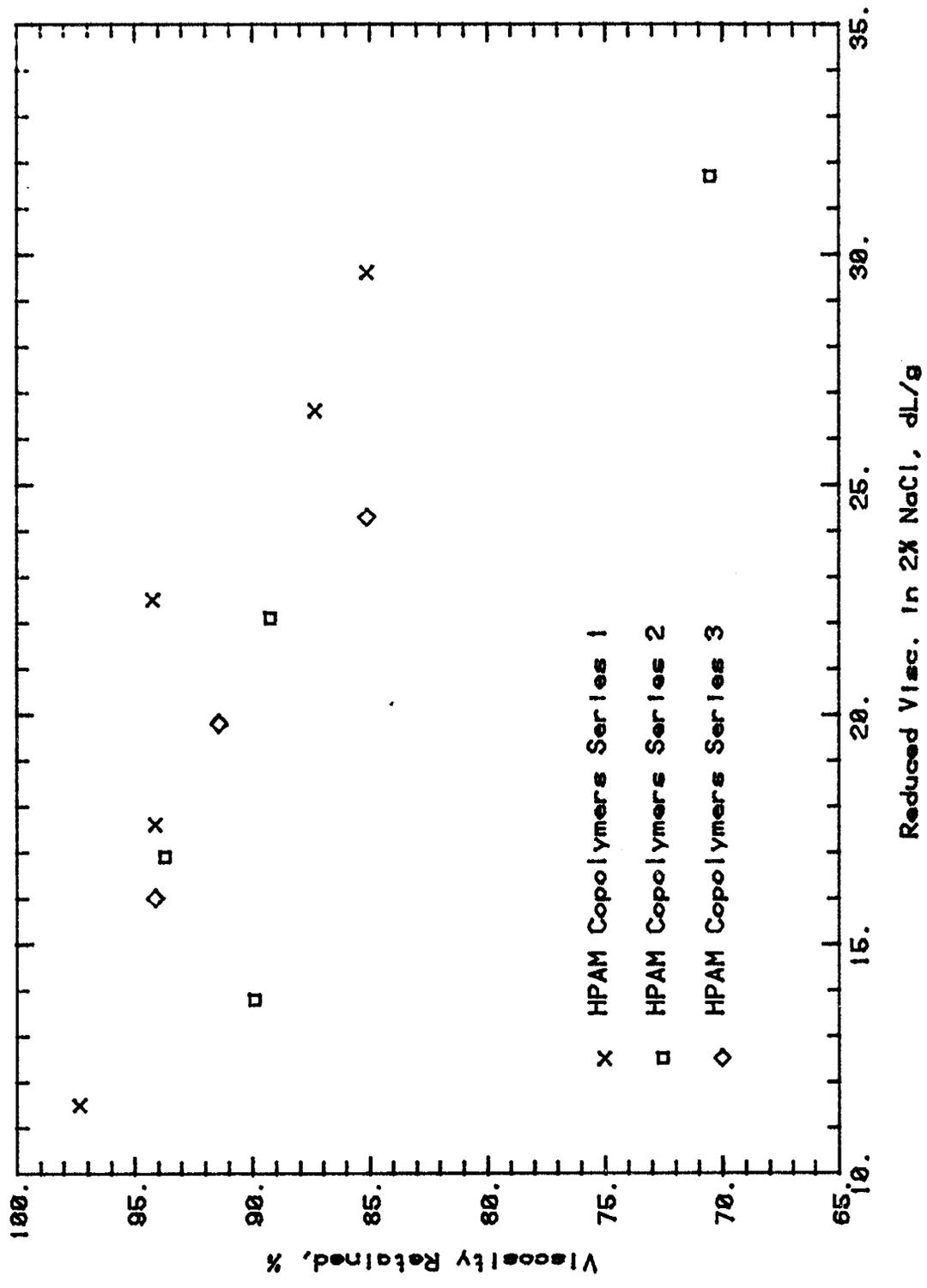


Figure 11. Viscosity Retained after Shear in 0.01% NaCl

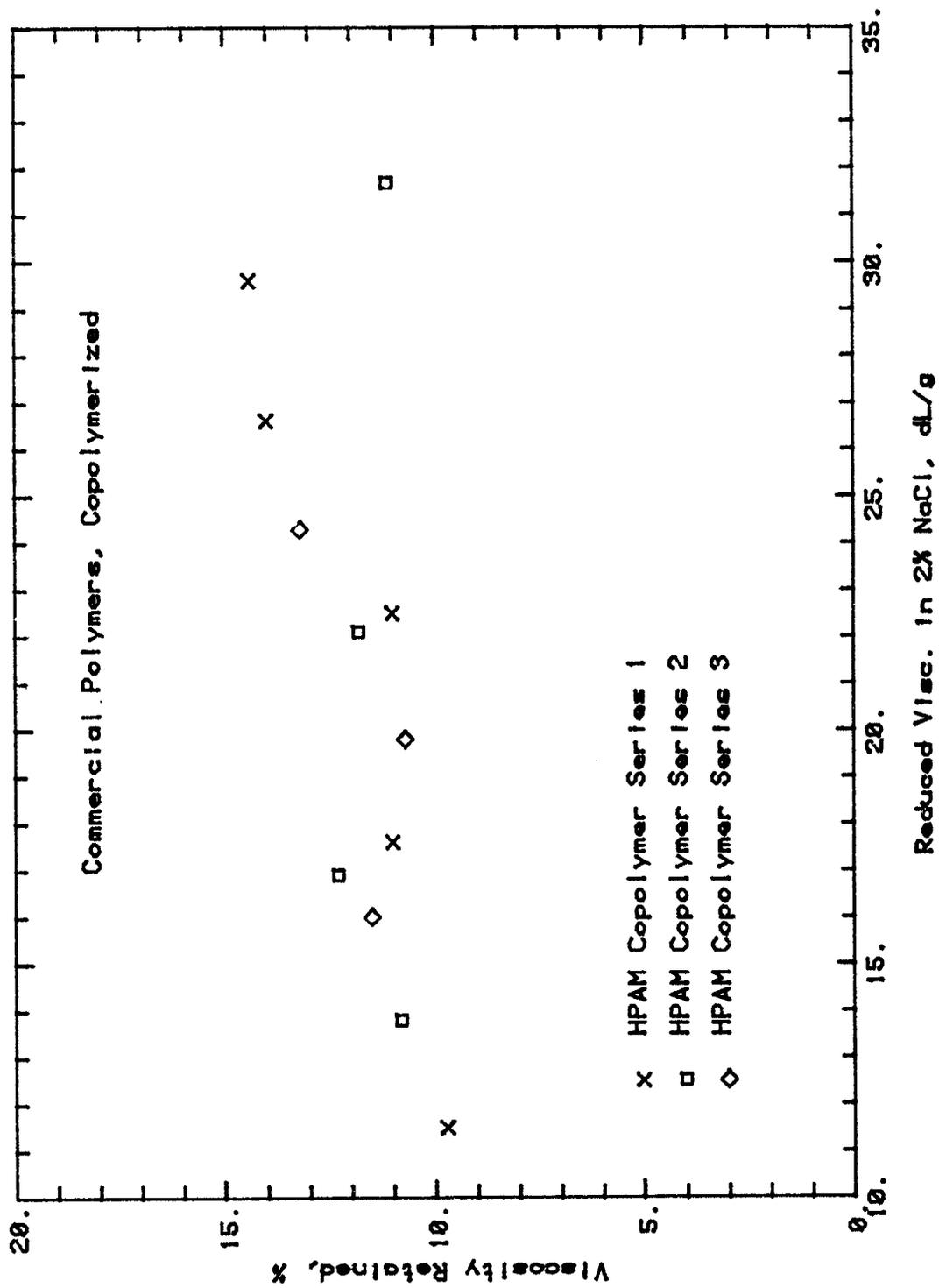
