WATER-SOLUBLE ACRYLAMIDE COPOLYMERS CONTAINING SUCCINIMIDE OR PYRROLIDINE RINGS

by

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Abstract

Acrylamide copolymers containing succinimide or pyrrolidine rings in the polymer backbone were prepared to determine if the bridging ability of polyacrylamide flocculants could be improved by stiffening the polymer chains. The five-membered rings were introduced by the free radical copolymerization of acrylamide with sodium N-(4-sulfophenyl)maleimide, p-maleimidobenzoic acid, sodium N,N-diallylsulfanilate, and N,N-diallylaniline. All of the copolymers were characterized by elemental analysis, photoacoustic FTIR, ^{13}C NMR, gel permeation chromatography, and viscometry. In addition, sufficient data were obtained for the copolymerization of acrylamide with sodium N-(4-sulfophenyl)maleimide to calculate reactivity ratios for that system.

Poly(acrylamide-co-sodium N-(4-sulfophenyl)maleimide) performed poorly compared to commercial partially hydrolyzed polyacrylamides (HPAM), when used to flocculate a 3% Ca-montmorillonite suspension at pH 4.0 and pH 7.5. Poly(acrylamide-co-sodium N-(4-sulfophenyl)malemide), poly(acrylamide-co-p-maleimidobenzoic acid), and poly(acrylamide-co-sodium N,N-diallylsulfanilate) behaved as dispersants instead of flocculants, when tested on a 3% kaolinite suspension at pH 4.6. The molecular weights of the copolymers were too low for polymer bridging between the

clay particles to occur. Although the copolymers were reasonably effective dispersants, they were not as effective as a commercial polyacrylate dispersant unless used at dosages at least four times higher than that of the commercial dispersant.

Poly(acrylamide-co-N,N-diallylaniline) was not sufficiently water-soluble to be useful as a flocculant.

It was concluded from the results of the polymerization and flocculation experiments that effective high molecular weight anionic flocculants can not be prepared by the copolymerization of acrylamide with maleimide or diallyl monomers. The copolymerization rates of maleimide and diallyl monomers are too low.

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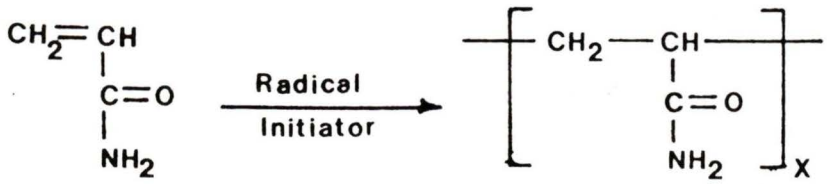
Dedicated to the memory of Dr. W. M. Leung.

1. Introduction

1.1. Polyacrylamide and Acrylamide Copolymers

Polyacrylamide and acrylamide copolymers are amongst the most commonly used and commercially important water-soluble polymers. These polymers have a wide range of applications including use as flocculants, dispersants, and viscosity control agents.[1]

Polyacrylamide can be prepared by the free radical polymerization of acrylamide monomer 1 in the absence of oxygen.[1-3]



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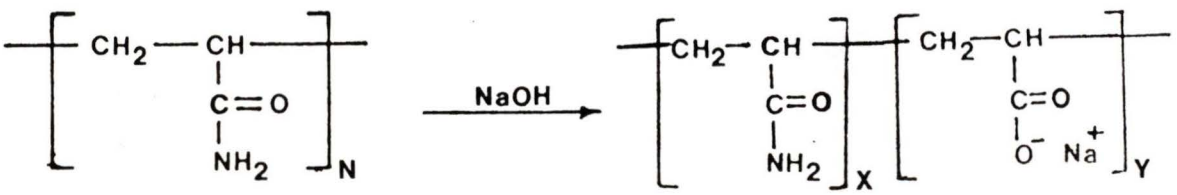
Normally, the polymerization is carried out in water using water-soluble peroxide initiators, or in water-in-oil emulsions using oil-soluble peroxide or azo compounds as initiators. Weight average molecular weights as high as 4 to 20 million can be achieved, depending on the reaction conditions. Lower molecular weights can be obtained by polymerizing acrylamide in the presence of chain transfer

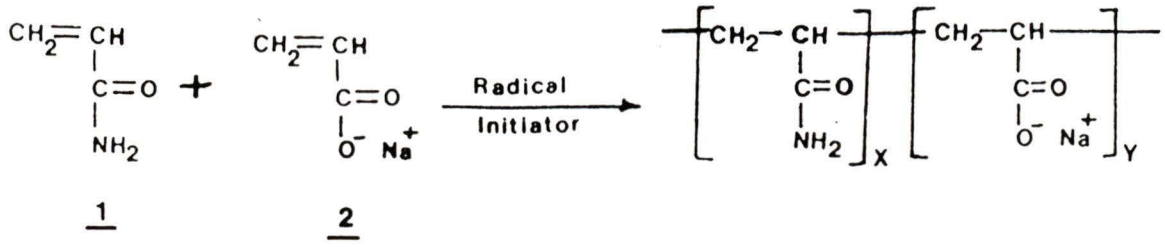
agents such as alcohols or by using high initiator concentrations. Polyacrylamide is classified as a nonionic homopolymer since it contains no ionic functional groups and consists of a single repeating monomer unit.

Acrylamide copolymers are prepared either by the chemical modification of polyacrylamide or by copolymerization of acrylamide with a second type of vinyl monomer.[4] These copolymers can be nonionic, cationic, or anionic, depending on the functional groups present in the second type of repeating unit.

Most anionic acrylamide copolymers contain either carboxylate or sulfonate functional groups.[4] The most frequently used anionic acrylamide copolymer is poly(acrylamide-co-acrylic acid), which can be prepared by the polymerization of acrylamide, followed by hydrolysis,



or by the copolymerization of acrylamide 1 with acrylic acid or acrylate salts 2.



1 2

High molecular weight (>1 million) anionic acrylamide copolymers with low to intermediate charge densities (ca. 5 to 50 mole % anionic) are useful as flocculants and viscosity control agents, whereas low molecular weight (<100,000) anionic acrylamide copolymers with high charge densities (ca. >50 mole % anionic) are used as dispersants.[4-6]

The majority of the commercial cationic copolymers contain quaternized amine functional groups.[4] Copolymers containing unquaternized tertiary amine groups are available, but are less commonly used since the charge and solubility of both the monomers and polymers are pH-dependent. Most cationic acrylamide copolymers contain about 10 mole % or less cationic monomer units. Unlike anionic copolymers, all molecular weight ranges of cationic copolymers usually act as flocculants since the solid particles in the majority of suspensions bear negative surface charges.

1.2.Copolymerization Reactivity Ratios[7]

The composition of an acrylamide copolymer, like any copolymer, is usually found to be different than that of the comonomer feed from which it was produced. The ratio and distribution of the comonomer units along the copolymer chains depends on the relative reactivities of the comonomers for that particular copolymer system and can not be predicted from the homopolymerization rates of the individual monomers.

Copolymerization of two monomers, M_1 and M_2, results in two propagating species: one is a polymer chain with an M_1 unit at the propagating end, and the other is a polymer chain with an M_2 unit at the propagating end. The two propagating species can be represented as $M_1^{\cdot}$ and $M_2^{\cdot}$. If it is assumed that the reactivity of the propagating species depends only on the monomer unit at the end of the polymer chain, then four reactions are possible.

$$M_1^{\cdot} + M_1 \xrightarrow{k_1} M_1^{\cdot}$$
$$M_1^{\cdot} + M_2 \xrightarrow{k_2} M_2^{\cdot}$$
$$M_2^{\cdot} + M_1 \xrightarrow{k_3} M_1^{\cdot}$$
$$M_2^{\cdot} + M_2 \xrightarrow{k_4} M_2^{\cdot}$$

If the assumption about the reactivity of the propagating species is valid, then the mole fraction of monomer M_1 in the copolymer is given by

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (1\text{-}1)$$

where f_1 and f_2 are the mole fractions of monomers M_1 and M_2, respectively, in the feed, while r_1 and r_2 are parameters known as the copolymerization reactivity ratios of M_1 and M_2, respectively. (See reference 6 for derivation of Eq. 1-1).

The copolymerization reactivity ratio r_1 is defined as the ratio of the rate constant of the propagating chain $M_1^{\cdot}$ adding monomer M_1 to the rate constant for the same chain adding monomer M_2. Reactivity ratio r_2 is defined in an analogous manner.

$$r_1 = \frac{k_1}{k_2} \qquad (1\text{-}2)$$

$$r_2 = \frac{k_4}{k_3} \qquad (1\text{-}3)$$

An r_1 value greater than unity means that the propagating polymer chain $M_1^{\cdot}$ preferentially adds monomer M_1, whereas a value less than unity means that $M_1^{\cdot}$ preferentially adds monomer M_2. Usually, r_1 and r_2 are evaluated by determining the copolymer composition for several different

comonomer feed compositions. The extent of copolymerization should represent no more than 5 to 10% conversion since the composition of the comonomer feed will vary with the extent of polymerization.

A variety of methods of data analysis may be applied to determine the reactivity ratios of a new copolymer system.[7] The Kelen-Tudos[8] linear graphic method was selected for use here to determine the reactivity ratios of sodium N-(4-sulfophenyl)maleimide 3 and acrylamide 1 because it is easy to use and is a significant improvement on the older Fineman-Ross[9] and Mayo-Lewis[10] methods. Also, it seems to be a commonly used method.[11]

1.3. Flocculation

One of the major uses of polyacrylamides is for solid-liquid separations in mineral processing and wastewater treatment. A specific application in this area is the removal of coal fines and clays from the wastewater of coal washing plants.[12] Coarse particles (>100 μm) can be separated by gravity settling alone, but the finer particles (<100 μm) may settle very slowly, or not at all, without the assistance of flocculants because of their size, density, and surface properties.[13]

Most particles tend to develop a net negative surface charge when dispersed in water.[3,13,14] The negative charge arises from the ionization of surface functional groups such

as hydroxyl and carboxyl groups, isomorphic substitution in the solid lattice, and preferential adsorption of ions or ionizable species.[3] Cations in solution near a particle migrate to the solid surface, forming a rigid cation layer (Stern layer) around the particle that partially neutralizes the negative surface charge. The surface charge is not completely neutralized because the cations in the Stern layer prevent additional cations from diffusing to the surface of the particle by mutual electrostatic repulsion. Anions concentrate in the diffuse layer surrounding the positive Stern layer because of electrostatic attraction, giving the diffuse layer a net negative charge. The rigid Stern layer and the outer diffuse layer comprise what is referred to as the electric double layer (Fig. 1).

The stability of a solid particle suspension will depend on the sum of the electrostatic repulsive forces of overlapping electric double layers and attractive London-Van der Waals forces between the particles. In general, the repulsive forces predominate at intermediate distances while the attractive forces predominate at small and large distances.[14]

Cationic polymers destabilize suspensions of negatively charged particles by charge neutralization and, if the molecular weights are sufficiently high, by bridging.[3,15] Cationic polymers adsorb onto the negatively charged sites on particles in an aqueous suspension, thereby neutralizing

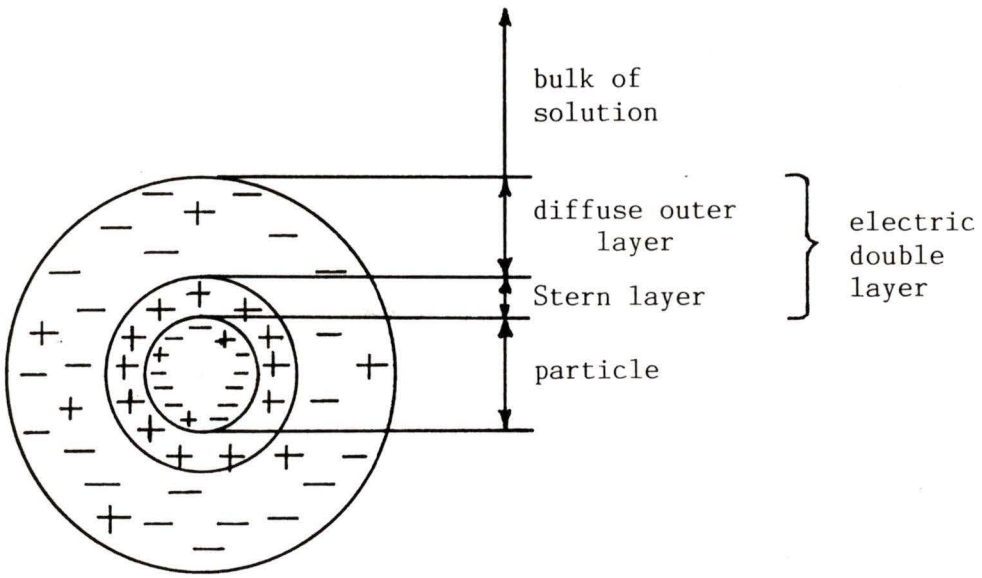


Fig. 1: Schematic illustration of the electric double layer surrounding a colloid partical suspended in solution.

the charges at these sites and allowing London-van der Waals attractive forces to cause the particles to aggregate. If the polymer is of a type with a high cationic charge density, it may not even be necessary for polymer to attach to all of the negatively charged sites of each particle to achieve overall neutralization of the surface charge of the particles. The high cationic charge density of the polymer can not only neutralize the charge on the sites that the polymer actually attaches to, but may also provide sufficient excess cationic charge to compensate for the remaining negatively charged sites. Thus the surface of each particle will be covered with positively and negatively charged patches that can bind electrostatically to the appropriately charged patches on the surfaces of the other particles (Fig. 2). When high molecular weight cationic polymers are used, the polymer chains may be sufficiently long that segments of a polymer chain can attach to the surface of one particle and extend to the surfaces of one or more other nearby particles, forming bridges that tie the particles together. Therefore, destabilization of the suspension by bridging also does not require complete neutralization of the negative surface charges of the particles.

The principle mechanism by which high molecular weight nonionic and anionic polymers destabilize most suspensions is by bridging (Fig. 3).[15-17] Bridging can occur only if

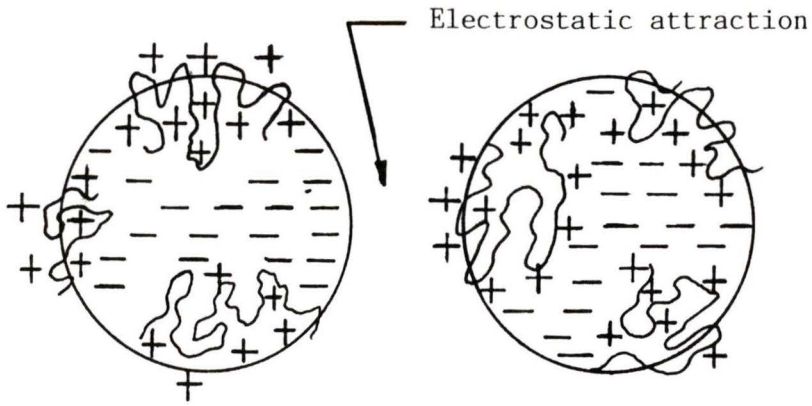


Fig. 2: "Electrostatic patch" mechanism for cationic flocculants.[15]

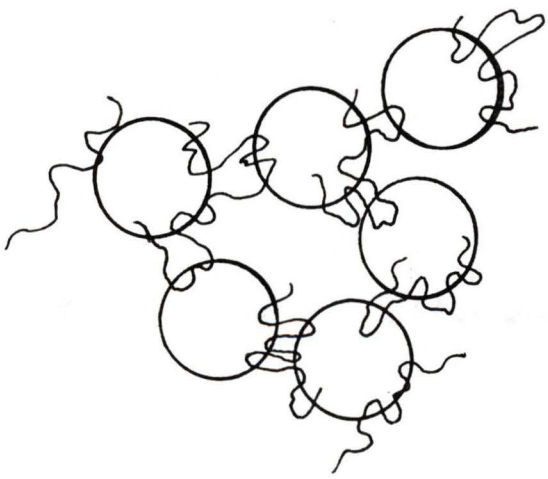


Fig. 3: Bridging mechanism.[15]

the distance that an adsorbed polymer chain extends from the surface of a particle is greater than the minimum distance of approach of the particles. Nonionic and anionic polymers can adsorb onto particles possessing a net negative surface charge by one or more of the following mechanisms: 1) hydrogen bonding, 2) London-van der Waals interactions, 3) complexation between anionic functional groups of the polymers and divalent or trivalent cations adsorbed on the surfaces of the particles, and 4) electrostatic bonding between the anionic functional groups and positively charged surfaces on the particles.[16,17]

1.4. Dispersion Stabilization

At low dosages cationic polymers destabilize suspensions by decreasing the negative surface charge of the particles. However, at high dosages cationic polymers can act as stabilizers by reversing the surface charge of the particles so that mutual repulsive forces again predominate over London-van der Waals attractive forces.[3,14] Also, under diffusion controlled conditions, the adsorption rate of polymers onto particle surfaces is usually faster than the collision rate of the particles.[15] Therefore, high dosages of polymer may saturate the surfaces of the suspension particles before polymer bridging can occur, or possibly cause steric stabilization (Fig. 4). Steric stabilization involves repulsive forces that prevent the

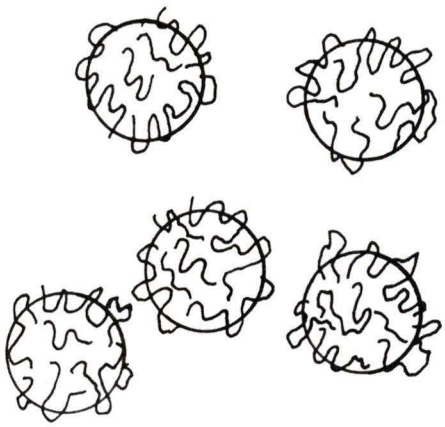


Fig. 4: Restabilization by surface saturation.[15]

interpenetration of the adsorbed polymer layers of particles. Interpenetration of the polymer layers is unfavourable if it results in losses in configurational entropy and solvation enthalpy of the polymer chains.

Low molecular weight anionic polyacrylamides usually tend to act as dispersants because the polymer chains are too short to form bridges between particles. Adsorption of the polymers increases the electrostatic repulsive forces between negatively charged particles, thus stabilizing the suspension.[5]

1.5 Purpose of Research

The purpose of this project was to determine if the introduction of five-membered rings into the backbone of acrylamide copolymers would improve the bridging ability of the copolymers.

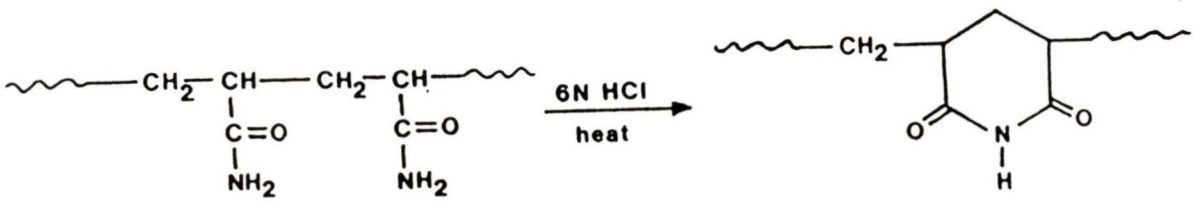
In order for polymer bridging between particles to occur, the absorbed polymer must extend far enough from the surface of a particle to attach to the surfaces of other particles, and there must be sufficient unoccupied surface available on the particles for adsorption of segments of extended polymer chains.[15] A study of the flocculation of clay suspensions by polyacrylamide by Michaels[18] showed that the bridging ability of the polymer increased with increasing polymer chain length. Also, bridging was greater if partially hydrolyzed polyacrylamide was used because

mutual repulsion between the carboxylate groups increased the hydrodynamic volume of the polymer, and the anionic character of the polymer reduced the degree of polymer adsorption on negatively charged particles, leaving unoccupied surface available for adsorption of segments of extended polymer chains.

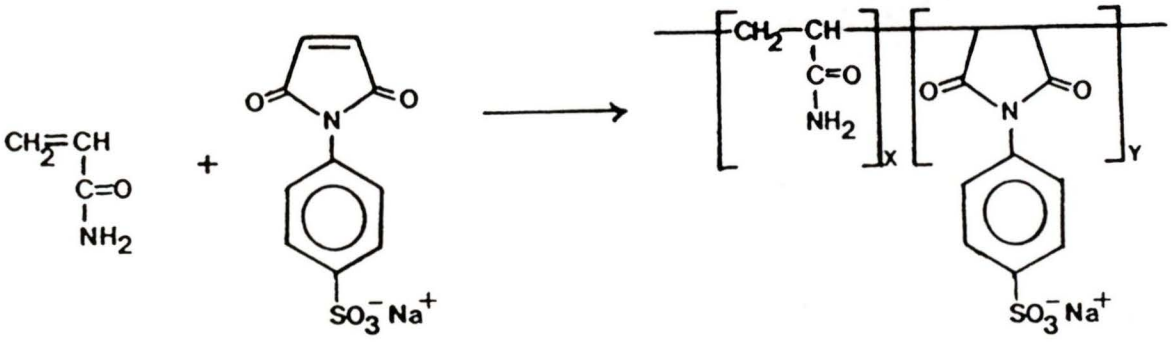
A problem with partially hydrolyzed polyacrylamide is the sensitivity of the polymer to pH, ionic strength, and divalent cations. The hydrodynamic volume of the polymer decreases with decreasing pH because of protonation of the carboxylate groups and decreases in the presence of inorganic salts because of shielding of the carboxylate groups by cations.[15,16] The reduction in the hydrodynamic volume can decrease the bridging ability of the polymer.[19] It also causes large losses in the viscosities of solutions containing partially hydrolyzed polyacrylamide, which is undesirable when the polymer is used as a viscosity control agent in enhanced oil recovery.[6,20] The presence of high concentrations of divalent cations such as calcium can also be a problem because the polymer may precipitate.

An alternative method of increasing the hydrodynamic volume of polyacrylamides may be to introduce five- or six-membered rings into the polymer chains to stiffen the polymer backbone.[20,21] Imide rings can be introduced by heating aqueous solutions of polyacrylamide in the presence of a strong acid to bring about intramolecular

cyclization.[20,22]



Imide rings can also be introduced by copolymerization of acrylamide monomer 1 with a water-soluble imide monomer such as sodium N-(4-sulfophenyl)maleimide (SPMI) 3.



1 3

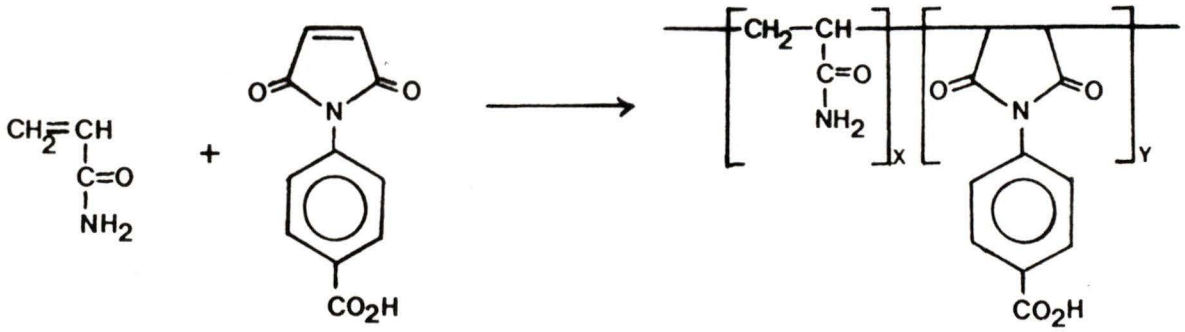
Shepitka et al.[23] reported that poly(acrylamide-co-sodium N-(4-sulfophenyl)maleimide) (PAMSM) was unsuitable for use as a viscosity control agent because the molecular weights obtained were too low and the imide ring was susceptible to hydrolysis. However, no experimental data were presented to support these statements. It was thought possible that even though the polymer was unsuitable for use as a viscosity control agent, the molecular weight of

copolymers with a low SPMI content (ca. 5 to 10 mole %) might be high enough for them to function as flocculants. Also, the low hydrolytic stability of the imide ring might not be a problem if these copolymers were used within a few hours or days after being dissolved in water, which is the recommended practice for most flocculants available as dry powders.[24]

One of the advantages of sulfonate-containing polymers compared to carboxyl-containing polymers is that the sulfonate groups remain ionized even at low pH. Also, unlike carboxylated polymers, sulfonate-containing polymers do not precipitate when used in aqueous suspensions containing high concentrations of divalent cations like calcium.[25] It was for these reasons that sodium N-(4-sulfophenyl)maleimide 3 was selected for copolymerization with acrylamide.

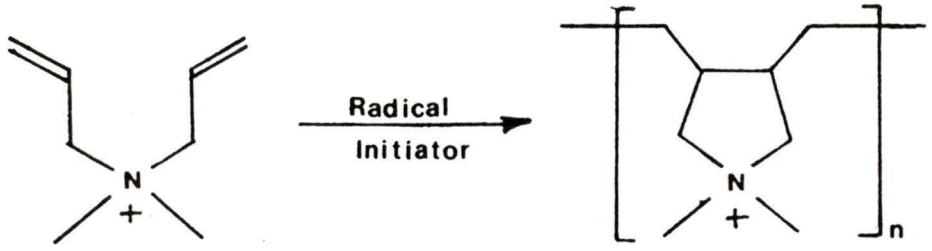
As the project progressed, however, the PAMSM copolymers that were prepared were found to be poor flocculants when tested on clay suspensions. It was thought that electrostatic repulsive forces between the strongly anionic sulfonate groups and the negatively charged surfaces of the clay particles may have been too large for sufficient adsorption of the PAMSM copolymers to occur. Therefore, acrylamide 1 was also copolymerized with p-maleimidobenzoic acid 4 to determine if replacement of the strongly ionic sulfonate group of the imide units with the weaker carboxyl

group would improve the performance of the acrylamide-imide copolymer.



1 4

A solution to the problem with the hydrolytic instability of the five-membered imide ring of the acrylamide-imide copolymers would be to copolymerize acrylamide with monomers that introduce pyrrolidine rings into the polymer backbone. Butler[26] and others[27] have shown that dimethylallylammonium salts 5 cyclopolymerize in the presence of free radical initiators to give linear, water-soluble homopolymers **containing pyrrolidine rings.**



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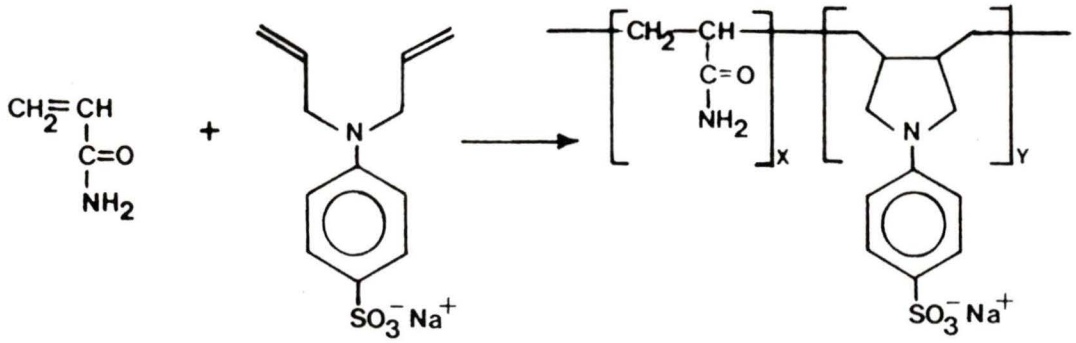
Dimethyldiallylammonium salts will also undergo cyclo-polymerization when copolymerized with acrylamide, yielding

cationic copolymers that are of commercial importance as flocculants.[28]

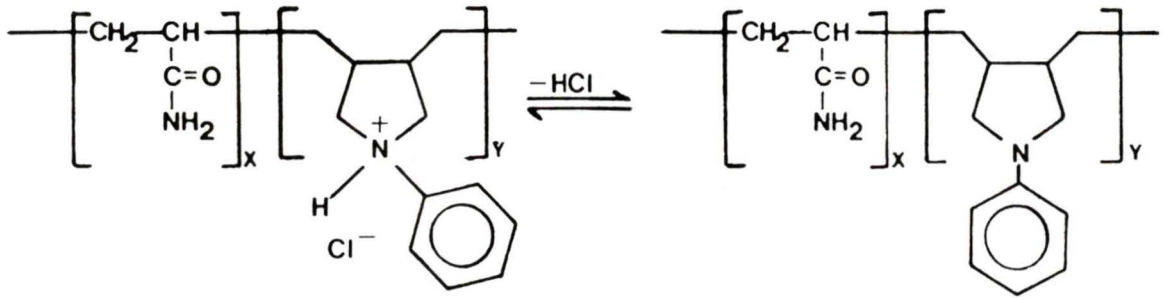
Numerous other diallyl monomers[29], including N,N-diallylaniline[30] 6, have also been shown to cyclopolymerize to give homopolymers containing pyrrolidine rings. Therefore, it seemed likely that sodium N,N-diallylsulfanilate 7 could also be copolymerized with acrylamide to produce an anionic copolymer.



1 7

Neither the homopolymer nor copolymers of sodium N,N-diallylsulfanilate 7 have been reported in the literature. There is one reference to the use of sodium sulfanilate monomer for the printing of textile fibers and fabrics.[31] No monomer preparative procedure was given.

Poly(acrylamide-co-N,N-diallylaniline) has not been reported in the literature, either. This copolymer would be expected to be nonionic at neutral and alkaline pH, and cationic at low pH.


CH2
CH
C=O
NH2
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N
Y
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CH
C=O
NH2
X
N
Y

1.6. Glossary of Acronyms

AM	- acrylamide
CMA	- p-carboxymaleanilic acid
CSA	- p-carboxysuccinanilic acid
DAA	- N,N-diallylaniline
DAS	- sodium N,N-diallylsulfanilate
HPAM	- partially hydrolyzed polyacrylamide
MBA	- p-maleimidobenzoic acid
PAM	- polyacrylamide
PAMDAA	- poly(acrylamide-co-N,N-diallylaniline)
PAMDAS	- poly(acrylamide-co-sodium N,N-diallylsulfanilate)
PAMMBA	- poly(acrylamide-co-p-maleimidobenzoic acid)
PAMSM	- poly(acrylamide-co-sodium N-(4-sulfophenyl)-maleimide)
SBA	- p-succinimidobenzoic acid
SPMA	- sodium N-(4-sulfophenyl)maleamic acid
SPMI	- sodium N-(4-sulfophenyl)maleimide
SPSA	- sodium N-(4-sulfophenyl)succinic acid
SPSI	- sodium N-(4-sulfophenyl)succinimide

2. Experimental

2.1. Chemicals

Fisher reagent grade acrylamide (m.p. found: 84-85°C (uncalib.), 84.2°C (DSC); Fisher lit. m.p. 84.2-84.8°C) was used without further purification. Aldrich sulfanilic acid (99%) was used to prepare sodium N-(4-sulfophenyl)maleimide 3 while BDH A.C.S. reagent grade sulfanilic acid (99+%) was used to prepare sodium N,N-diallylsulfanilate 7. Maleic anhydride (99%), allyl bromide (99%), acetic anhydride (A.C.S. reagent grade), potassium persulfate (A.C.S. reagent grade, 99+%), and p-aminobenzoic acid (99%) were from Aldrich. Methanol, acetone, glacial acetic acid, aniline, hydrochloric acid, sodium acetate, sodium hydroxide, sodium chloride, sodium carbonate, sodium bicarbonate, potassium orthophosphate, and potassium dihydrogen orthophosphate were all Fisher A.C.S. reagent grade. Denatured ethanol (15% methanol) was from Anachemia. Dimethylsulfoxide was Chemonix A.C.S. reagent grade and was distilled over CaH_2 under vacuum before use. Succinic anhydride (99%) was from Terochem. Azobisisobutyronitrile (AIBN) was from Fluka and was recrystallized twice from methanol before use. Hydrogen peroxide was BDH (ca. 60% w/v) that was standardized with sodium thiosulfate before use.

Copolymerizations of acrylamide with sodium N-(4-sulfophenyl)maleimide 3 were carried out under UHP nitrogen (<5

ppm O_2, Linde) that was first passed through two scrubbers filled with a solution made up from 1 g of sodium anthraquinone β-sulfonate (Aldrich), 8 g of sodium dithionite (Fisher), and 10 g of sodium hydroxide dissolved in 200 mL of water, and then passed through a third scrubber containing 200 mL of saturated aqueous lead acetate (Aldrich) to trap any hydrogen sulfide released by the oxygen scrubbers.[32] The oxygen scrubbers were not used for the copolymerizations of acrylamide with p-maleimidobenzoic acid 4, sodium N,N-diallylsulfanilate 7, and N,N-diallylaniline 6.

Percol 351 (nonionic polyacrylamide, 20 million mol. wt.) and Percol E24 (10% hydrolyzed polyacrylamide, 15 million mol. wt.) were obtained from Allied Colloids (Canada) Limited. Praestol 2935/73 (37% hydrolyzed polyacrylamide, 4 to 6 million mol. wt.) was obtained from Stockhausen Chemische.

Ca-montmorillonite used for the flocculation experiments was from Clay Minerals Source, Clay Minerals Repository, Apache County, Arizona, U.S.A. Kaolinite used for the flocculation and dispersion experiments was Hydrite R (lot 1745, 82% less than 2 microns) obtained from Georgia Kaolin Company, Inc., Union, N.J., U.S.A.

2.2. Equipment

All glassware used for copolymerizations was soaked in alcoholic NaOH, rinsed with de-ionized water, soaked in 4 N HCl, rinsed with de-ionized water again, and finally oven dried at 120°C.

The photoacoustic-FTIR (PAS-FTIR) spectra of the monomers and copolymers were recorded using a Bruker 113v FTIR spectrometer, together with a Princeton Applied Research Corporation Model 6003 photoacoustic cell and Model 6005 preamplifier. Most of the spectra were obtained by averaging 10 to 16 - 250 scan files, recorded at a resolution of 4 cm^{-1} with a mirror velocity of 0.059 cm/s. The carrier gas above the samples in the photoacoustic cell was nitrogen.

The infrared transmission spectra of monomers were run as KBr pellets (ca. 1 to 2 wt % monomer) using a Perkin-Elmer 283 infrared spectrometer.

The 90 MHz ^{1}H NMR spectra were run on a Perkin-Elmer R32 spectrometer using the HDO peak (δ 4.65) as the chemical shift reference. The 250 MHz ^{1}H and 62.9 MHz ^{13}C NMR spectra were run on a Bruker WM250 NMR equipped with a 5.9 T superconducting magnet, using tetramethylsilane (TMS, δ 0.0) as the external chemical shift reference. All spectra were run at ambient temperature.

The 50.3 MHz ^{13}C NMR spectra were run on a Bruker CXP200 spectrometer equipped with a 4.7 T superconducting

magnet. Other general operating details include a spectral width of 25,000 kHz, quadrature detection, 10 Hz filter width, and 12 bit digitizer resolution. Spectra were run using broad band proton decoupling, a pulse width of 12 μs (45 degrees), a dead time delay of 60 μs, and a recycle delay of 1 s, unless stated otherwise. A few drops of methanol (δ 49.3) were used as an internal chemical shift reference reference for the ^{13}C NMR spectra of the PAMSM monomers and copolymers. Tetrachloroethane-d_2 (TCE, δ 74.4) was used as an external chemical shift reference for the spectra of most of the other monomers and copolymers. The methyl resonance (δ 39.5) of DMSO was used as an internal reference for the spectra of the PAMMBA monomers run in that solvent.

Gel permeation chromatography was done using an apparatus consisting of a Waters 501 HPLC pump, a Rheodyne Model 7125 syringe loading sample injector with a 100 μL sample loop, a Spectra-Physics SP8400 variable wavelength detector set at 208 or 274 nm, and a Linear Instruments Corporation chart recorder. The PAMSM copolymers were chromatographed on a Varian 7.5 mm I.D. by 30 cm TSK-GEL G5000 PW column at a flow rate of 1.5 mL/min, using aqueous 0.005 M sodium sulfate as the mobile phase. The PAMMBA and PAMDAS copolymers were chromatographed on a 4 mm I.D. by 25 cm TSK-GEL TOYOPEARL HW-40S column at a flow rate of 0.4 mL/min, using aqueous 0.01 M Na_2SO_4 as the mobile phase.

Low angle laser light scattering measurements were made with a Chromatix KMX-6 spectrophotometer using a static cell. Refractive index increments (dn/dc) were measured with a Chromatix KMX-16 laser differential refractometer.

Viscosity measurements were made with Ubbelohde dilution viscometers on dilute aqueous polymer solutions containing 0.50 M NaCl at pH 7.0 $\pm$ 0.2 and 25.0 $\pm$ 0.05^{o}C.

Elemental analyses were carried out by D. Mahlow Ltd., Edmonton, Alberta.

Melting points were determined using a Reichert hot stage microscope equipped with an Omega Engineering Model 199 Chromel-Alumel thermocouple for temperature readout and are uncorrected.