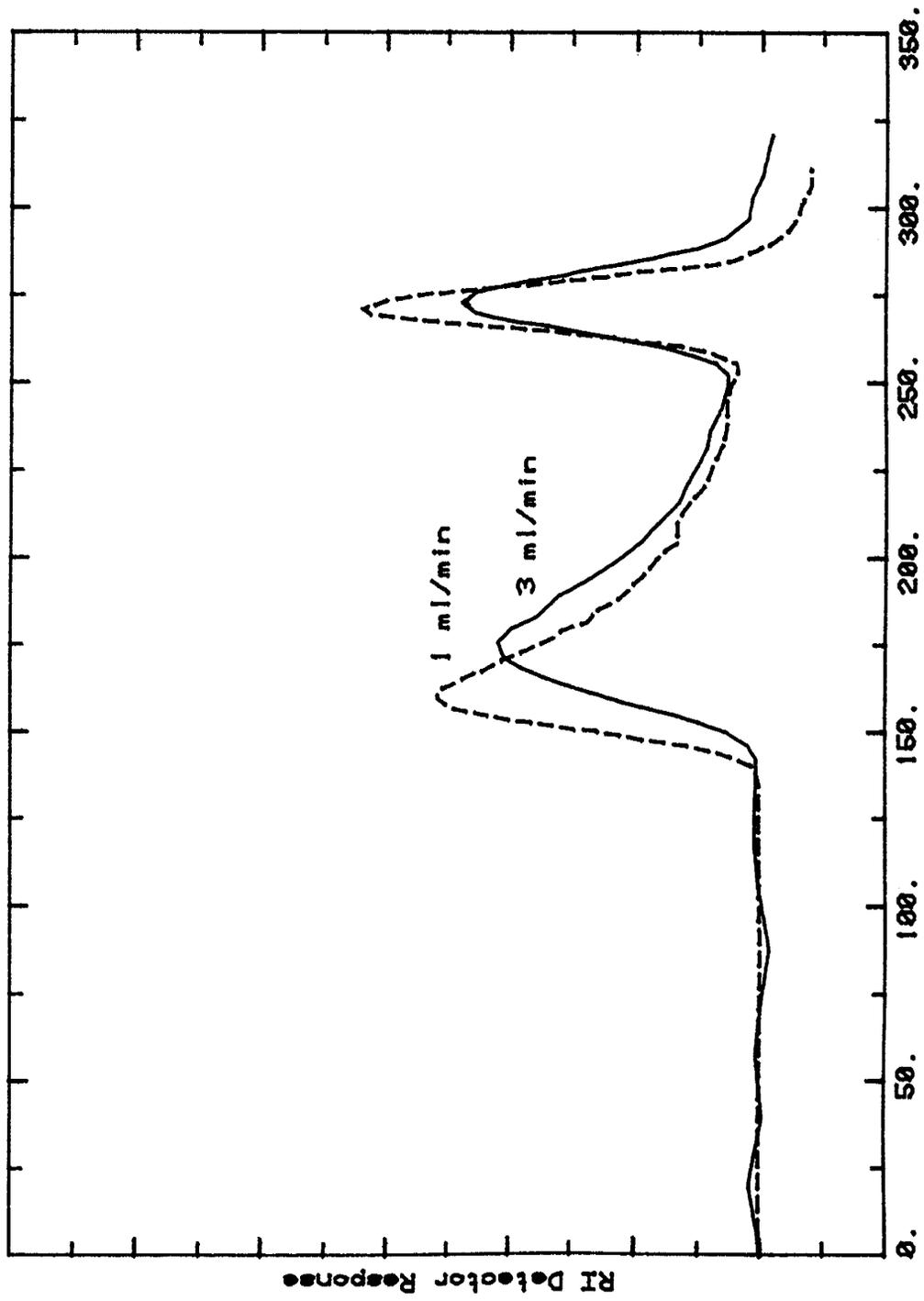


Figure 12. Viscosity Retained when Salinity is Increased from 0.01% NaCl to 2% NaCl



Retention Volume (ml)