Copolymer samples were freeze dried on a Labconco Model 75200 freeze drier.

Turbidities of clay suspensions were measured with a Hach Model 2100A turbidimeter that had an operating range of 0 to 1000 nephelometric turbidity units (NTU).

Additional information about the equipment and procedures used to characterize samples is given in the following experimental sections.

2.3. Poly(acrylamide-co-sodium N-(4-(sulfophenyl)maleimide) (PAMSM)

2.3.1. Preparation of Monomers

Sodium Sulfanilate 8

Sulfanilic acid (99%) sold by Aldrich was contaminated by purple impurities. Infrared spectroscopy indicated that the impurities consisted of polysulfonated, oxidized, or ring-fused aromatic amines because the intensities of the N-H stretching bands relative to the S=O stretching bands were less for the impurity than for sulfanilic acid.

Sulfanilic acid was converted to its sodium salt 8 and purified after preliminary smaller scale tests using the following procedure. Approximately 700 g (4.04 mol) of sulfanilic acid was dispersed in 2 L of distilled water. Then 161.7 g (4.04 mol) of NaOH dissolved in 250 mL of de-ionized water was added and the pH of the solution was adjusted to about 11 with 1.0 M NaOH. Powdered activated charcoal (50 g) was added and the solution was heated to near boiling for one hour. The hot solution was gravity-filtered, another 30 g of powdered activated charcoal was added and the solution was heated for a further hour. The hot solution was again gravity filtered and the filtrate evaporated to a slurry of about 300 mL on a rotary evaporator at about 60^{o}C. Next, the solution was heated to boiling and sufficient water (ca. 500-600 mL) was added to

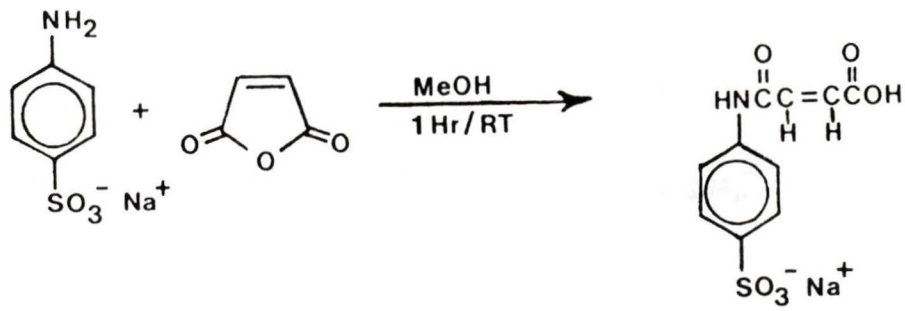
dissolve all of the sodium sulfanilate. The solution was allowed to cool slowly to room temperature and then placed in an ice-water bath. White crystals of the purified sodium sulfanilate 8 were filtered off, air dried overnight, and then dried in a vacuum oven at 100°C for 24 hours.

^{13}C NMR (50.3 MHz, H_2O, int. ref. MeOH): 115.4 (aromatic C's ortho to $-NH_2$), 127.2 (aromatic C's meta to $-NH_2$), 132.6 (aromatic C para to $-NH_2$), 149.9 (aromatic C ipso to $-NH_2$).

ANAL. Calcd. for $C_6H_6NNaO_3S$: C, 36.92%; H, 3.10%; N, 7.18%; S, 16.43%; Found: C, 31.24%; H, 4.35%; N, 6.14%; S, 12.92%; Calcd. for $C_6H_6NNaO_3 \cdot 2H_2O$: C, 31.17%; H, 4.36%; N, 6.06%; S, 13.87%.

ANAL. of BDH sulfanilic acid, Calcd. for $C_6H_7NO_3S$: C, 41.61%; H, 4.07%; N, 8.09%; S, 18.51%; Found: C, 41.66%; H, 4.09%; N, 8.04%; S, 17.36%.

Sodium N-(4-Sulfophenyl)maleamic Acid (SPMA) 10[33,34]



8 **9** **10**

A solution of maleic anhydride 9 (68 g, 0.60 mol) in 200 mL of methanol was added slowly, with rapid stirring, to a solution of sodium sulfanilate dihydrate 8 (100 g, 0.43 mol) in 2.0 L of methanol. The mixture was stirred at room temperature for about one hour. Crude, yellow sodium N-(4-sulfophenyl)maleamic acid 10 precipitated and was recovered by filtration.

The procedure was repeated twice more, and the combined samples were stirred in about 600 mL of methanol and filtered. Then the maleamic acid 10 was stirred in about 1.0 L of acetone, filtered, and air dried overnight. The purified product was dried in a vacuum oven for 24 hours at 65°C; yield 317 g (1.08 mol, 84%).

PAS-FTIR: ν (cm^{-1}) 3500-2800 (carboxylic acid O-H), 3284 (N-H), 3061 (aromatic C-H), 1722 (carboxylic acid C=O), 1635 (amide I: C=O), 1529 (amide II: mostly N-H bending), 1188 (asymmetric S=O), 1043 (symmetric S=O).

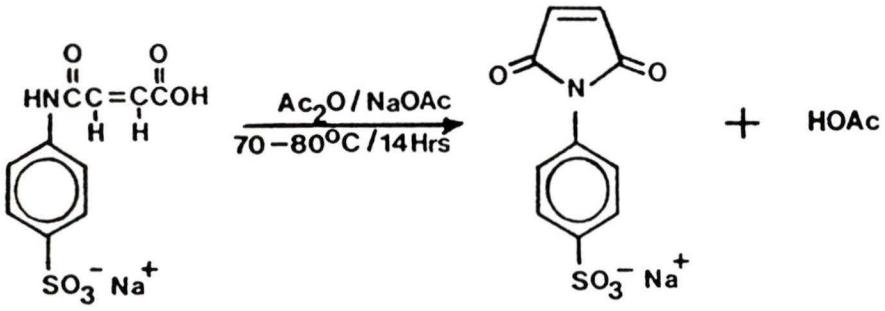
^{1}H NMR (90 MHz, D_2O, ref. HDO): δ 6.29 (d, J = 8 Hz,

1 H, alkene), 6.53 (d, J = 8 Hz, 1 H, alkene), 7.63 (d, J = 6 Hz, 2 H, aromatic), 7.74 (d, J = 6 Hz, 2 H, aromatic).

^{13}C NMR (50.3 MHz, D_2O, int. ref MeOH): δ 121.4 (aromatic C's ortho to N), 126.8 (aromatic C's meta to N), 130.7 (alkene C), 132.7 (alkene C), 139.4 (aromatic C-N and C-S), 166.1 (amide C=O), 169.7 (carboxylic acid C=O).

ANAL. Calcd. for $C_{10}H_8NNaO_6S$: C, 40.68%, H, 2.75%; N, 4.78%; S, 10.93%. Found: C, 38.85%; H, 3.43%; N, 4.54%; S, 9.52%. Calcd. for $C_{10}H_8NNaO_6S \cdot H_2O$: C, 38.59%, H, 3.24%; N, 4.50%; S, 10.30%.

Sodium N-(4-sulfopheny)maleimide (SPMI) 3[33,34]



10 3

A slurry of SPMA 10 (200 g, 0.68 mol) and anhydrous sodium acetate (30 g, 0.37 mol) in 2.5 L of acetic anhydride was stirred for 14 hours at 70 to 80°C under nitrogen. Then the slurry was cooled to room temperature and filtered. The pale yellow solid was stirred in about 1 L of acetone at room temperature, refiltered, and then air dried overnight.

Approximately 40 g fractions of the dry solid were

dissolved in 100 mL of distilled water and the pH adjusted to 2.0 with 6 N HCl to convert the sodium acetate to acetic acid and sodium chloride. Acetic acid and water were removed under reduced pressure at approximately 30°C on a rotary evaporator. Only 40 g portions of the crude product were used in each preparation to minimize the time that the imide 3 was dissolved in water because SPMI 3 slowly hydrolyzes to the maleamic acid 10, sodium sulfanilate 8, and maleic acid.

All of the fractions of solid recovered after evaporation were combined, stirred in about 2.0 L of hot glacial acetic acid and filtered to remove undissolved SPMI 3 and sodium chloride. The filtered solid was stirred in another 2.0 L of hot glacial acetic acid and refiltered. The filtrates were combined and evaporated on a rotary evaporator at 30 to 35°C, to yield a pale yellow solid. The solid was recrystallized on cooling from about 3.0 L of near boiling 85% denatured ethanol (15% de-ionized water). A silver nitrate test indicated that no residual sodium chloride was present. The recrystallized, pale yellow SPMI 3 was dried for 3 days at 60°C in a vacuum oven; yield 82.6 g (44%).

The ^{1}H NMR spectrum (200 MHz, D_2O) indicated that the purified SPMI 3 contained approximately 5% residual SPMA 10, some of which was produced by the hydrolysis of SPMI 3 while the spectrum was run.

PAS-FTIR: ν (cm^{-1}) 3473 (N-H of residual SPMA), 3090 (aromatic C-H), 1775 (imide C=O), 1709 (imide C=O), 1196 (asymmetric S=O), 1047 (symmetric S=O).

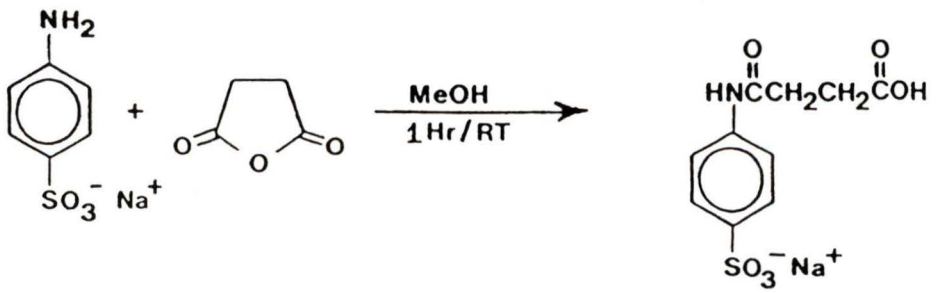
^{1}H NMR (90 MHz, D_2O, int. ref. HDO): δ 6.94 (s, 2 H, alkene), 7.44 (d, J = 9 Hz, 2 H, aromatic), 7.92 (d, J = 9 Hz, 2 H, aromatic).

^{13}C NMR (50.3 MHz, H_2O, ext. ref. TCE): δ 127.6 (aromatic C's ortho to N), 127.8 (aromatic C's meta to N), 134.2 (aromatic C-S), 135.5 (alkene C's), 143.1 (aromatic C-N), 172.8 (imide C=O's).

UV (H_2O): λ_{max}=192 nm (ϵ = 38300 L mol^{-1} cm^{-1}) λ_{max}=222 nm (ϵ = 20400 L mol^{-1} cm^{-1}).

ANAL. Calc. for $C_{10}H_6NNaO_5S$: C, 43.64%; H, 2.20%; N, 5.09%; Na, 8.35%. Found: C, 43.32%; H, 2.20%; N, 5.06%; Na, 8.05%.

Sodium N-(4-sulfophenyl)succinic Acid (SPSA) 12



8 **11** **12**

A slurry of partially dissolved succinic anhydride 11 (7.0 g, 0.0714 moles) in 100 mL of methanol was added to a

solution of sodium sulfanilate dihydrate 8 (10.0 g; 0.0433 moles) in 300 mL of methanol. The succinic anhydride completely dissolved. A white precipitate which formed while the solution was stirred at room temperature for about 1 hour, was recovered by filtration and air dried overnight; yield 9.5 g. ^{1}H NMR showed that the sample contained 1.8 moles of methanol per mole of SPSA 12, so the actual yield of SPSA 12 free of solvent was 7.86 g (62%). About 1.5 g of the sample was dried for 3 days at 65°C under vacuum and then stored over Drierite in a desiccator.

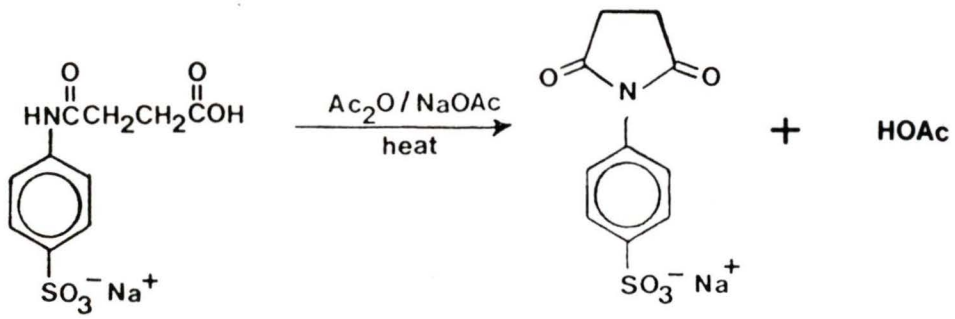
PAS-FTIR: (cm^{-1}) 3500-2400 (carboxylic acid O-H), 3338 (amide N-H), 1734 (carboxylic acid C=O), 1680 (amide I: C=O), 1599 (amide II: mostly N-H bending), 1337 (aryl C-N), 1246 (C-O), 1180 (asymmetric S=O stretch), 1042 (symmetric S=O stretch).

^{1}H NMR (90 MHz,D_2O, int. ref. HDO): δ 2.59 (s, 4 H, $-CH_2CH_2-$), 7.44 (d, J = 8, 2 H, aromatic), 7.68 d(dd, J = 8, 2 H, aromatic).

^{13}C NMR (50.3 MHz, H_2O, int. ref. MeOH): δ 29.4 ($-CH_2-$), 31.4 ($-CH_2-$), 121.3 (aromatic C's ortho to N), 126.7 (aromatic C's meta N), 138.9 (aromatic C-S), 140.1 (aromatic C-N), 173.9 (amide C=O), 177.4 (carboxylic acid C=O).

ANAL. Calc. for $C_{10}H_{10}NNaO_6S$: C, 40.68%; H, 3.41%; N, 4.75%; S, 10.86%. Found: C,40.47%; H, 3.37%; N, 4.52%; S, 9.92%.

Sodium N-(4-sulfophenyl)succinimide (SPSI) 13



12 13

A slurry of 9.00 g of crude SPSA 12 (7.53 g SPSA; 0.0255 moles) and sodium acetate (0.50 g) in 80 mL of acetic anhydride was stirred for 12 hours at 80°C to 85°C under nitrogen. The methylene ^{1}H NMR resonances of an aliquot of the mixture showed that about 50% of the succinic acid 12 had cyclized. Another 70 mL of acetic anhydride was added and the mixture was heated to about 125°C for a further 2.5 hours, when an ^{1}H NMR spectrum indicated completion of the reaction. The reaction mixture was filtered and the recovered solid was air dried overnight.

Next, the solid was dissolved in about 100 mL of de-ionized water and the pH was adjusted to 1.8 with 6 N HCl to convert the sodium acetate to acetic acid. The acetic acid and water were removed under reduced pressure on a rotary evaporator at about 30 to 35°C, to yield a white solid.

About half of the solid dissolved when it was added to 250 mL of hot glacial acetic acid. The solution was filtered to remove the undissolved SPSI 13 and sodium

chloride. The filtrate was evaporated on the rotary evaporator, yielding SPSI 13 contaminated with some residual sodium chloride. The imide 13 was precipitated twice from 90% denatured ethanol/10% water using crystallization techniques, which produced a white gel rather than a crystalline solid. The filtered gel was dried overnight at 60°C under vacuum, yielding 0.78 g (2.8 mol; 11% yield) of white, powdered SPSI 13.

The crude SPSI 13 product that did not dissolve in hot glacial acetic acid was precipitated twice by cooling hot, saturated solutions in 90% ethanol/10% water and the final product dried at 60°C under vacuum. Yield was a further 2.65 g (37%; total yield 48%).

PAS-FTIR: ν (cm^{-1}) 3060 (aromatic C-H); 2993 and 2941 (aliphatic C-H); 1780 (imide C=O, 5-membered ring); 1709 (imide C=O); 1188 (asymmetric S=O); 1047 (symmetric S=O).

^{1}H NMR (90 MHz, D_2O, int. ref. HDO): δ 2.88 (s, 4 H, $-CH_2CH_2-$), 7.41 (d, J = 6, 2 H, aromatic), 7.95 (d, J = 6, 2 H, aromatic).

^{13}C NMR (50.3 MHz, H_2O, int. ref. MeOH): δ 28.7 ($-CH_2-$'s), 127.1 (aromatic C's ortho to N), 127.8 (aromatic C's meta to N), 134.1 (aromatic C-S), 143.6 (aromatic C-N), 180.7 (imide C=O's).

ANAL. Calcd. for $C_{10}H_8NNaO_5S$: C, 43.32%; H, 2.91%; N, 5.05%; S, 11.56%. Found: C, 40.91%; H, 3.09%; N, 5.59%; S, 9.16%.

2.3.2. Imide Monomer Hydrolytic Experiments

Effect of NaOD on the Rate of Hydrolysis of SPMI 3

Solutions were prepared by dissolving 75 mg of sodium N-(4-sulfophenyl)maleimide 3 in 0.6 mL of D_2O containing 0.0, 0.013, 0.13, or 1.3 moles of sodium hydroxide per mole of SPMI 3, in four 5 mm NMR tubes. The 90 MHz ^1H NMR spectra of these solutions were recorded at 25°C using a Perkin-Elmer R32 NMR spectrometer, within 15 minutes of preparation of each solution and then daily thereafter, over a period of 5 days. The samples were stored in the dark at room temperature (ca. 23°C) between taking spectra. The degree of saponification and hydrolysis of SPMI 3 was determined by comparing the peak area for the SPMI 3 alkene protons with the peak areas for the alkenes protons of two of the hydrolysis products, SPMA 10 and maleic acid. The other hydrolytic product observed was sodium sulfanilate 8.

Effect of Temperature on the Rate of Hydrolysis of SPMI 3

Solutions of the 75 mg of SPMI 3 in 0.6 mL of D_2O were made up in two 5 mm NMR tubes and ^1H NMR spectra were run on these within 35 minutes of preparation. One hour after the solutions were prepared, one was immersed in a 40°C bath, and the other in a 60°C water bath, both in the light. Another three spectra were obtained from each sample during the next 50 hours at 25°C. The degree of hydrolysis of SPMI

3 was determined by comparing the peak area for the alkene protons of SPMI 3 with the peak areas for the alkene protons of three of the hydrolysis products, SPMA 10, maleic acid 19, and fumaric acid 20. The other product was sodium sulfanilate 8.

Effect of NaOD on the Rate of Hydrolysis of SPSI 13

SPSI 13 (75 mg) was dissolved in 0.6 mL of D_2O containing 1.3 moles of sodium hydroxide per mole of the imide and the ^1H NMR spectrum was recorded about 15 minutes later.

Effect of Temperature on the Rate of Hydrolysis of SPSI 13

Solutions of 75 mg of SPSI 13 in 0.06 mL of D_2O were placed in each of the two 5 mm NMR tubes and ^1H NMR spectra recorded within fifteen minutes of preparation. Then one of the samples was stored at room temperature (ca. 23°C) in the dark while the other sample was immersed in a 60°C water bath in the light. NMR spectra were taken on each sample at 25°C every few days over a period of 18 days.

2.3.3. Preparation and Characterization of Poly(acrylamide-co-sodium N-(4-sulfophenyl)maleimide) (PAMSM)

Nitrogen was bubbled through 200 mL of distilled deionized water in a 250 mL flask in a 30°C water bath for at least 1 hour, to remove dissolved oxygen. Then the de-

oxygenated water was transferred with a syringe to septum-capped 25 mL round bottom flasks containing sodium N-(4-sulfophenyl)maleimide 3, acrylamide 1, and potassium persulfate under nitrogen. Table 1 gives the quantities of reagents used. The flasks were immersed in the 30°C water bath for a minimum of 20 minutes to a maximum of 140 minutes. The solutions were stirred continuously during that time using hydromagnetic stirrers (GFS Chemicals). At the end of the polymerizations, the final pH of each of the solutions was measured and then 0.20 g of hydroquinone was added to each solution to stop further polymerization.

Solutions PAMSM-1 to -6 were dialyzed using Spectra/Por 3 dialysis tubing (3500 molecular weight cut-off, MWCO) in jars containing 300 mL of de-ionized water. Separate jars were used to prevent cross contamination from diffusion of monomer and low molecular weight copolymer. The dialyses were kept near 0°C to prevent further polymerization and to minimize hydrolysis of the imide rings in the copolymers. The dialysate was replaced five to six times during a period of 53 to 63 hours, and was analyzed by UV spectroscopy (λ = 200 nm) to monitor the progress of the dialysis. About 7 mL of each dialyzed solution was saved for use in flocculation tests. The remainder (ca. 60 to 70 mL) was freeze dried for two to three days. The yields of freeze dried copolymer given in Table 1 have been corrected

Table 1: Copolymerization of Acrylamide (AM) and Sodium N-(4-sulfophenyl)maleimide (SPMI) at 30°C

Copolymer	Wt. AM (g)	mmoles AM	Wt. SPMI (g)	mmoles SPMI	Wt. $K_2S_2O_8$ (g)	Vol. Water (mL)	Polymn. Time (min.)	Final pH	Yield (%)
PAMSM-1	4.155	58.46	0.847	3.08	0.0500	13.8	20	n/m	16
PAMSM-2	3.470	48.82	1.504	5.47	0.0501	12.2	33	3.30	15
PAMSM-3	2.540	35.73	2.460	8.94	0.0505	10.0	41	3.13	11
PAMSM-4	1.882	26.48	3.121	11.34	0.0503	8.5	47	n/m	6.0
PAMSM-5	1.027	14.48	3.975	14.44	0.0505	7.0	40	2.93	3.4
PAMSM-6	0.394	5.54	4.860	17.66	0.0509	8.0	40	2.90	1.5
PAMSM-7	3.473	48.86	1.504	5.47	0.0051	10.0	30	n/m	2.6
PAMSM-8	1.028	14.47	3.979	14.46	0.0503	7.0	98	2.85	4.1
PAMSM-9	0.395	5.56	4.606	16.74	0.0511	8.0	140	2.69	1.7

n/m: Not measured.

for the amount of dialyzed solution that was saved.

Solutions PAMSM-7 to -9, which were prepared at a later date, were dialyzed using Spectra/Por 6 dialysis tubing (1000 MWCO). The dialysate (300 mL de-ionized water) was replaced 13 times over a period of 10 days.

Aqueous solutions containing 0.2 to 0.3 mg of freeze dried copolymer per 1.0 mL of 0.005 M Na_2SO_4 were chromatographed on a 7.5 mm I.D. by 30 cm TSK-GEL G5000PW column to determine the residual monomer content of the copolymer samples. The solutions were chromatographed at a flow rate of 1.5 mL/min, using 0.005 M Na_2SO_4 as the mobile phase.

The ^{13}C NMR spectra of 2 to 10% by weight aqueous solutions of copolymers PAMSM-1 to -4 were recorded at ambient temperature on a Bruker CXP200 NMR. A few drops of D_2O were added to each of the samples to provide an internal deuterium lock. Refer to Section 2.2 for further information about the experimental procedures.

Viscosity measurements were made on aqueous solutions of PAMSM-1, -2 and -3 containing 0.0025, 0.0029, 0.0033, 0.0040, and 0.0050 g of copolymer per mL of 0.50 M NaCl at pH 7.0 $\pm$ 0.2 and 25.0 $\pm$ 0.05^{o}C. Intrinsic viscosities were determined by extrapolating plots of reduced viscosity versus concentration to zero concentration. Viscosity average molecular weights of the copolymers were estimated using the Mark-Houwink relationship reported by Klein and Conrad[35] for polyacrylamide in 0.5 M NaCl at 25^{o}C, with

concentration in g/cm^3.

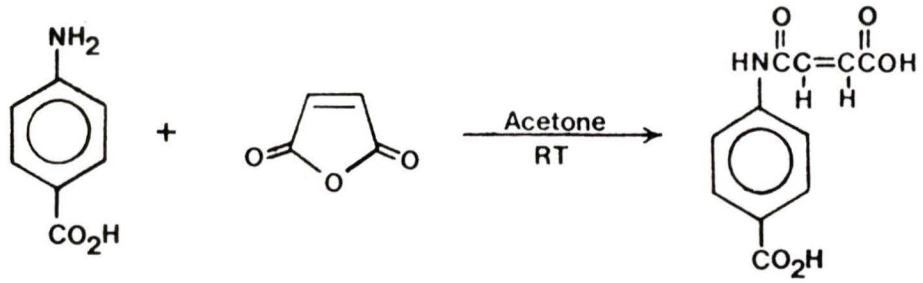
$$[\eta] = 7.19 \times 10^{-3} M^{0.77} \qquad (2\text{-}1)$$

Low angle laser light scattering measurements were made on a series of solutions of PAMSM-1 and PAMSM-3 containing 10 to 90 mg of copolymer per mL of aqueous 0.010 M Na_2SO_4. The solutions were filtered through Millipore Millex-PF 0.8 μm filter units before the Raleigh factors were measured. The measurements were repeated a few days later on different subsamples of the same copolymers.

2.4. Poly(acrylamide-co-p-maleimidobenzoic acid) (PAMMBA)

2.4.1. Preparation of Monomers

p-Carboxymaleanilic Acid (CMA) 15[36]



14 9 15

Maleic anhydride 9 (148.3 g, 1.51 mol), dissolved in 400 mL of acetone, was added to p-aminobenzoic acid 14 (200 g, 1.46 mol) dissolved in 3.0 L of acetone at room temperature. A yellow precipitate began to form within a few minutes. After stirring for 3 hours at room temperature, the solid was filtered and then stirred and refiltered twice from 2 x 500 mL of acetone. The yield of p-carboxymaleanilic acid (CMA) 15 after vacuum drying at 60°C was 314.1 g (91.6%); m.p. 215-219°C (lit.[36] 214-217°C).

PAS-FTIR: ν (cm^{-1}) 3500-2500 (carboxylic acid O-H), 3283 (amide N-H), 3050 (aromatic and alkene C-H), 1695 (carboxylic acid and amide C=O), 1626 (alkene C=C), 1582 (aromatic C=C), 1549 (amide II: N-H), 1296 (C-O), 675 (C-H bending).

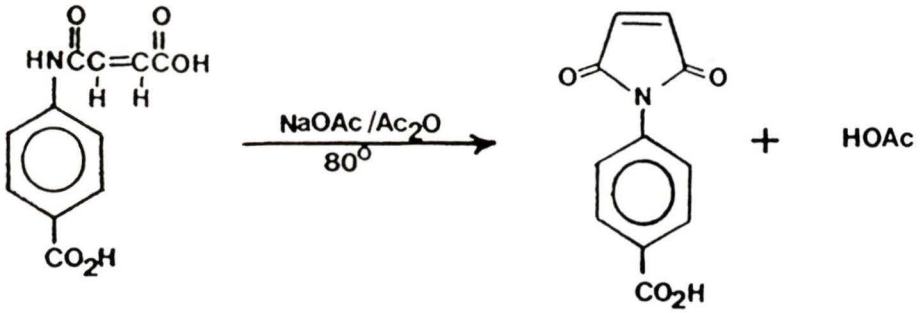
^{13}C NMR (50.3 MHz, DMSO): δ 118.2 (aromatic C's

ortho to N), 125.0 (aromatic C-CO_2H), 129.5 (aromatic C's ortho to -CO_2H), 131.3 (alkene C's), 141.6 (aromatic C-N), 162.9 (amide C=O), 165.8 (-CO_2H's).

^{13}C NMR (50.3 MHz, H_2O, pH 6.7, ext. ref. TCE): 121.2 (aromatic C's ortho to N), 125.4 (alkene C), 131.0 (aromatic C's ortho to -CO_2^-), 132.1 (aromatic C-CO_2^-), 138.3 (alkene C), 141.1 (aromatic C-N), 166.8 (amide C=O), 174.8 and 175.4 (-CO_2^-'s).

ANAL. Calcd. for $C_{11}H_9NO_5$: C, 56.17%; H, 3.86%; N, 5.96%; Found: C, 56.30%; H, 3.94%; N, 5.97%.

p-Maleimidobenzoic Acid (MBA) 4[36-38]



15 4

p-Carboxymaleanilic acid 15 (314.1 g, 1.34 mol) was dispersed in 500 mL of acetic anhydride containing 40.0 g of anhydrous sodium acetate. The maleanilic acid gradually dissolved while the mixture was heated with stirring at 80°C for 3 hours. The hot solution was poured into 1 L of room temperature de-ionized water to precipitate the product 4, which was filtered and then dried overnight at 60°C under

vacuum. The p-maleimidobenzoic acid 4 was recrystallized from hot denatured ethanol (15% methanol); yield 125.2 g (43.2%), m.p. 235-238°C (lit.[36] 235-237°C, lit.[37] 240-241°C, lit.[38] 208-210°C, lit.[39] 234°C).

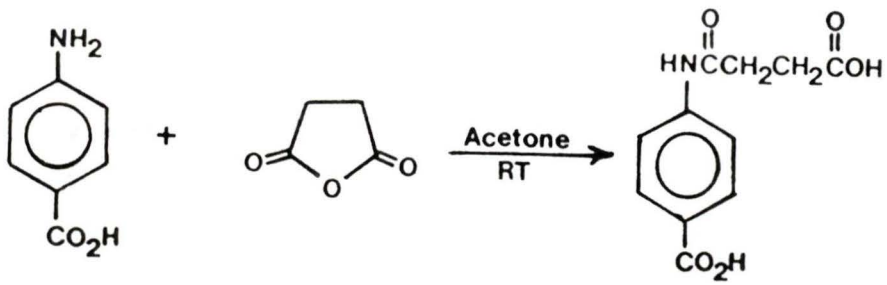
PAS-FTIR: ν (cm^{-1}) 3476 (N-H of residual CMA), 3500-2700 (carboxylic acid O-H), 1776 (C=O stretching characteristic of a 5-membered imide ring), 1709 (overlapping imide and carboxylic acid C=O stretching bands), 1603 (aromatic C=C), 1516 (aromatic C=C), 1217 (carboxylic acid C-O).

^{13}C NMR (50.3 MHz, DMSO): δ 125.0 (aromatic C's ortho to N), 125.6 (aromatic -C-N), 128.9 (aromatic C's ortho to $-CO_2H$), 133.7 (alkene C's), 134.4 (aromatic C-CO_2H), 165.7 ($-CO_2H$), 168.4 (imide C=O's).

^{13}C NMR (50.3 MHz, H_2O, pH 6.7, ext. ref. TCE): δ 127.8 (aromatic C's ortho to N), 130.8 (aromatic C's ortho to $-CO_2^-$), 133.6 (aromatic C-CO_2^-), 135.5 (alkene C's), 137.3 (aromatic C-N), 172.6 (imide C=O's), 175.3 (benzoate $-CO_2^-$).

ANAL. Calcd. for $C_{11}H_7NO_4$: C, 60.83%; H, 3.25%; N, 6.45%; Found: C, 61.31%; H, 3.34%; N, 6.46%.

p-Carboxysuccinanilic Acid (CSA) 16



14 11 16

Succinic anhydride 11 (16.9 g, 0.169 mol), dissolved in 200 mL of acetone, was added to p-aminobenzoic acid 14 (20.0 g, 0.146 mol) dissolved in 300 mL of acetone at room temperature. p-Carboxysuccinanilic acid (CSA) 16 precipitated while the mixture was stirred at room temperature for 3 hours to yield 21.5 g (62%) of white solid after vacuum drying at 60°C; m.p. 232-235°C (lit.[40] 225-226°C). Another 14.2 g of CSA 16 contaminated with excess succinic anhydride was recovered by evaporating the acetone.

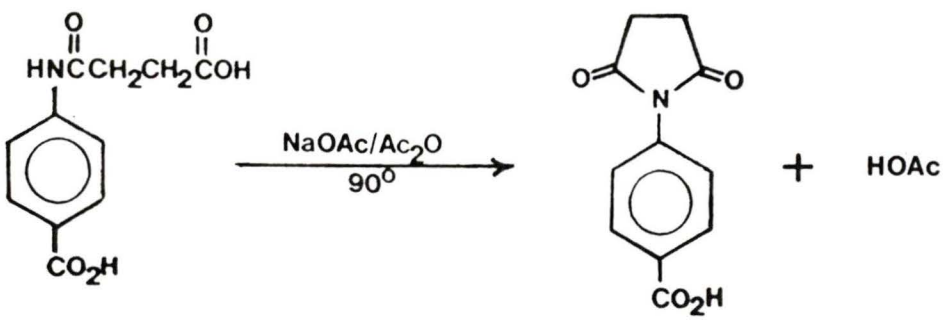
PAS-FTIR: ν (cm^{-1}) 3500-2500 (carboxylic acid O-H), 3310 (amide N-H), 3035 (aromatic C-H), 1699 (carboxylic acid C=O), 1670 (amide C=O), 1610 (aromatic C=C), 1597 (aromatic C=C), 1537 (aromatic C=C), 1298 (C-O).

^{13}C NMR (50.3 MHz, DMSO): δ 27.9 ($-\underline{C}H_2-CH_2-CO_2H$), 30.4 ($-\underline{C}H_2-CO_2H$), 117.4 (aromatic C's ortho to N), 124.1 (aromatic $-\underline{C}-CO_2H$), 129.3 (aromatic C's ortho to $-CO_2H$), 142.2 (aromatic C-N), 165.9 (aromatic $-CO_2H$), 169.7 (aliphatic $-CO_2H$), 172.6 (amide C=O).

^{13}C NMR (50.3 MHz, H_2O, pH 6.7, ext. ref. TCE): δ 33.4 ($-\underline{C}H_2-CH_2-CO_2H$), 33.9 ($-\underline{C}H_2-CO_2H$), 121.6 (aromatic C's ortho to N), 130.8 (aromatic C's ortho to $-CO_2H$), 133.3 (aromatic $-\underline{C}-CO_2H$), 140.7 (aromatic C-N), 175.6 ($-CO_2^-$'s), 181.8 (amide C=O).

ANAL. Calcd. for $C_{11}H_{11}NO_5$: C, 55.69%; H, 4.67%; N, 5.91%; Found: C, 55.64%; H, 4.84%; N, 5.90%.

p-Succinimidobenzoic Acid (SBA) 17



16 17

p-Carboxysuccinanilic acid 16 (15.0 g, 0.0632 mol) was dispersed in 50 mL of acetic anhydride containing 2.00 g of anhydrous sodium acetate. The suspension was heated at 90°C for 4 hours. Then, 100 mL of de-ionized water at room temperature was added to the hot slurry with rapid stirring, which completely dissolved the suspended solids. The product 17 was extracted from this solution with 3 x 150 mL of chloroform. A white solid (2.54 g) containing mostly sodium acetate was isolated by freeze drying the aqueous layer.

A white solid remained on removal of most of the chloroform on a rotary evaporator. The solid was filtered, rinsed with diethyl ether, stirred in approximately 200 mL of de-ionized water and refiltered. The yield after drying under vacuum at 60°C was 2.61 g (13.9%). The ^{13}C NMR and PAS-FTIR spectra of the solid showed that it was p-succinimidobenzoic acid (SBA) 20; m.p. 246-248°C.

Another 9.28 g of crude SBA was obtained by evaporating the acetic anhydride. The ^{13}C NMR spectrum indicated that the SBA was contaminated with about 10% CSA.

PAS-FTIR: ν (cm^{-1}) 3500-2500 (carboxylic acid O-H), 3483 (N-H of residual CSA), 1786 (imide C=O), 1705 (carboxylic acid and imide C=O), 1610 (aromatic C=C), 1587 (aromatic C=C), 1518 (aromatic C=C), 1292 (C-O).

^{13}C NMR (50.3 MHz, DMSO): δ 27.6 (methylene C's), 126.0 (aromatic C's ortho to N), 128.8 (aromatic C's ortho to $-CO_2H$), 129.5 (aromatic C-N), 135.7 (aromatic $-\underline{C}-CO_2H$), 165.7 ($-CO_2H$), 175.5 (imide C=O's).

^{13}C NMR (50.3 MHz, H_2O, pH 6.7, ext. ref. TCE): δ 29.3 (methylene C's), 127.6 (aromatic C's ortho to N), 130.8 (aromatic C's ortho to $-CO_2H$), 134.3 (aromatic $-\underline{C}-CO_2^-$), 138.2 (aromatic C-N), 175.2 ($-CO_2^-$), 181.7 (imide C=O's).

ANAL. Calcd. for $C_{11}H_9NO_4$: C, 60.27%; H, 4.14%; N, 6.39%; Found: C, 59.32%; H, 4.20%; N, 6.18%.

2.4.2. Preparation and Characterization of Poly(acrylamide-co-p-maleimidobenzoic acid) (PAMMBA)

Copolymerization in Glacial Acetic Acid: PAMMBA-1, -2, -3 and PAM-1

Nitrogen was bubbled through 200 mL of distilled glacial acetic acid for 45 minutes at 60°C. Then aliquots of the de-oxygenated acetic acid were transferred with a syringe to septum-capped, nitrogen purged flasks containing acrylamide 1 and p-maleimidobenzoic acid (MBA) 4. The solutions were stirred using hydromagnetic stirrers for 10 minutes at 60°C to dissolve the monomers and then 2.0 mL of a solution of AIBN dissolved in glacial acetic acid was added. The quantities of all reagents used are given in Table 2.