Figure 13. Dow Pusher 700 Chromatograms

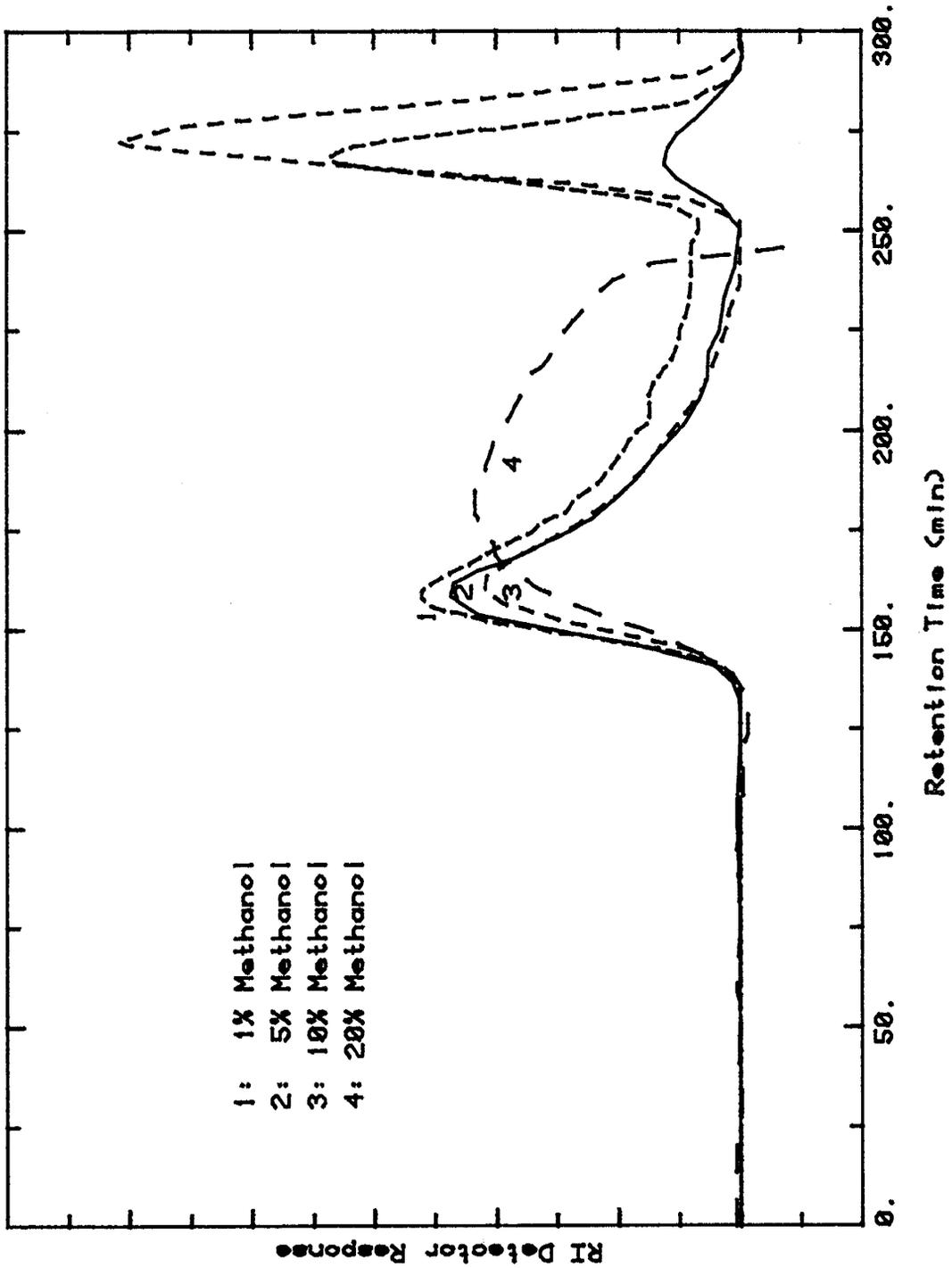
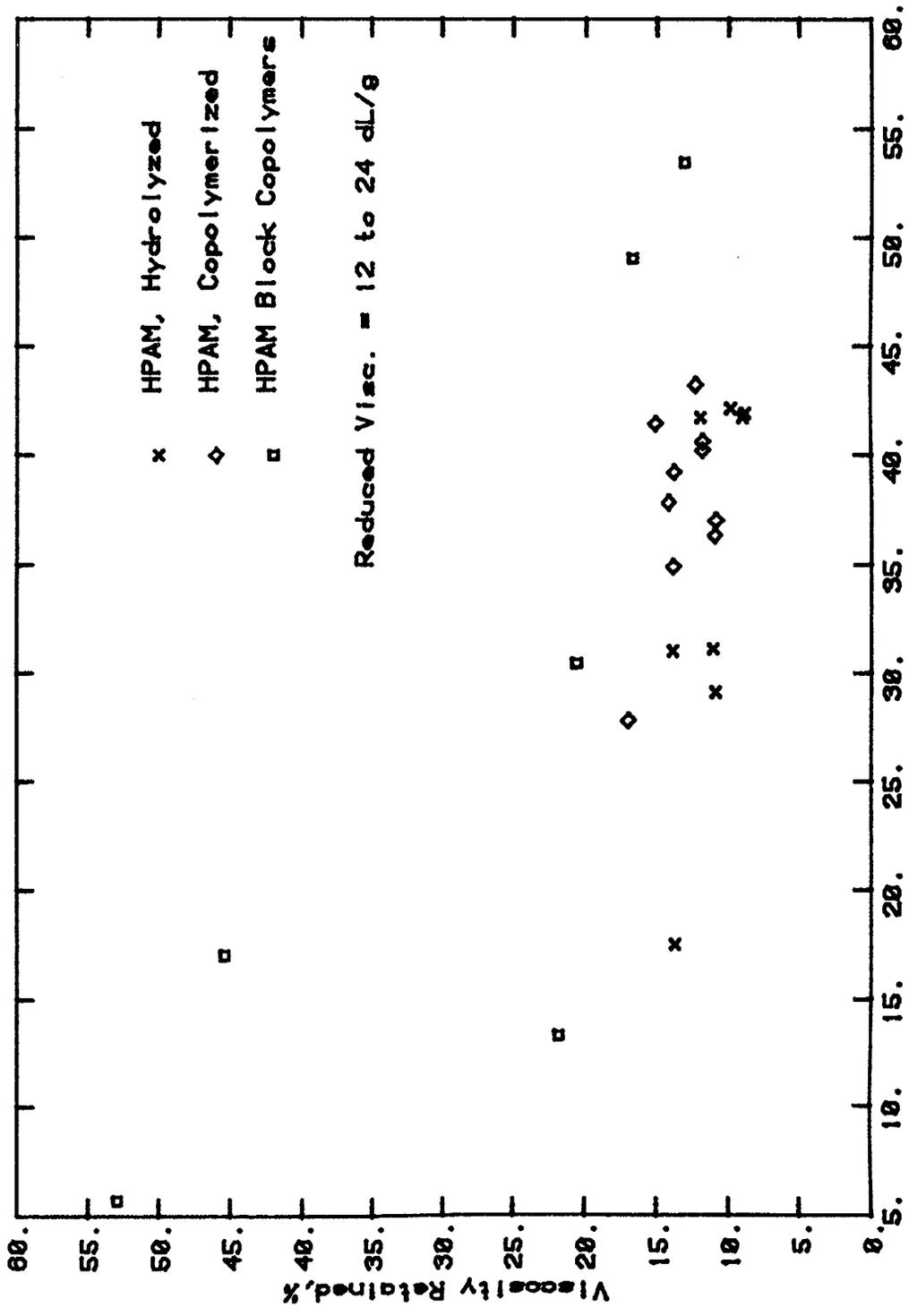


Figure 14. Dow Pusher 700, Varying Methanol Concentrations



Weight of Acid or Ammonium Salt, %

Figure 15. Viscosity Retained when Salinity is Increased from 0.01% NaCl to 2% NaCl

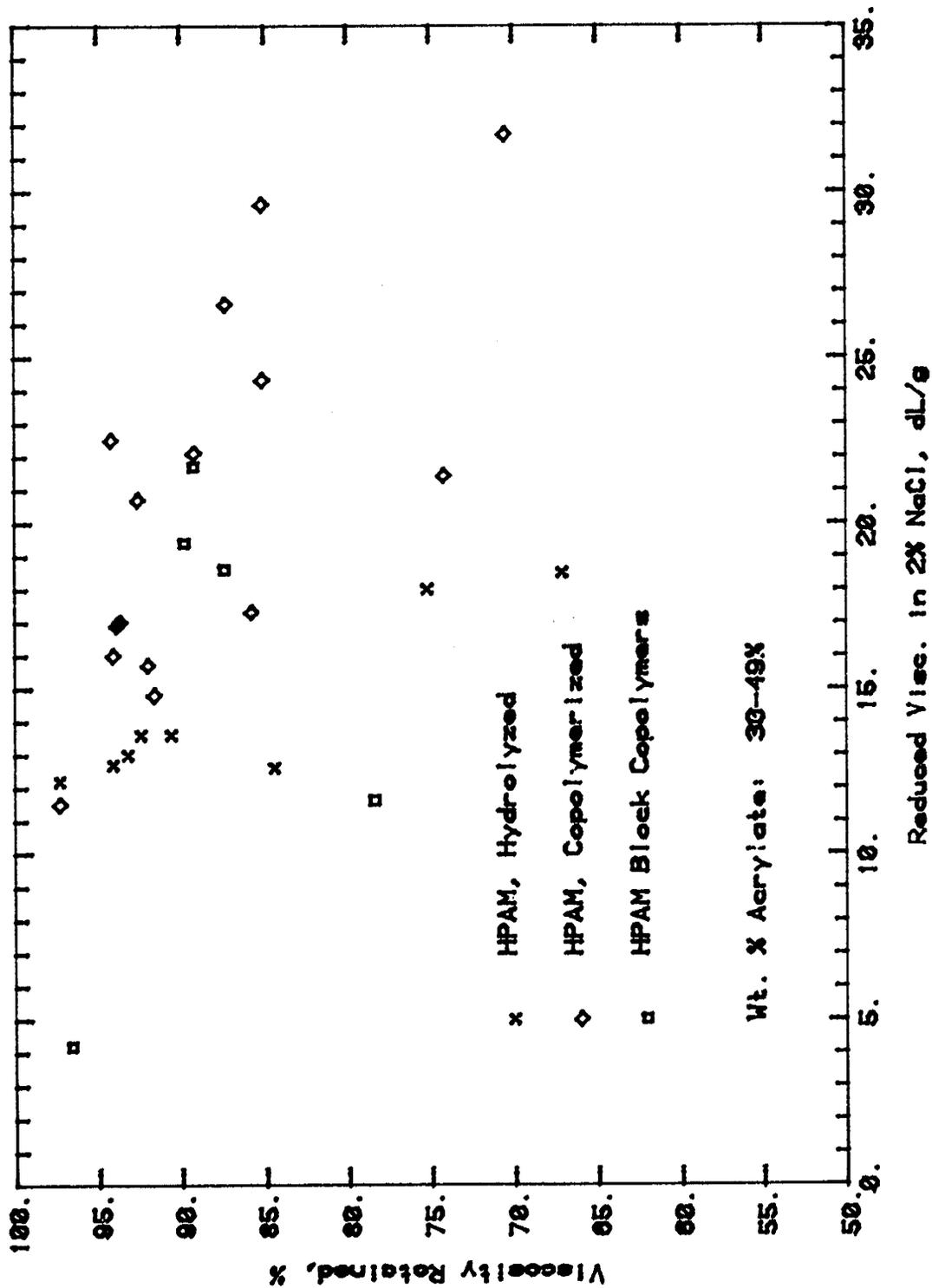