Solutions PAM-1 and PAMMBA-1 became viscous after 5 hours at 60°C while no significant change in the viscosities of PAMMBA-2 and PAMMBA-3 was observed. After 6.5 hours, each of the solutions were poured into 300 mL of methanol to precipitate the copolymers and the acetic acid-methanol was decanted. The copolymers were redissolved in about 20 mL of distilled water by adding a few drops of dilute $NaHCO_3$ solution to convert the MBA units to their water-soluble sodium salt form and reprecipitated in 300 mL of methanol. The copolymers were redissolved in water and reprecipitated with methanol once more before being freeze dried.

Table 2: Copolymerization of Acrylamide (AM) and p-Maleimidobenzoic Acid (MBA) in Glacial Acetic Acid at 60°C

Copolymer	Wt. AM (g)	Millimoles AM	Wt. MBA (g)	Millimoles MBA	Wt. AIBN (g)	Vol. AcOH (mL)	Polymn. Time (hr:min)	Yield (%)
PAMMBA-1	4.252	59.82	0.682	3.142	0.100	32	6:30	85
PAMMBA-2	3.649	51.33	1.241	5.714	0.100	42	6:30	59
PAMMBA-3	2.743	38.59	2.073	9.545	0.100	62	6:30	36
PAM-1	5.007	70.44	0	0	0.100	32	6:30	91
PAMMBA-4	8.511	119.7	1.368	6.299	0.020	62	14:15	57
PAMMBA-5	10.946	154.0	3.727	17.16	0.030	123	14:15	23
PAMMBA-6	8.239	115.9	6.219	28.64	0.030	183	14:30	10
PAM-2	10.001	140.7	0	0	0.020	62	14:15	69

Copolymerization in Glacial Acetic Acid: PAMMBA-4, -5, -6, and PAM-2

Solutions of acrylamide 1 and MBA 4 in acetic acid in septum-capped round bottom flasks were purged with UHP nitrogen for 15 minutes at room temperature. Next, nitrogen was bubbled through solutions PAMMBA-4, PAMMBA-5 and PAM-1 for 30 minutes at room temperature. Solution PAMMBA-3 had to be immersed in a 60°C water bath while the solution was sparged with UHP nitrogen to completely dissolve the comonomer. AIBN solution (2 mL) was added and then the flasks were immersed in a 60°C water bath for 14 to 14.5 hours. The quantities of all reagents used are given in Table 2.

The copolymers were precipitated in about 400 mL of methanol and decanted. Then the copolymers were dissolved in about 40 mL of water by adding a few drops of dilute $NaHCO_3$ solution, reprecipitated in 400 mL of acetone, and freeze dried.

Copolymerization in DMSO: PAMMBA-7, -8, -9, and PAM-3

Nitrogen was bubbled through 150 mL of reagent grade DMSO (Chemonix, vacuum distilled over CaH_2) for 30 minutes at room temperature. Then 30 mL aliquots of DMSO were transferred to nitrogen purged, septum-capped flasks containing acrylamide 1 and MBA 4. After bubbling nitrogen through each solution for 10 minutes, the flasks were

Table 3: Copolymerization of Acrylamide (AM) and p-Maleimidobenzoic Acid (MBA) in DMSO at 60°C

Copolymer	Wt. AM (g)	Millimoles AM	Wt. MBA (g)	Millimoles MBA	Wt. AIBN[a] (g)	Vol. DMSO (mL)	Polymn. Time (hr:min)	% Yield
PAMMBA-7	4.248	59.76	0.683	3.145	0.100	30.0	6:00	85
PAMMBA-8	3.674	51.69	1.231	5.667	0.100	30.0	6:00	29
PAMMBA-9	2.709	38.11	2.074	9.550	0.100	30.0	6:00	0
PAM-3	5.007	70.44	0	0	0.100	30.0	6:00	89

[a]Polymerizations were initiated with 2.0 mL of de-oxygenated acetic acid containing 0.0500 g AIBN/mL.

immersed in a 60°C water bath and 2.0 mL of a solution of AIBN in acetic acid was added to each. Table 3 gives the quantities of reagents used.

Initially the solutions were yellow, but gradually turned orange while they were heated at 60°C for 6 hours. Polymer precipitated when solutions PAMMBA-7 and -8 were poured into 200 mL of methanol, but only a turbid suspension was obtained when PAMMBA-9 was added. Copolymers PAMMBA-7 and -8 were redissolved in about 40 mL of water using a few drops of dilute aqueous $NaHCO_3$, and reprecipitated in 200 mL of methanol. The two copolymers were redissolved in water, reprecipitated in methanol, and freeze dried.

Attempted Copolymerization in 1.5:1 (v/v) DMSO:water

Nitrogen was bubbled through solutions of acrylamide 1, MBA 4, and $NaHCO_3$ dissolved in 1.5:1 (v/v) DMSO:water in nitrogen purged, septum-capped flasks for 15 minutes at room temperature. After adding H_2O_2 initiator, the flasks were immersed in a 60°C water bath for 6 hours. Initially, the solutions were yellow but gradually turned bright red during the 6 hours. Precipitates were obtained when the solutions were added to 200 mL of methanol. The precipitates were filtered, redissolved in about 10 mL of water using a few drops of dilute aqueous $NaHCO_3$, reprecipitated with 200 mL of methanol, washed with methanol, and then freeze dried. Quantitative details are given in Table 4.

Table 4: Attempted Copolymerization of Acrylamide (AM) and p-Maleimidobenzoic Acid (MBA) in 1.5:1 (v/v) DMSO:Water at 60°C

Copolymer	Wt. AM (g)	Millimoles AM	Wt. MBA (g)	Millimoles MBA	Vol. DMSO (mL)	Vol. H_2O (mL)	Polymn. Time (hr:min)	Yield (g)
PAMMBA-10	4.266	60.02	0.685	3.154	15.0	10.0	6:00	0.366[a]
PAMMBA-11	3.642	51.24	1.239	5.706	15.0	10.0	6:00	0.835[a]
PAMMBA-12	2.737	38.51	2.280	10.05	15.0	10.0	6:00	2.027[a]
PAM-4	5.002	70.37	0	0	15.0	10.0	6:00	3.470

[a]Yield: ^{13}C NMR showed that the precipitates were mostly p-maleimidobenzoic acid 4, p-carboxymaleanilic acid 15 and p-aminobenzoic acid 14, not copolymers.

Characterization of the PAMMBA Copolymers

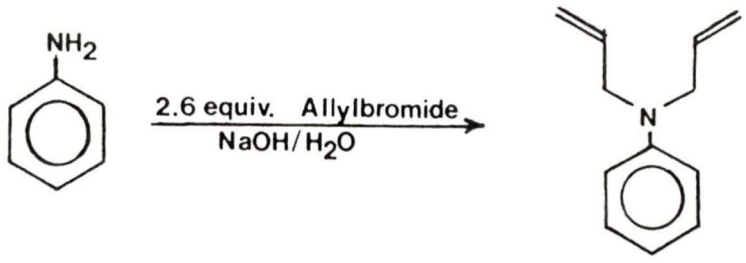
The residual monomer content of the copolymers was determined by gel permeation chromatography. The copolymers were chromatographed on a 4 mm I.D. x 25 cm Toyopearl TSK-GEL HW-40S column at a flow rate of 0.4 mL/min using aqueous 0.01 M Na_2SO_4 as the mobile phase. The injection concentration of the polymer solutions was 1.0 mg/mL and the injection volume was 100 µL.

The ^{13}C NMR spectra of 2 to 10% by weight solutions of the copolymers were recorded at ambient temperature on a Bruker CXP200 NMR. Aqueous 0.375 M KH_2PO_4/0.125 M K_3PO_4 buffer (pH 6.7) was used as the solvent for all of the samples since the chemical shifts are pH sensitive. A few drops of D_2O were added to each of the samples to provide an internal deuterium lock. Tetrachloroethane-d_2 was used as an external chemical shift reference. See Section 2.2 for further information about the experimental procedures.

Viscosity measurements were made on aqueous solutions of PAMMBA-1, -2, -4, -7, and -8 containing 0.003 to 0.03 g of copolymer per mL of 0.5 M NaCl at pH 7.0 $\pm$ 0.2 and 25.0 $\pm$ 0.05°C. Intrinsic viscosities were determined by extrapolation of plots of reduced viscosity versus concentration to zero concentration. Viscosity average molecular weights were estimated using the Mark-Houwink equation (Eq. 2-1) on page 40.

2.5. Poly(N,N-diallylaniline) (PDAA)

2.5.1. Preparation of N,N-Diallylaniline (DAA) 6 [41]



18 6

Allyl bromide (140.0 mL, 1.618 mol) and aqueous KOH (200 mL, 97.61 g/200 mL, 1.74 mol) were added dropwise simultaneously, over a period of 50 minutes, to freshly distilled aniline 18 (61.3 mL, 0.644 mol) and distilled water (25 mL) under nitrogen at room temperature. The solution was stirred for a total of 4 hours at room temperature and then was gently refluxed for 18 hours.

The organic layer was separated and dried over KOH pellets. Some of the unreacted allyl bromide, and allyl alcohol which results from hydrolysis of allyl bromide, were removed under vacuum at room temperature. The sample was distilled under vacuum (Precision pump), yielding 88.4 g of clear, colourless distillate (b.p. 78 - 81^{o}C under vacuum).

^{1}H NMR (250 MHz, $CDCl_3$, ext. ref. TMS): δ 3.95 (dt, J_{vic} = 4.8 Hz, $J_{allylic}$ = 1.6 Hz, 4 H, methylene H's), 5.15-5.19 (m, 2 H, alkene H's), 5.19-5.25 (m, 2 H, alkene H's), 5.82-5.96 (m, 2 H, alkene H's), 6.68-6.76 (m, 3 H,

aromatic H's), 7.19-7.27 (m, 2 H, aromatic H's).

^{13}C NMR (50.3 MHz, neat, ext. ref. TCE): δ 53.8 ($-CH_2-$), 113.9 ($=CH_2$), 116.7 (aromatic C's ortho to N), 117.7 (aromatic C para to N), 129.9 (aromatic C's meta to N), 135.5 (-CH=), 149.8 (aromatic C ipso to N).

ANAL. Calcd. for $C_{12}H_{15}N$: C, 83.19%; H, 8.73%; N, 8.09%; Found: C, 83.02%; H, 8.53%; N, 7.91%.

2.5.2. Preparation of Poly(N,N-diallylaniline) (PDAA)[42,43]

N,N-diallylaniline 6 (5.01 g, 28.9 mmol) was converted to its water-soluble hydrochloride salt by dropwise addition of concentrated hydrochloric acid. The solution was diluted to 12.0 mL with distilled water and the pH was adjusted to 0.65 with dilute HCl. Next, nitrogen was bubbled through the solution for 15 minutes in a septum capped flask at room temperature. Then 1.0 mL of nitrogen-sparged 4.25% (w/v) hydrogen peroxide was added and the flask was immersed in a 60°C water bath. After 25 minutes, the solution was made basic with sodium carbonate and extracted with chloroform. The organic layer was dried over magnesium sulfate and evaporated on a rotary evaporator. The brown residue was washed with petroleum ether, redissolved in chloroform and reprecipitated with petroleum ether.

PAS-FTIR: ν (cm^{-1}) 3057 and 3032 (aromatic C-H), 2922 (aliphatic C-H), 2856 (aliphatic C-H), 2827 (aliphatic C-H), 1600 (aromatic C=C), 1506 (aromatic C=C), 1480 (aromatic

C=C), 746 (C-H OOP bending), 690 (C=C OOP ring bending).

^{13}C NMR (62.9 MHz; $CDCl_3$; ext. ref. TMS): δ 26.8 (bridging $-CH_2-$'s of cis-pyrrolidine rings), 32.0 (bridging $-CH_2-$'s of trans-pyrrolidine rings), 41.6 (methine C's of cis-pyrrolidine rings), 44.7 (methine C's of trans-pyrrolidine rings), 51.8 ($-\underline{C}H_2-N$ of cis-pyrrolidine rings), 53.5 ($-\underline{C}H_2-N$ of trans-pyrrolidine rings), 111.3 (aromatic C's ortho to N), 115.4 (aromatic C para to N), 129.2 (aromatic C's meta to N), 147.8 (aromatic C ipso to N).

2.6. Preparation of Poly(acrylamide-co-N,N-diallylaniline) (PAMDAA)

Concentrated HCl was added dropwise to N,N-diallylaniline 6 and 40 mL of distilled water to convert the amine to its water-soluble HCl salt. Another 10 mL of distilled water was added and the solution was transferred to a septum-capped flask containing acrylamide monomer. Nitrogen (UHP) was bubbled through the solution for at least 15 minutes, 1.0 mL of de-oxygenated H_2O_2 solution was added and the flask was immersed in a 60°C water bath. The clear, colourless solution turned orange about 5 minutes after the flask was immersed in the water bath, indicating that diallyl radicals were being generated. The copolymerization was stopped about 35 minutes after the flask was placed in the bath by precipitating the copolymer in 200 mL of methanol. The copolymer was redissolved in water

Table 5: Copolymerization of Acrylamide (AM) and N,N-Diallylaniline (DAA) at 60°C

Copolymer	Wt. AM (g)	mmoles AM	Wt. DAA (g)	mmoles DAA	Wt. H_2O_2 (g)	Vol. H_2O (mL)	pH	Polymn. Time (min)	Yield (%)
PAMDAA-1	3.934	55.35	1.074	6.20	0.00425[a]	51.0	0.65	34	75
PAMDAA-2	3.107	43.71	1.902	10.98	0.00425[a]	51.0	0.65	35	46
PAMDAA-3	2.447	34.43	2.559	14.77	0.00425[a]	51.0	0.65	36	20
PAMDAA-4	3.101	43.62	1.924	11.11	0.0419[b]	51.0	0.61	20	83
PAMDAA-5	2.456	34.54	2.618	15.11	0.0419[b]	51.0	0.65	40	69

[a] 1.0 mL of aqueous 4.25 % H_2O_2

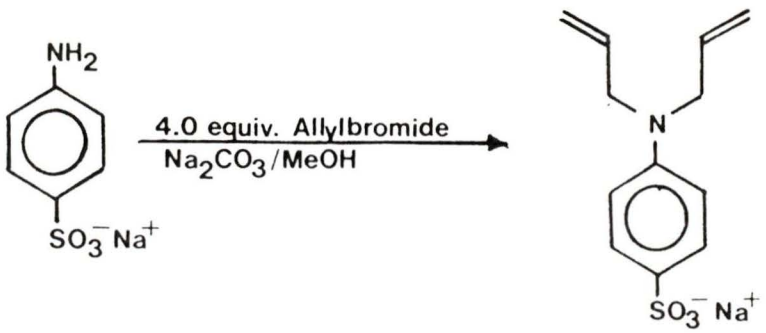
[b] 1.0 mL of aqueous 4.19 % H_2O_2

(pH < 2) and then reprecipitated with methanol twice. Finally, the copolymer was freeze dried. The quantities of acrylamide (AM), N,N-diallylaniline (DAA) 6, and H_2O_2 used and reaction conditions are summarized in Table 5.

Solution PAMDAA-1 gelled 34 minutes after it was immersed in the 60°C water bath, whereas solutions PAMDAA-2 and PAMDAA-3 were still free flowing. Solutions PAMDAA-4 and PAMDAA-5 turned to orange, insoluble gels.

2.7. Poly(acrylamide-co-sodium N,N-diallylsulfanilate) (PAMDAS)

2.7.1. Preparation of Sodium N,N-Diallylsulfanilate (DAS) 7



8 7

Sodium carbonate (131.6 g, 1.242 mol) was dispersed in 1.0 L of methanol containing sodium sulfanilate 8 (112.7 g, 0.577 mol). Allyl bromide (200 mL, 2.31 mol) was added with rapid stirring over a period of 10 minutes. The mixture was stirred at room temperature for 3 hours under nitrogen, and

then was gently refluxed for 18 hours. The white, insoluble material, which was mostly sodium carbonate and sodium bromide, was filtered off and the filtrate was evaporated under vacuum. The solid from the evaporated filtrate was redissolved in 500 mL of de-ionized water and extracted 3 times with 200 mL of diethyl ether to remove allyl bromide and methyl diallyl ether. The pH of the aqueous layer was lowered to 2.3 using hydrobromic acid, to convert the remaining sodium carbonate to sodium bromide, carbon dioxide and water. Then the solution was freeze dried for 3 days: yield 291.2 g (37.2 wt % DAS, 62.8 wt % NaBr; calculated from an average of the elemental analyses and titrations given below).

IR (KBr): ν (cm^{-1}) 3500-3100 (water O-H), 3080 (vinyl C-H), 2990 (methylene C-H), 1640 (allyl C=C), 1595 (aromatic C=C), 1200 (asymmetric S=O and aromatic C-N), 1030 (symmetric S=O), 990 (C-H OOP bending characteristic of a monosubstituted alkene), 680 (S-O).

^{1}H NMR (90 MHz, D_2O, ext. ref. TMS) δ 4.12 (d, J = 7 Hz, 4 H, $-CH_2-$), 5.28 (dd, J_{trans} = 14 Hz, J_{gem} = 4 Hz, 2 H, vinyl H's cis to methylene groups), 5.35 (dd, J_{cis} = 5 Hz, J_{gem} = 4 Hz, 2 H, vinyl H's trans to methylene groups), 5.40-6.00 (m, 2 H, vinyl H's gem to methylene groups), 7.38 (d, J_{ortho} = 9 Hz, 2 H, aromatic H's ortho to N), 7.92 (d, J_{ortho} = 9 Hz, 2 H, aromatic H's ortho to sulfonate group).

^{13}C NMR (50.3 MHz, H_2O, int. ref. methanol): 52.4

(vinyl -CH=), 111.8 (vinyl $=CH_2$), 113.8 (aromatic C's ortho to N), 127.0 (aromatic C's ortho to sulfonate group), 130.1 (aromatic C-N), 150.5 (aromatic C-S).

ANAL. Calcd. for $C_{12}H_{14}NNaO_3S$: C, 52.35%; H, 5.13%; N, 5.09%, S, 11.65%; Found: C, 19.36%; H, 2.18%; N, 1.84%; S, 3.97%; Cald. for 37.0 wt % DAS, 63.0 wt % NaBr: C, 19.36%; H, 1.90%; N, 1.88%; S, 4.36%.