Figure 10. Viscosity Retained after Shear in 0.01% NaCl

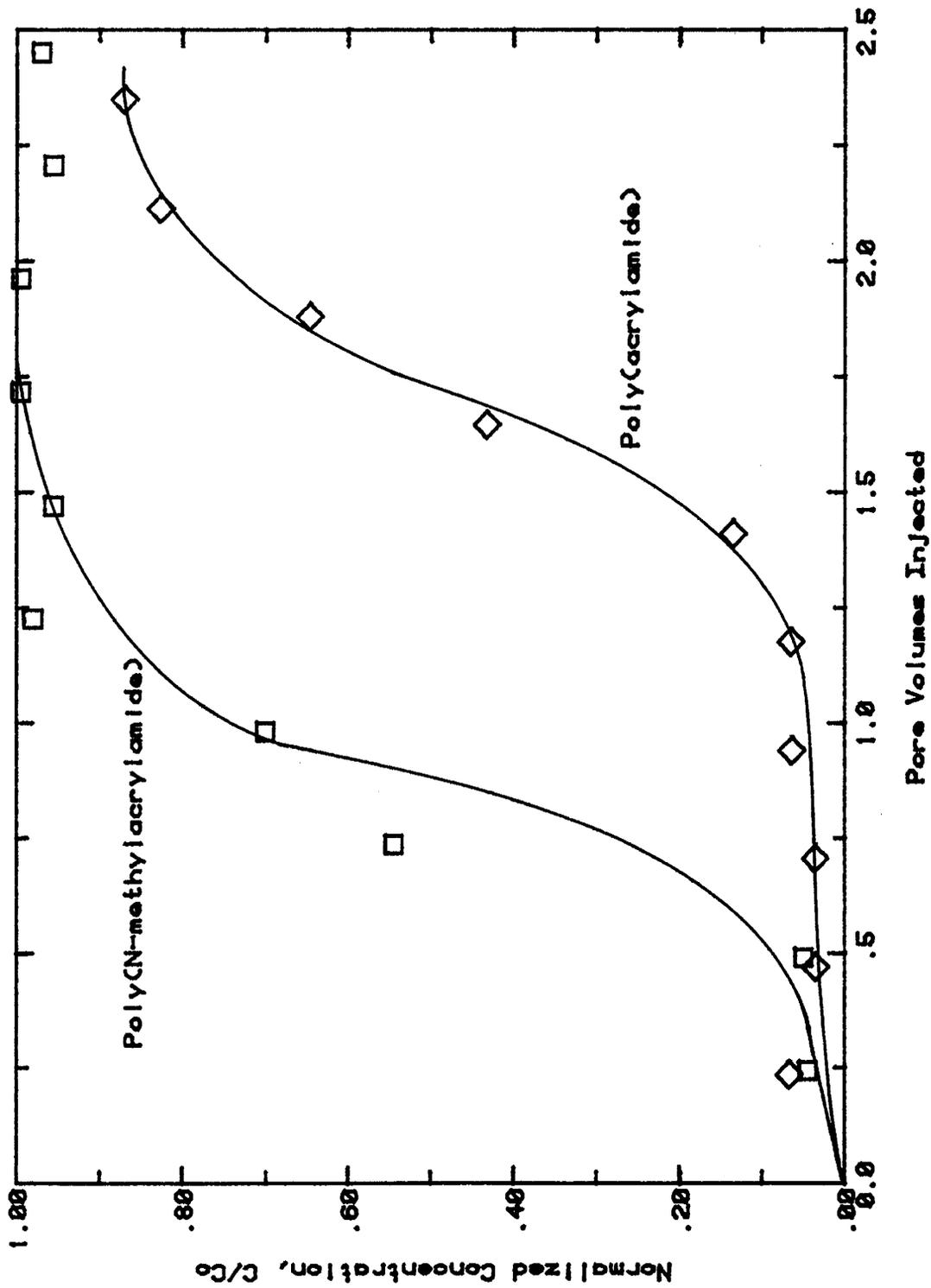


Figure 17. Polymer Breakthrough Curves for Homopolymer

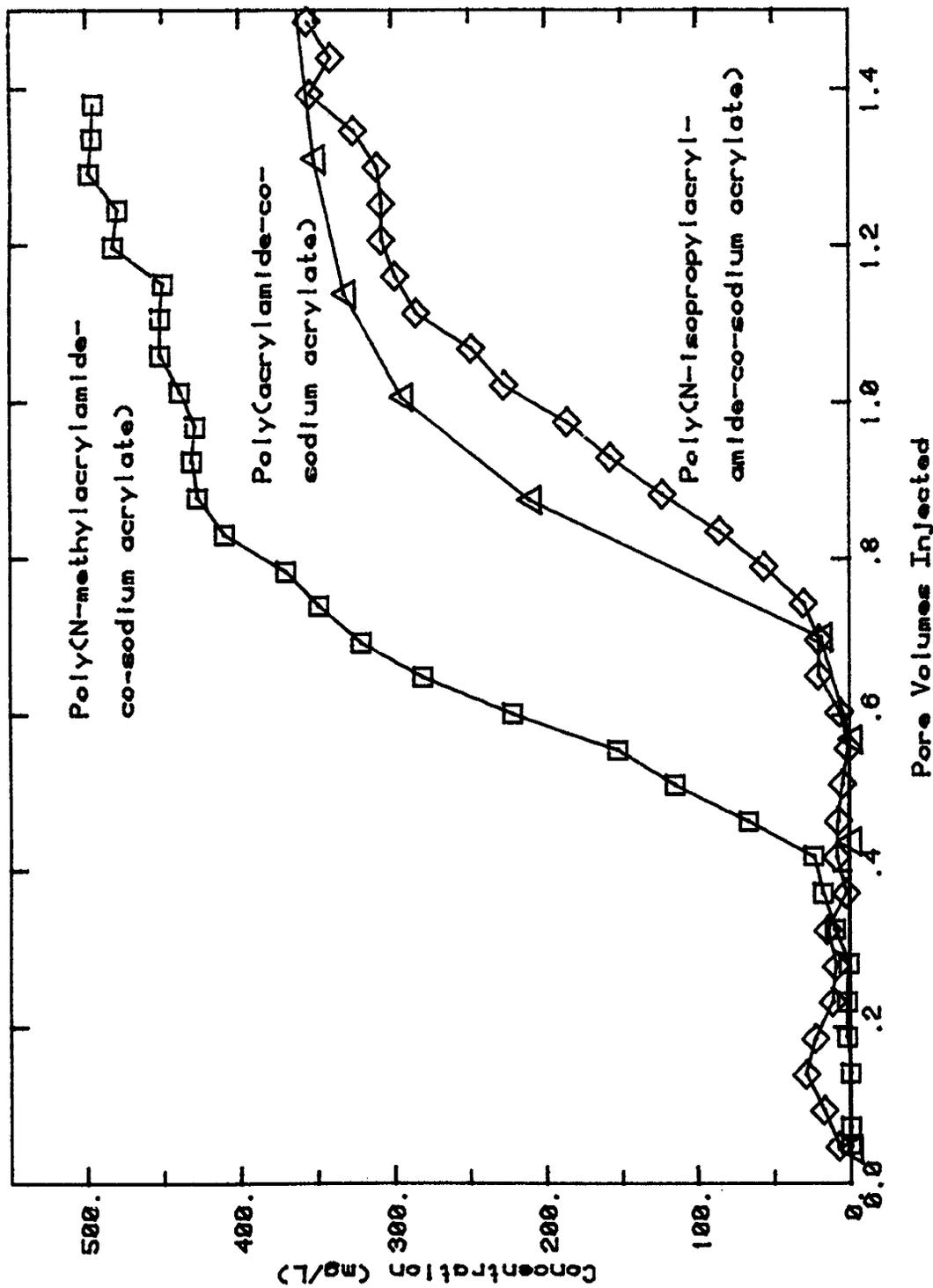
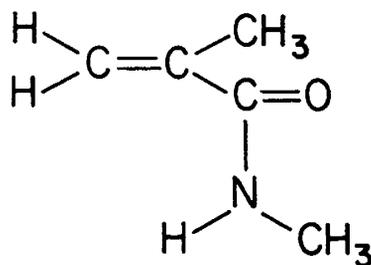