$AgNO_3$ Titrations: 62.6 wt % NaBr, 62.8 wt % NaBr.

2.7.2. Preparation and Characterization of Poly(acrylamide-co-sodium N,N-diallylsulfanilate) (PAMDAS)

Solutions containing sodium N,N-diallylsulfanilate 7 dissolved in 20 mL of distilled water, with the pH adjusted to 1.9 with dilute HCl, were transferred to septum-capped flasks containing acrylamide monomer. Nitrogen was bubbled through each solution for at least 15 minutes. Then the flasks were immersed in a 60°C water bath and 1.0 mL of initiator solution was added. After 11.5 to 15 hours, the flasks were removed from the water bath, 200 mg of hydroquinone was added, and the solutions were dialyzed in 300 mL of distilled water at about 5°C using Spectra/Por 6 dialysis tubing (1000 MWCO). The dialysate was replaced 15 to 20 times over a period of 5 to 7 days. Finally, the solutions were freeze dried. The quantities of reagents used for the copolymerizations are given in Table 6.

Aqueous solutions containing 1.0 mg of copolymer per mL

Table 6: Copolymerization of Acrylamide (AM) and Sodium N,N-Diallylsulfanilate (DAS) at 60°C

Copolymer	Wt. AM (g)	mmoles AM	Wt. DAS (g)	mmoles DAS	Wt. Initiator (g)	Vol. H_2O (mL)	pH	Polymn. Time (hr:min)	Yield (%)
PAMDAS-1	3.575	50.30	1.43	5.19	0.0413[a]	21.0	1.9	15:00	53
PAMDAS-2	1.981	27.87	3.09	11.2	0.0413[a]	21.0	1.9	15:00	12
PAMDAS-3	1.111	14.64	3.86	14.0	0.0413[a]	21.0	1.9	15:00	9
PAMDAS-4	0.327	4.60	4.67	17.0	0.0422[a]	21.0	1.9	11:30	4
PAMDAS-5	3.587	50.46	1.42	5.16	0.00422[a]	21.0	1.9	12:00	20
PAMDAS-6	1.981	27.87	3.01	10.9	0.00422[a]	21.0	1.9	12:00	4
PAMDAS-7	1.099	15.46	3.95	14.3	0.00422[a]	21.0	1.9	12:00	2
PAMDAS-8	3.574	50.28	1.41	5.12	0.0503[b]	21.0	2.0	14:00	9
PAMDAS-9	1.980	27.85	3.02	11.0	0.0503[b]	21.0	1.9	14:00	3
PAMDAS-10	1.111	15.63	3.90	14.2	0.0503[b]	21.0	2.0	14:00	2

[a]Initiator: H_2O_2

[b]Initiator: $K_2S_2O_8$

of 0.01 M Na_2SO_4 were chromatographed on a 4 mm I.D. by 25 cm Toyopearl TSK-GEL HW-40S column to determine the residual monomer content of the copolymer samples. The solutions were chromatographed at a flow rate of 0.4 mL/min, using aqueous 0.01 M Na_2SO_4 as the mobile phase.

Viscosities of five aqueous solutions of PAMDAS-1 (3.9% DAS) containing 0.003 to 0.015 g of polymer per mL of 0.5 M NaCl were measured at pH 6.7 $\pm$ 0.2 and 25.0 $\pm$ 0.05^{o}C. The intrinsic viscosity was determined by extrapolation of a plot of reduced viscosity versus concentration to zero concentration. Then the weight average molecular weight of the copolymer was calculated using Eq. 2-5 on page 40.

2.8. Flocculation Tests

2.8.1. Preparation of Flocculant Solutions

Copolymers PAMSM-1 (7% imide, ca. 1.8 million mol. wt.), PAMSM-2 (15% imide), and PAMSM-3 (25% imide, ca. 600,000 mol. wt.) were tested along with three commercial flocculants: Percol 351 (nonionic polyacrylamide, 20 million mol. wt.), Percol E24 (10% HPAM, 15 million mol. wt.), and Praestol 2935/73 (37% HPAM, 4-6 million mol. wt.). Stock polymer solutions were prepared by dissolving an exact amount of polymer in the 0.020 to 0.040 g range in 40.0 mL of de-ionized water. The suspensions of the commercial

polymers were stirred at high speed for a few minutes to disperse the polymer, then stirred at low speed for about 2 hours, and finally left to stand overnight. The PAMSM copolymers dissolved quickly, so their solutions were prepared only about 30 minutes before the flocculation experiments were started.

The copolymer solution saved from the dialysis of copolymer PAMSM-1 was also tested to determine if freeze drying had any effect on the performance of the copolymer, and to confirm that 30 minutes was sufficient time to dissolve the copolymer before use. This solution, which is referred to as PAMSM-1b in this report, was diluted with de-ionized water so that the polymer concentration was the same as the concentration of the solution prepared from the freeze dried copolymer. The label PAMSM-1a refers to the solution prepared from the freeze dried copolymer.

2.8.2. Flocculation Tests on a 3% Ca-Montmorillonite Suspension

A stock suspension of Ca-montmorillonite was prepared by dispersing 60.0 g of the clay in 500 mL of de-ionized water. The suspension was left to stand for 11 days to hydrate the clay. Another 1500 mL of de-ionized water was then added to the suspension. The suspension was stirred rapidly with an overhead stirrer while 100 mL aliquots were transferred by pipette to 100 mL graduated settling

cylinders.

Flocculation tests were done at pH 7.5, which was the natural pH of the suspension, and at pH 4.0 using dilute HCl to adjust the pH to this value. Settling rates were determined by incremental addition of the polymer solutions to the cylinders. After each addition the cylinders were stoppered and inverted ten times to mix the polymer and then left to stand in a vertical position. The rate of descent of the supernatant-pulp interface was recorded, starting from the 100 mL mark. The turbidity of 20 mL of the supernatant, pipetted from the 70 mL mark of the cylinders, was measured with a turbidimeter. The turbidity was measured either six minutes after the polymer was added, or for very slowly settling samples, after the interface had descended below the 50 mL level. Excess volume was removed as clear supernatant before each addition of polymer solution so that the solution level remained at the 100 mL mark. The polymer dosages are reported as milligrams of polymer per kilogram of clay (i.e. ppm).

2.8.3. Flocculation Tests on a 3% Kaolinite Suspension

Flocculation tests were also conducted on a 3% by weight suspension of Hydrite R (kaolinite). A stock kaolinite suspension was prepared by dispersing 120 g of the clay in 1000 mL of de-ionized water. The suspension was left for 8 days to hydrate the clay. Another 1000 mL of de-

ionized water was then added to the suspension. The suspension was stirred rapidly with an overhead stirrer while 50 mL aliquots were transferred by pipette to 100 mL graduated cylinders. The aliquots were then diluted to 100 mL with de-ionized water.

Flocculation tests were done at pH 4.5, the natural pH of the suspension. Settling rates and turbidity measurements were performed in the same manner as the tests involving Ca-montmorillonite.

2.8.4. Flocculation Tests on a 3% Hematite Suspension

PAMSM-1a (7% imide), PAMSM-3 (25% imide), Praestol 2935/73 (37% HPAM), and polystyrene sulfonate (Polysciences: 500,000 mol. wt.) were tested on a 3% by weight hematite suspension at pH 4.5, 6.0 and 8.7, at dosages ranging from 30 ppm up to 1000 ppm. The tests were done in 100 mL graduated settling cylinders.

2.9. Dispersion Experiments

2.9.1. Polymer Solutions

Solutions of PAMMBA-1, -2, -3, -7 and -8, and PAMDAS-1, -2 and -3 were prepared by dissolving an exact amount (ca. 40 mg) of the copolymers in 40.0 mL of de-ionized water one day before use. The pH of the solutions was adjusted to

5.8 $\pm$ 0.2 with dilute NaOH or HCl. A solution of DISPEX N-40 (Allied Colloids), which is a polyacrylate dispersant containing 40 wt % active solids, was prepared by diluting 1.000 g of the solution in 200 mL of de-ionized water.

2.9.2. Effect of the Copolymer Compositions on the Effectiveness of the Copolymers as Dispersants

Tests to determine the effect of the compositions of the PAMMBA and PAMDAS copolymers on the stability of a kaolinite suspension were done using a one year old stock suspension of Hydrite R, containing 120 g of clay per 2000 mL of de-ionized water. The pH of the suspension was 4.78 when diluted with an equal volume of de-ionized water.

Tests were performed in 100 mL settling cylinders containing 50.0 mL of the stock suspension, 44.0 mL of de-ionized water and 6.0 mL of polymer solution. The cylinders were inverted 40 times after the polymer solution was added and then set upright. The turbidities of the samples were determined after 1, 2, 4, 8, 24, and 48 hours by pipetting 2.0 mL aliquots from the 60 mL level of the cylinders and diluting the aliquots with de-ionized water to reduce the turbidities to below 1000 NTU.

The effect of the PAMMBA copolymers on the stability of the suspension was also determined by recording the level of the interface between the settled or rapidly settling clay particles, and the turbid supernatant.

2.9.3. Effect of Copolymer Dosage on the Dispersion Stability

The performance of PAMMBA-3 was compared with DISPEX N-40 (Allied Colloids) at dosages of 250, 500, 1000, and 2000 ppm.

A 2.5 month old suspension of Hydrite R containing 120 g of clay per 1000 mL of de-ionized water was used to determine the effect of polymer dosage on the stability of kaolinite suspensions. Tests were done in 100 mL graduated settling cylinders containing 25 mL of the stock suspension, 72.0 to 74.7 mL of de-ionized water, and 370 to 3000 micro-litres of polymer solution. The cylinders were inverted 20 times to mix the polymers and then set upright. The turbidities and interface levels were determined in the same manner as described in Section 2.9.2.

3. Results and Discussion

3.1. Preparation and Characterization of the Monomers and Copolymers

3.1.1. Poly(acrylamide-co-sodium N-(4-sulfophenyl)maleimide) (PAMSM)

Preparation and Characterization of the Monomers

The preparations of the monomers proceeded smoothly to give well characterized products. The only problem encountered in the analyses was that the sulfur micro-analyses gave results that were invariably low by about 10% of the calculated sulfur content. Test samples of pure sulfanilic acid and its sodium salt dihydrate (Section 2.3.1) also gave sulfur analyses for both that were about 93% of the calculated sulfur content, with accurate values for C, N, and H. Hence, this difficulty is ascribed to an idiosyncracy of the method used to determine the sulfur content rather than to impure, or incorrect products. The sulfur analyses of the copolymers also seem to be about 10% too low when the C/S and S/N ratios are compared to the C/N ratios.

The PAS-FTIR and ^{13}C NMR spectra of the monomers are shown in Figs. 5 to 9. No ^{13}C NMR data was found in the literature for the monomers so the ^{13}C resonances reported