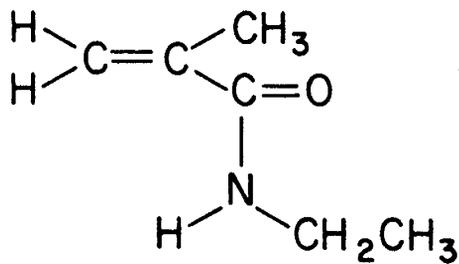
Figure 18. Polymer Breakthrough Curves for Copolymers

Figure 19

Hydrophobic N-Substituted Methacrylamides



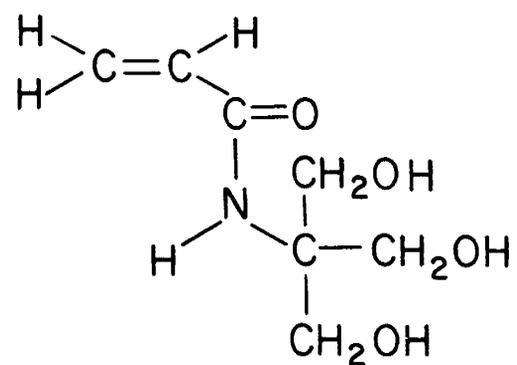
N-methylmethacrylamide



N-ethylmethacrylamide

Figure 20

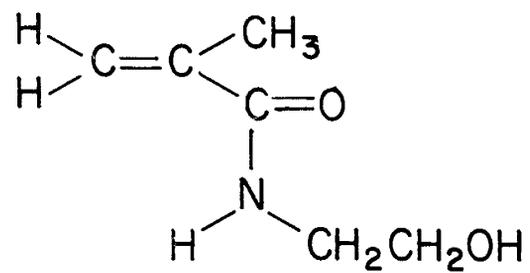
Trihydroxy N-Substituted Acrylamide



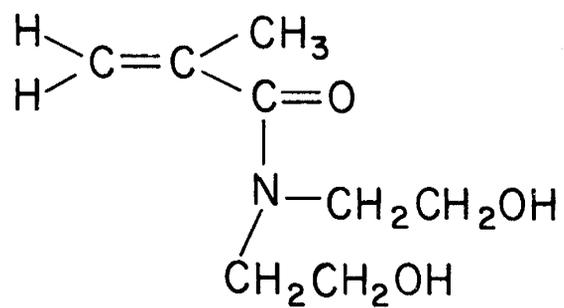
N-(tris(hydroxymethyl)aminomethane) acrylamide

Figure 21

Mono- and Dihydroxy N-Substituted Methacrylamide



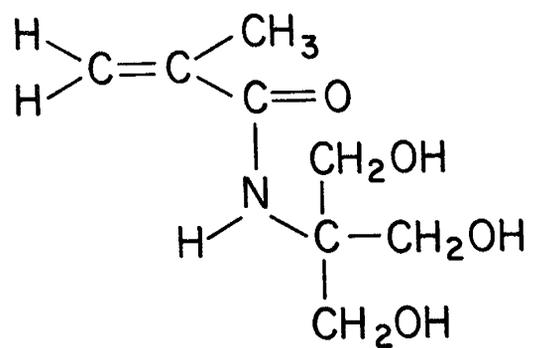
N-(2-hydroxyethyl) methacrylamide



N,N(di-2-hydroxyethyl) methacrylamide

Figure 22

Trihydroxy N-Substituted Methacrylamide



N-((trihydroxymethyl)methyl) methacrylamide

Figure 23

Copolymerization of Maleic Anhydride with Acrylic Acid

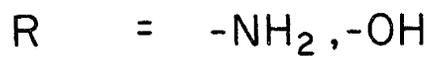
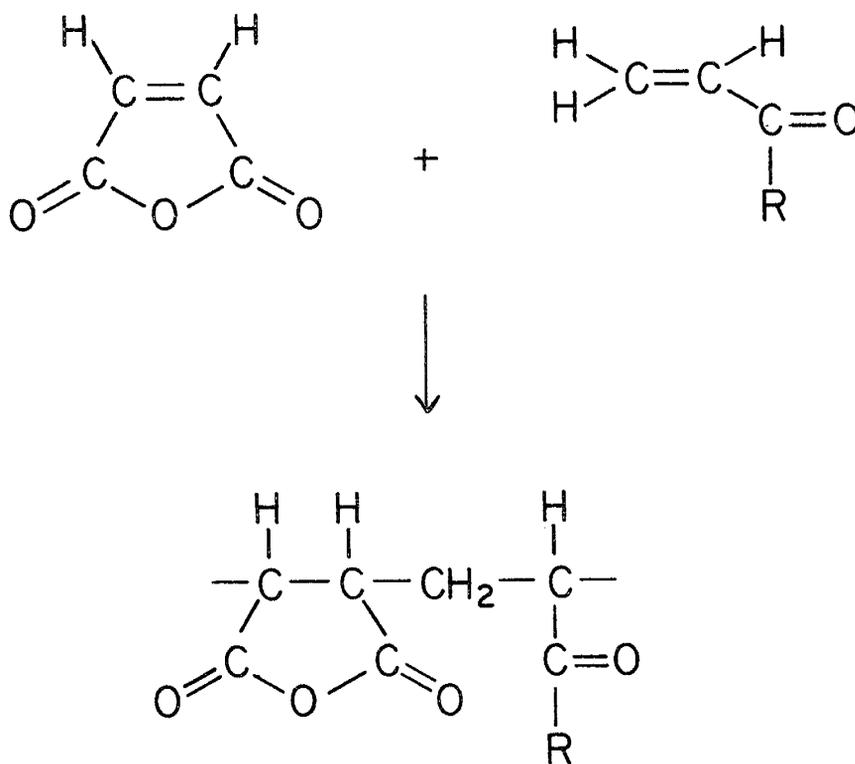


Figure 24

Copolymerization of Maleic Anhydride with Styrene

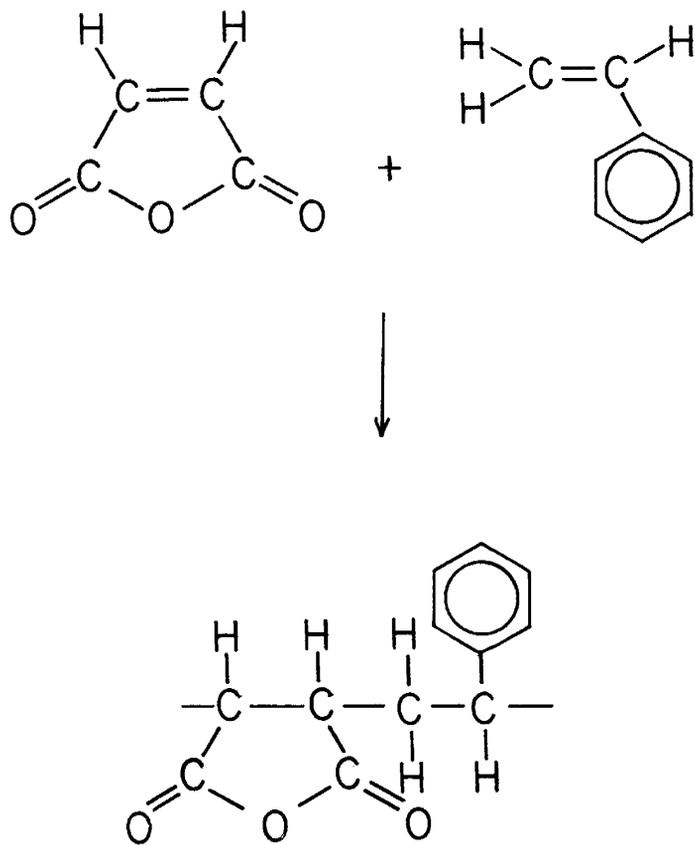
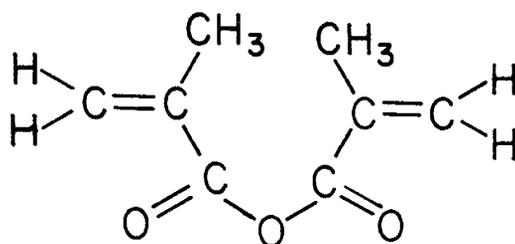


Figure 25

Copolymerization of Methacrylic Anhydride with Methacrylic Acid



+

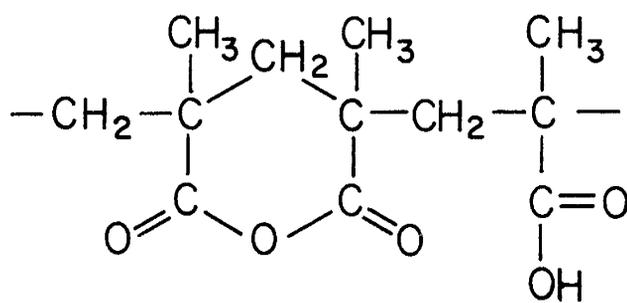
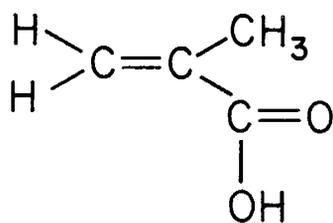


Figure 26

Copolymerization of Maleimide (and N-methyl or N-phenyl derivatives)  
with Acrylic Acid