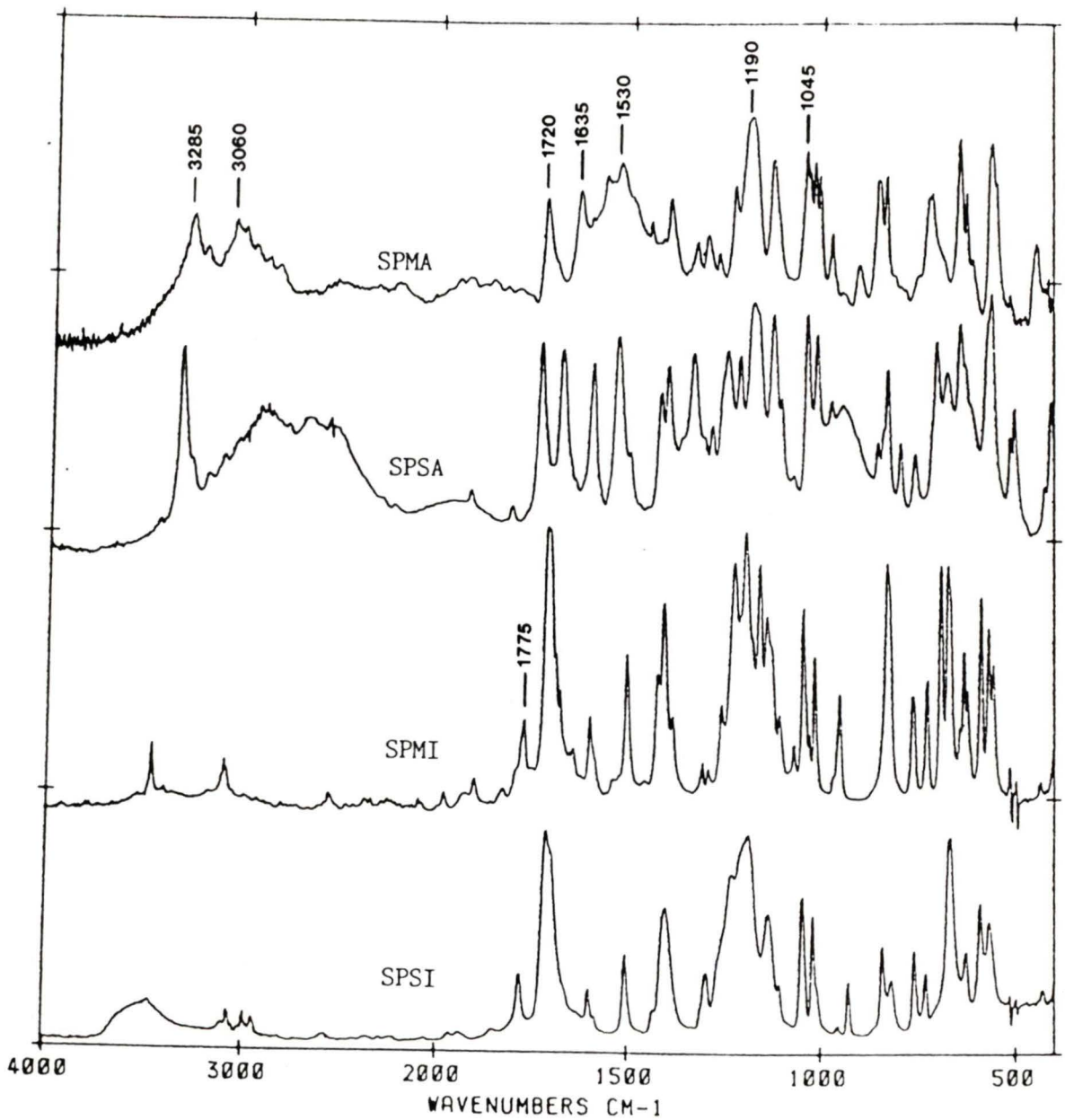


Fig. 5: PAS-FTIR Spectra of the PAMSM Monomers

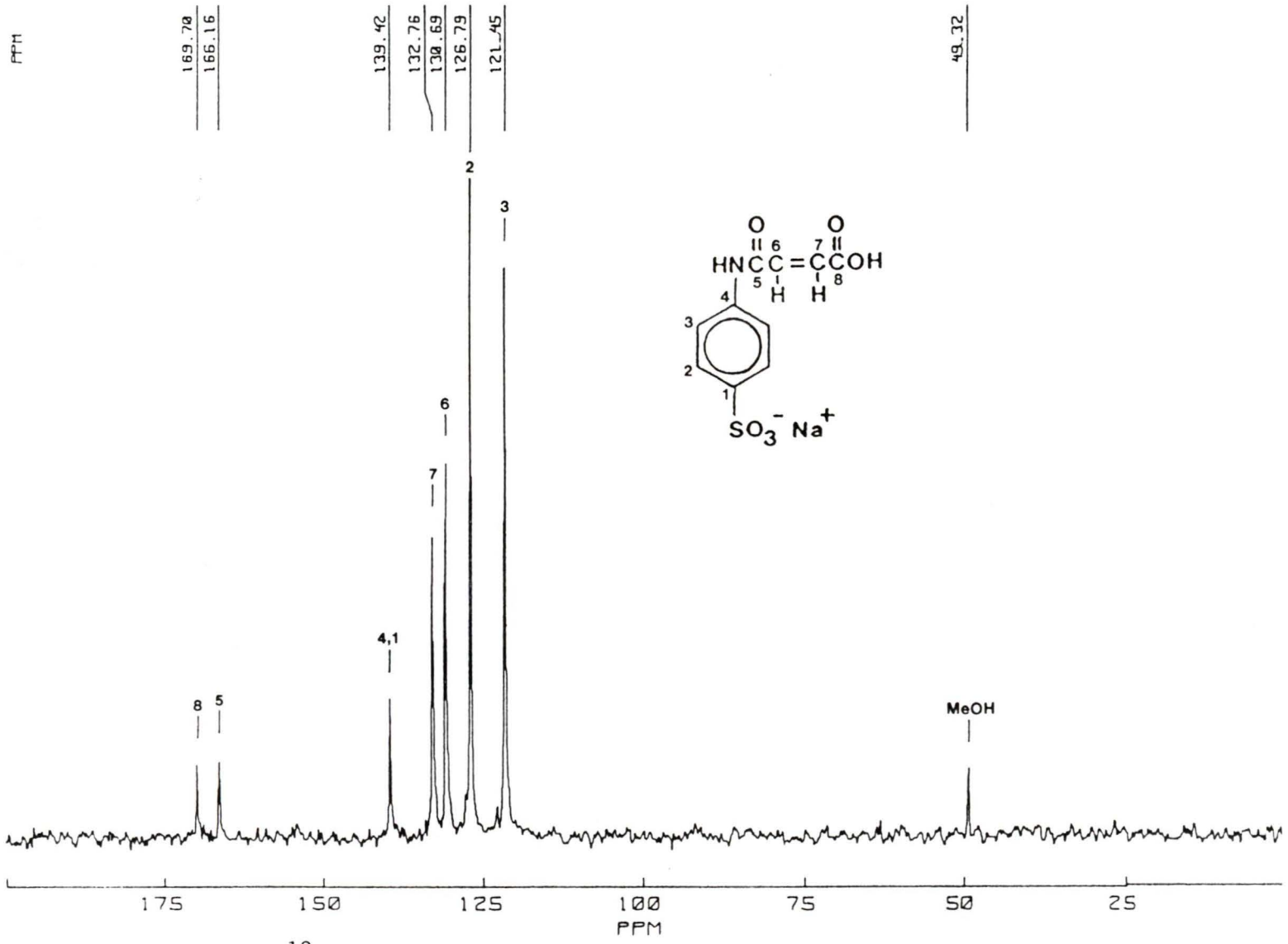


Fig. 6: ^{13}C NMR Spectrum of Sodium N-(4-sulfophenyl)maleamic Acid 10

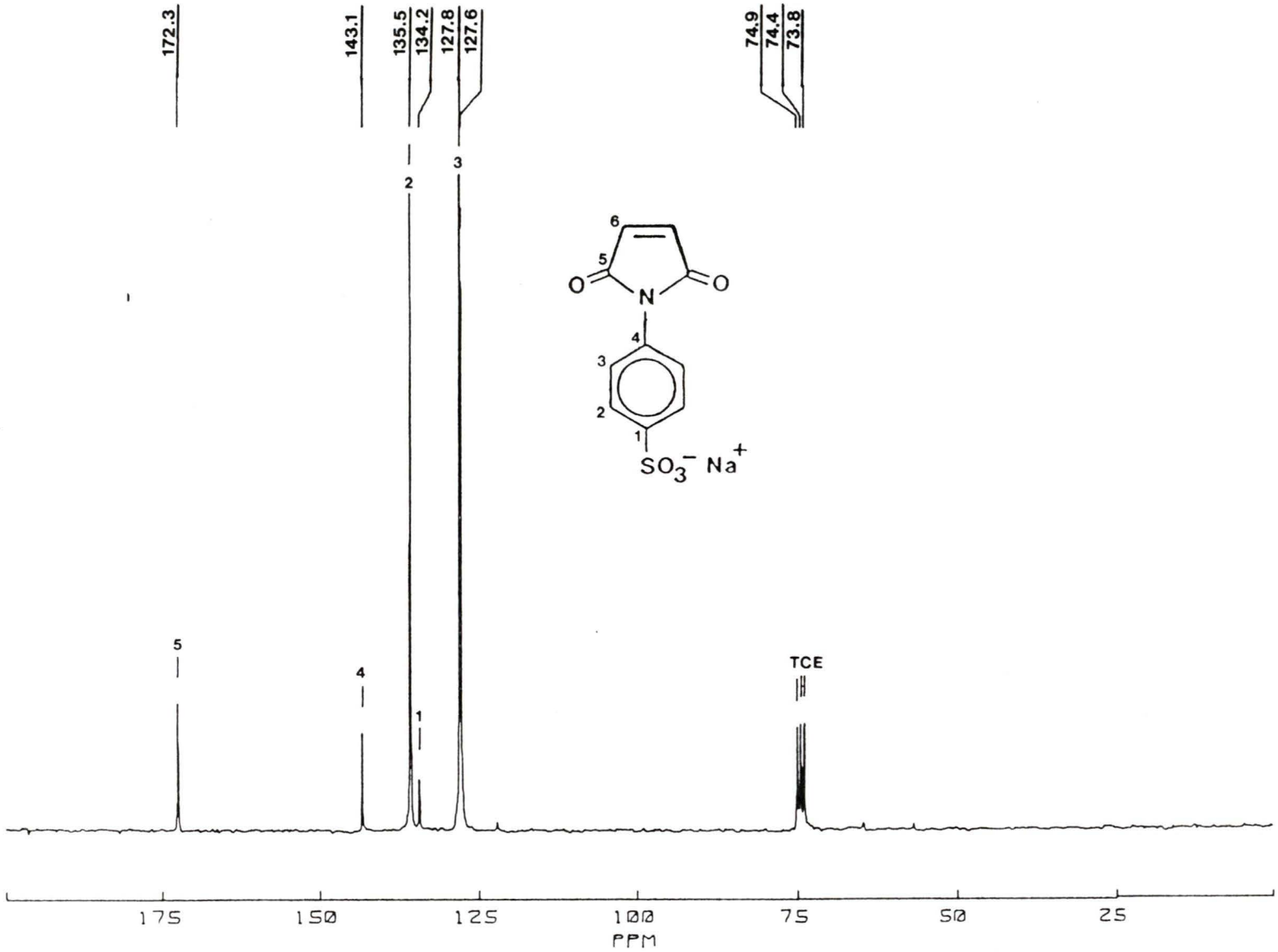


Fig. 7: ^{13}C NMR Spectrum of Sodium N-(4-sulfophenyl)maleimide 3

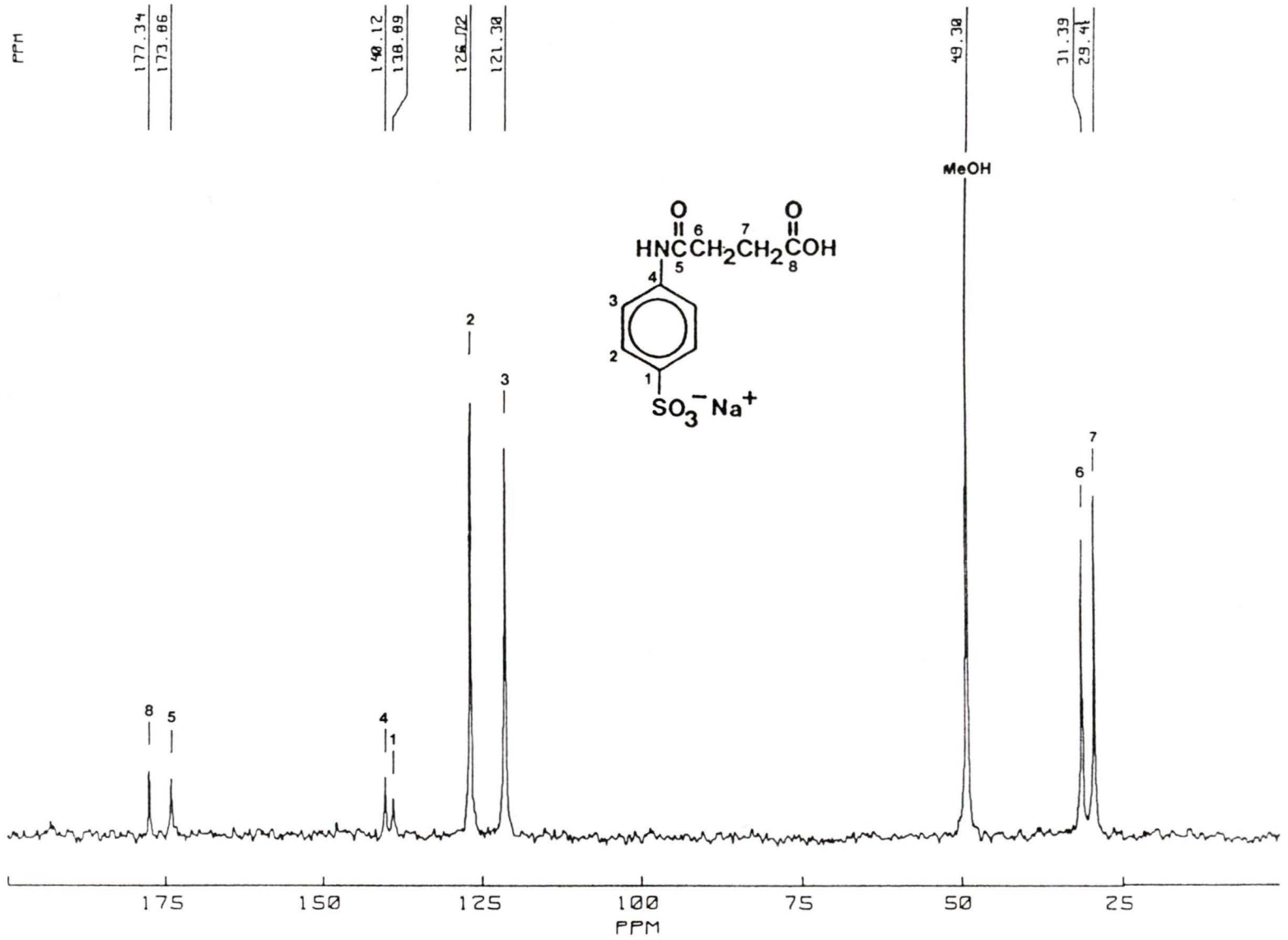


Fig. 8: ^{13}C NMR Spectrum of Sodium N-(4-sulfophenyl)succinic Acid 12

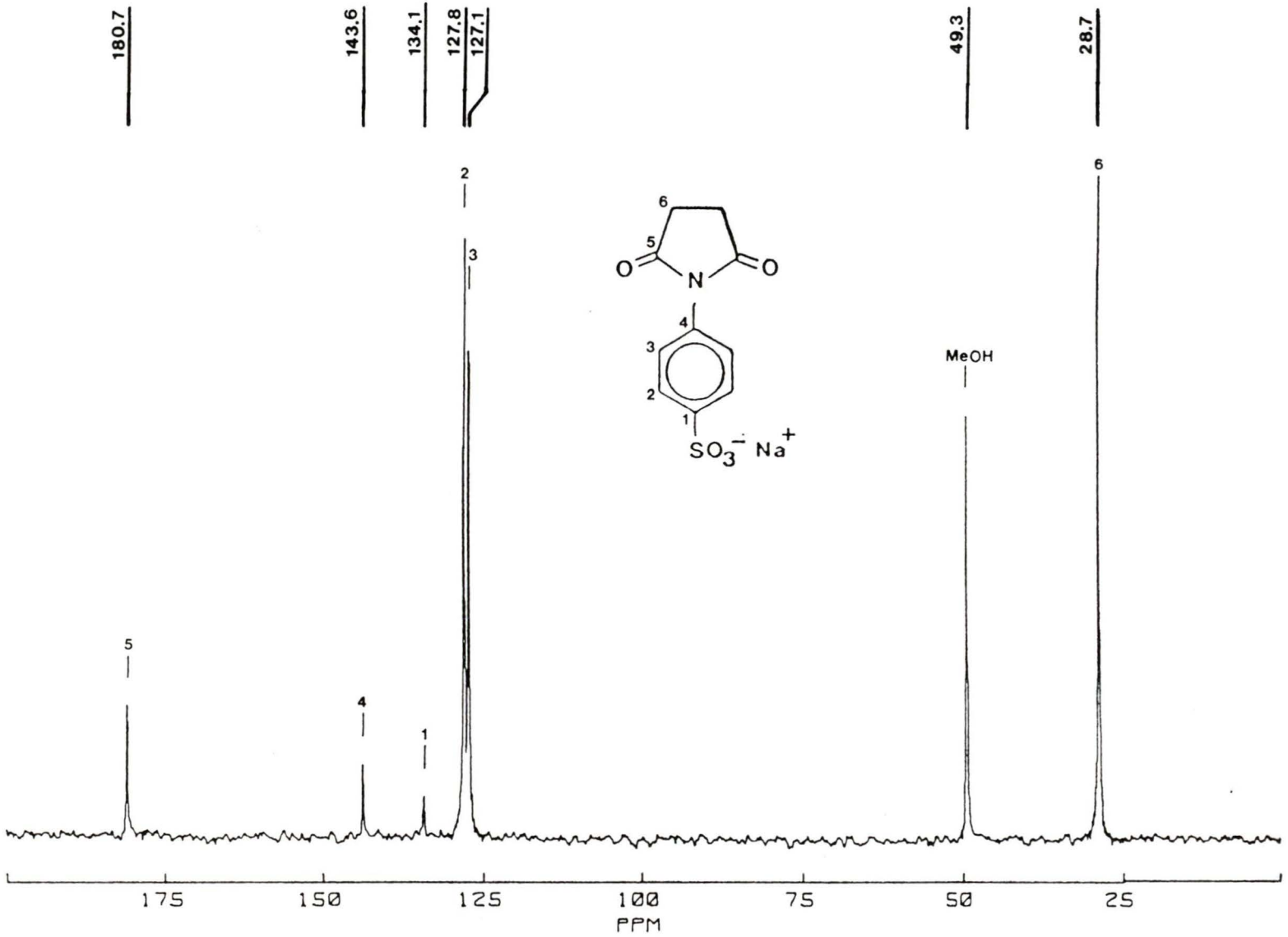
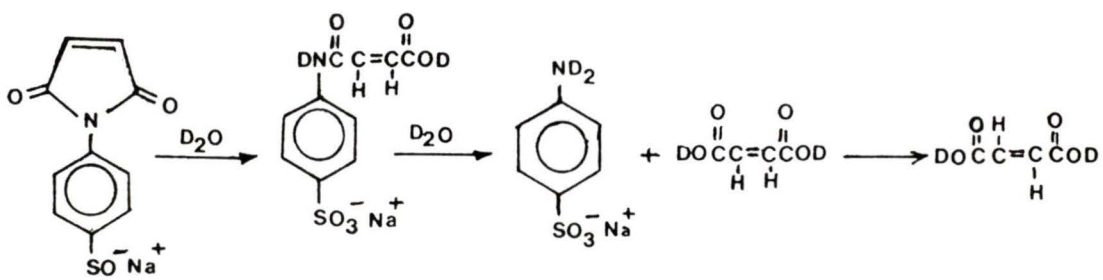


Fig. 9: ^{13}C NMR Spectrum of Sodium N-(4-sulfophenyl)succinimide 13

here were assigned by comparison with the spectra of structurally similar compounds[44,45] and by using tabulated HOSE codes ("Hierachically Ordered Spherical Description of Environment").[46]

Hydrolytic Stability of Sodium N-(4-sulfophenyl)maleimide (SPMI) 3



3 10 8 19 20

SPMI 3 underwent partial hydrolysis over a period of a few days when dissolved in D_2O alone to give a mixture of sodium N-(4-sulfophenyl)maleamic acid (SPMA) 10, sodium sulfanilate 8 and maleic acid 19 (Fig. 10). SPMI 3 was immediately saponified when dissolved in D_2O containing 1.3 moles of sodium hydroxide per mole of the imide, yielding SPMA 10. For smaller proportions of sodium hydroxide the extent of immediate saponification of SPMI 3 was equal, within experimental error, to the molar ratio of sodium hydroxide to the maleimide. The remaining SPMI 3 underwent slower hydrolysis over a period of a few days to give a mixture of SPMA 10, sodium sulfanilate 8, and maleic acid

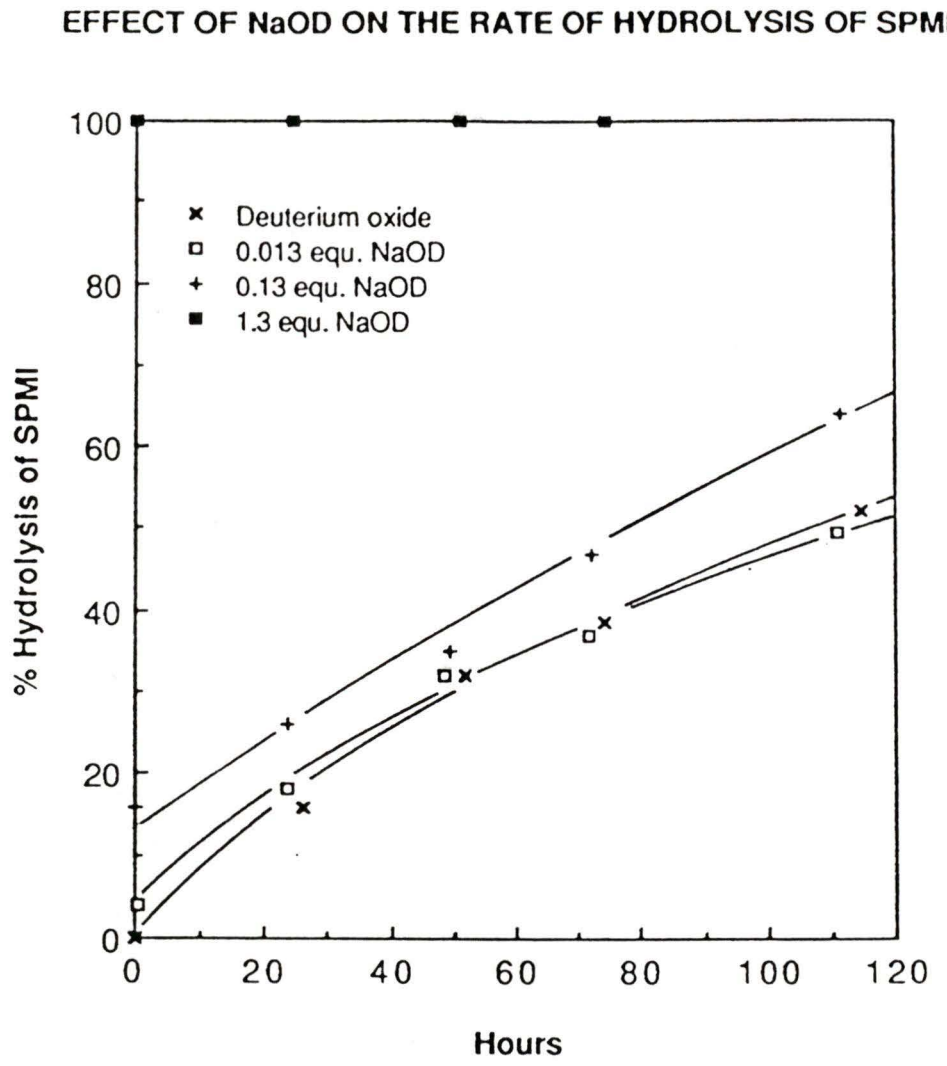


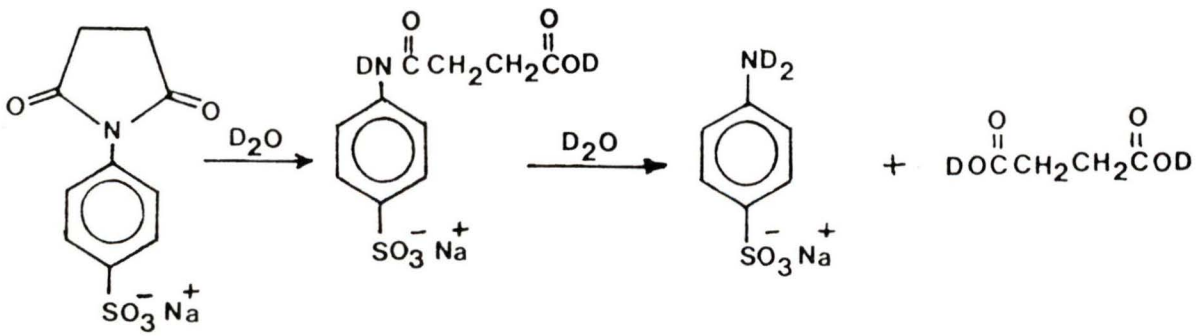
Fig. 10: Effect of NaOD on the Rate of Hydrolysis of SPMI 3 in D_2O at 23°C

19.

The rate of hydrolysis of SPMI 3 in D_2O alone increased as the temperature was increased from 23°C to 40°C to 60°C (Fig. 11). The maleimide 3 was partially hydrolyzed to give a mixture of SPMA 10, sodium sulfanilate 8, maleic acid 19, and fumaric acid 20. Fumaric acid was produced in the experiments at 40°C and 60°C by the cis-trans isomerization of maleic acid.