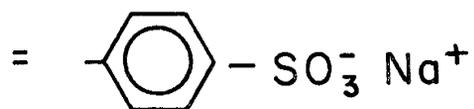
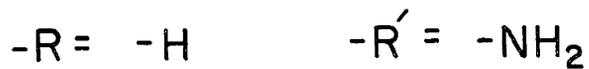
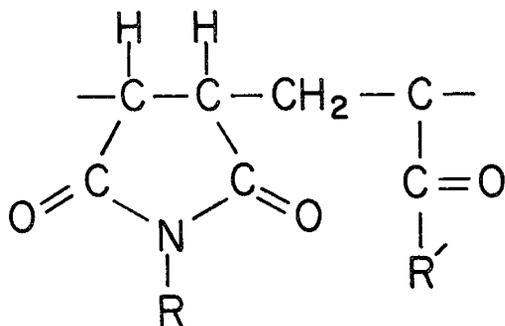
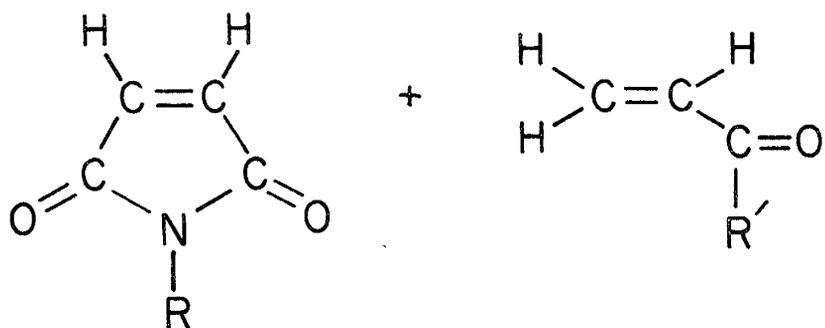
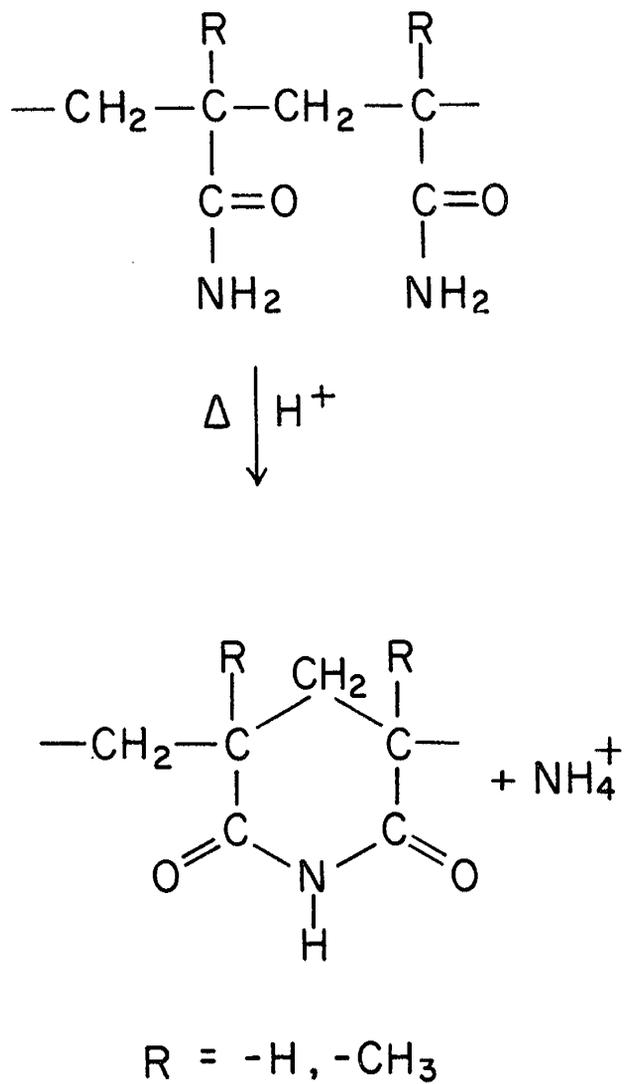
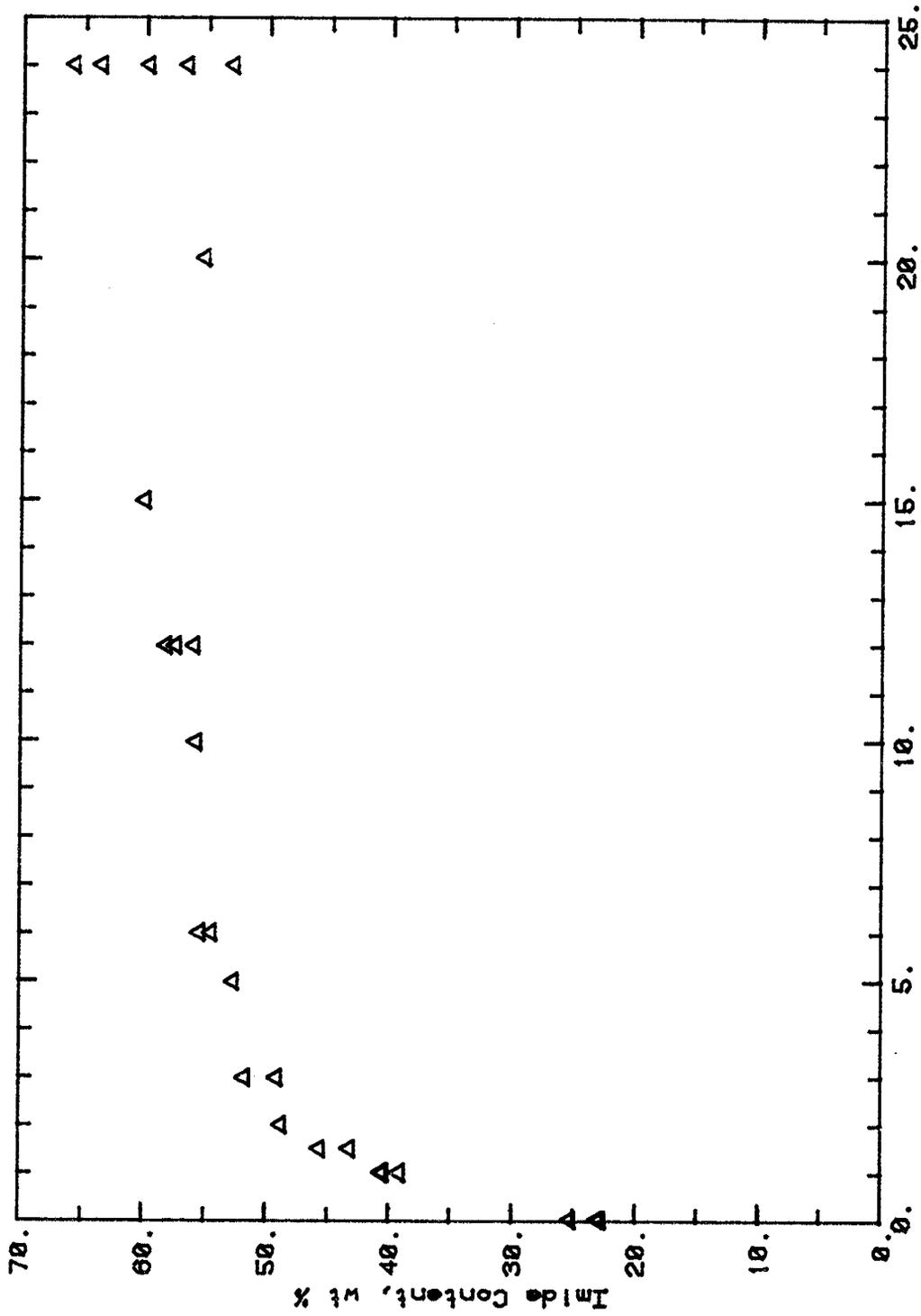


Figure 27

Acid Catalyzed Cyclo-Imidization of Methacrylamide





Time at 80°C ± 2°C, hours

Figure 28. Imide Formation Versus Time

Figure 29

Changes in Infrared Carbonyl Adsorption During Acid-Catalyzed Imidization