The results of these experiments demonstrated the need to copolymerize SPMI 3 with acrylamide 1 at as low a temperature as possible (i.e. approx. 30°C) to minimize hydrolysis of the imide monomer.

Hydrolytic Stability of Sodium N-(4-Sulfophenyl)succinimide (SPSI) 13



13 12 8 21

SPSI 13 immediately reacted when dissolved in D_2O containing 1.3 moles of NaOH per mole of the imide, to give a mixture of sodium N-(4-sulfophenyl)succinic acid (SPSA)

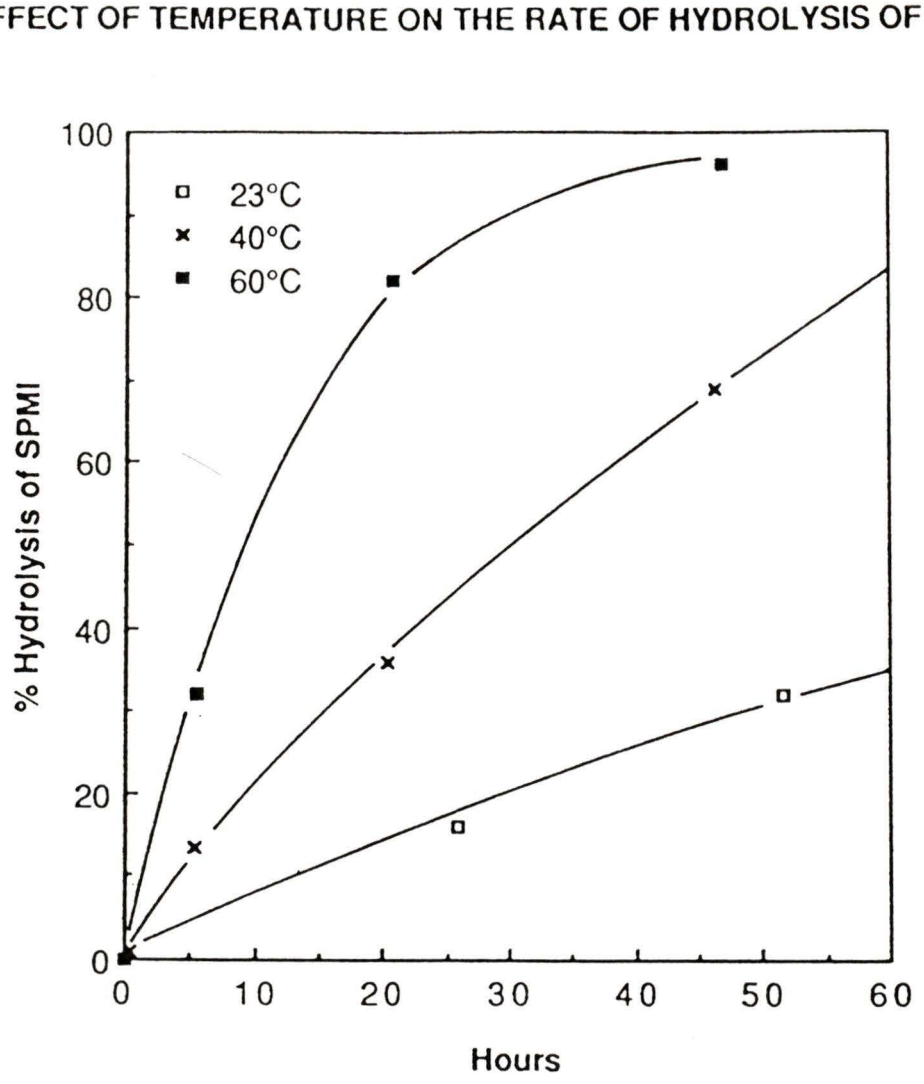


Fig. 11: Effect of Temperature on the Rate of Hydrolysis of SPMI 3 in D_2O

12, sodium sulfanilate 8 and succinic acid 21. This indicates that the imide rings in the imide-amide copolymer PAMSM, which are similar in structure to SPSI 13, would be rapidly saponified under alkaline conditions, destroying any rigidity that the imide rings may have provided in the copolymer chains.

Approximately 1% of SPSI 13, was hydrolyzed after 18 days in D_2O at room temperature (ca. 23°C) while 29% of the imide was hydrolyzed after 18 days in D_2O at 60°C (Fig. 12). This showed that, as anticipated, the saturated succinimide ring of SPSI 13 was much more stable than the unsaturated maleimide ring of SPMI 3. It was also an indication that the saturated imide rings of PAMSM might be sufficiently stable for the copolymer to be useful as a flocculant, especially near 25°C.

Obviously, more rigorous control of factors such as pH and ionic strength would be necessary to determine the rate constants for hydrolysis of these imide monomers. However, the purpose of this experiment was only to determine the relative stabilities of the monomers before copolymerization experiments were performed. A more detailed study of the rates of hydrolysis of imidosulfonate surfactants has been done by Stournas.[47]

EFFECT OF TEMPERATURE ON THE RATE OF HYDROLYSIS OF SPSI

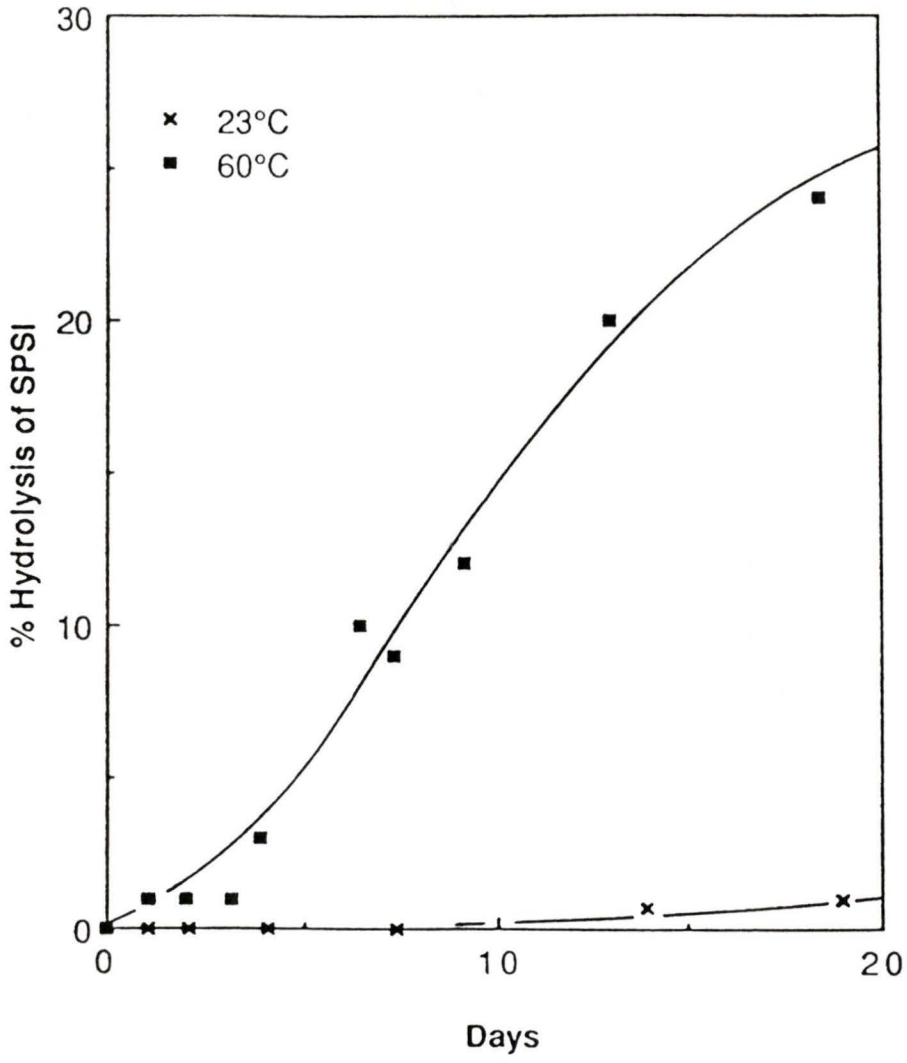


Fig. 12: Effect of Temperature on the Rate of Hydrolysis of SPSI 13 in D_2O

Preparation and Characterization of Poly(acrylamide-co-sodium N-(4-sulfophenyl)maleimide (PAMSM)

The residual monomer content of the dialyzed PAMSM copolymers was determined by gel permeation chromatography using a 7.5 mm I.D. by 30 cm TSK-GEL G5000PW column and 0.005 M Na_2SO_4 as the eluent. An ionic strength of 0.05 M Na_2SO_4 was found to be unsuitable because the retention times of the copolymers with high imide content were increased to the point where the copolymer and monomer peaks could not be resolved.

The copolymers had retention times ranging from 3.4 minutes for PAMSM-1 to 4.3 minutes for PAMSM-6. All of the copolymer samples were contaminated with traces of residual monomers, as small peaks were also eluted at 7 and 8 minute retention times. The five possible impurities that had retention times of 7 or 8 minutes were SPMI 3 (8 min), SPMA 10 (7 min), sodium sulfanilate 8 (7 min), maleic acid 19 (7 min) and acrylamide 1 (7 min). The ^{13}C NMR spectra of the copolymers indicated that the main impurity in the copolymers, besides SPMI 3, was SPMA 10. Therefore, the impurity eluted at 7 minutes was assumed to be SPMA 10 for calculation of the imide content of the copolymers from the C, N, and S elemental analyses. The amounts of residual SPMI 3 and SPMA 10 monomer were determined by comparing the peak areas of the impurities with the peak areas of solutions containing known concentrations of SPMI 3 and SPMA 10. In

Table 7: Composition of the PAMSM Copolymers

Copolymer	Feed Ratio AM:SPMI	Wt% C	Wt% N	Wt% S	Wt% Total Imide	Wt% Residual SPMI	Wt% Residual SPMA	Wt% Imide	Mole % Imide
PAMSM-1	95:5	43.72	14.22	2.55	25.1 ± 0.9	1.3	0.6	23.7	7.4
PAMSM-2	90:10	41.42	11.46	4.18	42.9 ± 1.8	1.5	1.3	41.3	15.4
PAMSM-3	80:20	39.56	9.47	5.35	56.3 ± 2.1	0.5	0.6	55.8	24.6
PAMSM-4	70:30	39.59	8.10	6.46	67.6 ± 3.1	2.1	3.9	65.6	33.0
PAMSM-5	50:50	38.58	7.23	n/m	76.8	1.8	2.5	75.8	44.7
PAMSM-6	24:76	38.52	5.72	n/m	89.8	6.9	12.3	87.4	64.3
PAMSM-7	90:10	42.79	11.37	4.72	45.1 ± 1.0	0.0	0.5	44.9	17.4
PAMSM-8	50:50	39.83	7.03	6.88	72.6 ± 4.0	0.0	0.3	72.3	40.2
PAMSM-9	25:75	39.06	5.48	9.13	89.4 ± 1.7	0.0	2.4	89.1	67.9

n/m: Not measured.

Wt% Total Imide: Wt% of copolymerized SPMI, residual SPMI monomer and residual SPMA monomer reported as wt% SPMI. Values reported are the averages of the wt% imide calculated using the C/N, C/S, and S/N ratios. The error limits are expressed as one standard deviation of the three values calculated for each copolymer.

Wt% Residual SPMI and SPMA: Determined by GPC.

Wt% Imide: Wt% of copolymerized SPMI in the copolymers.

Mole % Imide: Mole % of copolymerized SPMI in the copolymers.

this way it was calculated that the copolymers contained 0.4 to 6.9% by weight residual SPMI 3 and 0.6 to 12.3% by weight SPMA 10 (Table 7).

The total weight percentage of sodium N-(4-sulfophenyl)maleimide (SPMI) 3 in the copolymers, including both copolymerized and residual monomer, was calculated using the elemental analysis. These ratios were used because of the variability of the absolute C, N, and S values due to traces of residual water. Also, using these ratios eliminated error that may have been caused by the presence of any copolymerized or residual sodium N-(4-sulfophenyl)maleamic acid (SPMA) 10, which differs in its molecular formula from that of the imide 3 by the equivalent of one water molecule. The weight percentage of copolymerized SPMI 3 was calculated by subtracting the weight percentage of residual SPMI 3 and SPMA 10 monomer, determined by GPC, from the average of the total weight percentage of SPMI 3 calculated using Eqs. 3-1, 3-2, and 3-3.

$$\frac{\text{Wt\% SPMI}}{\text{Wt\% AM}} = \frac{(3)(12.01)(275.21) - (C/N)(14.01)(275.21)}{(C/N)(14.01)(71.08) - (10)(12.01)(71.08)} \qquad (3\text{-}1)$$

$$\frac{\text{Wt\% SPMI}}{\text{Wt\% AM}} = \frac{(3)(12.01)(275.21)}{(C/S)(32.06)(71.08) - (10)(12.01)(71.08)} \qquad (3\text{-}2)$$

$$\frac{\text{Wt\% SPMI}}{\text{Wt\% AM}} = \frac{(S/N)(14.01)(275.21)}{(32.06)(71.08) - (S/N)(14.01)(71.08)} \qquad (3\text{-}3)$$

Then the weight percentages of copolymerized SPMI 3 and acrylamide (AM) 1 were substituted into Eq. 3-4 to calculate the mole % of copolymerized SPMI 3.

$$\text{Mole \% SPMI} = \frac{(100)}{1 + \dfrac{(275.21)(\text{Wt\% AM})}{(71.08)(\text{Wt\% SPMI})}} \qquad (3\text{-}4)$$

GPC and the elemental analyses indicated that PAMSM copolymers containing 7.4 mole % to 64 mole % SPMI 3 were obtained using initial monomer feed ratios of 5:95 to 76:24 SPMI 3 to acrylamide (AM) 1 (Tables 1, 7). The yield of copolymer obtained decreased from 16 to 1.5% as the initial monomer feed ratio of SPMI 3 to acrylamide increased. This was probably because SPMI 3 is a 1,2-disubstituted alkene monomer, which would be expected to have a lower rate of propagation than acrylamide because of steric hindrance.[51] Steric hindrance would tend to slow propagation in favour of termination or chain transfer reactions.

Comparison of the PAS-FTIR spectra of the copolymers (Fig. 13) with the spectrum of polyacrylamide confirmed that an acrylamide polymer was produced. The strong stretching bands at 3348 and 3208 cm^{-1} are the asymmetric and symmetric N-H stretching bands, respectively, of the acrylamide units in the copolymer. The amide I C=O stretching vibration and the

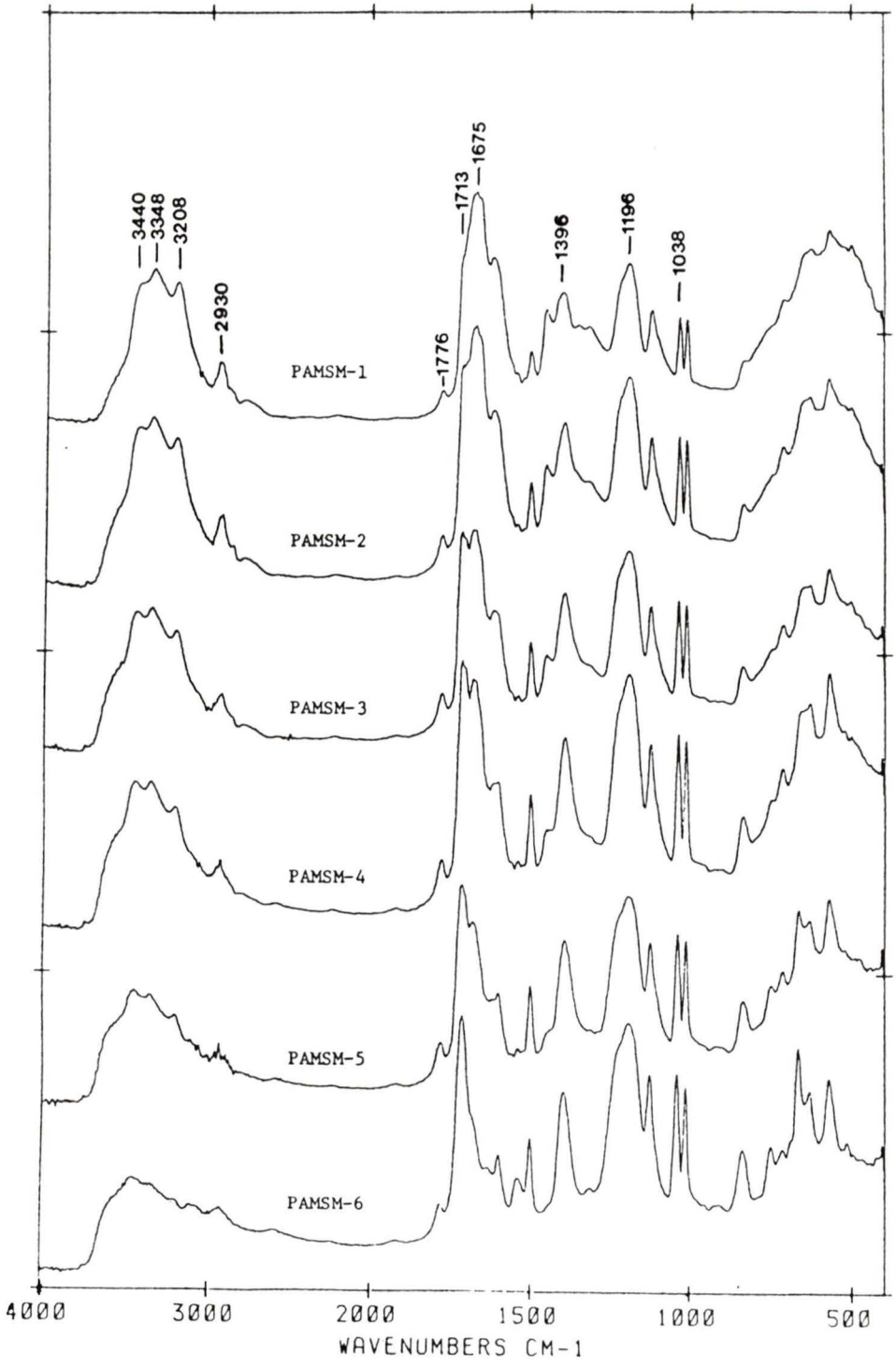


Fig. 13: PAS-FTIR Spectra of the PAMSM Copolymers

amide II N-H bending vibration of the acrylamide units occur at 1675 and 1610 cm^{-1}, respectively. Methylene C-H stretching is observed at 2930 cm^{-1}.

Comparison of the PAS-FTIR spectra of the copolymers with the spectra of monomeric sodium N-(4-sulfophenyl)-maleimide (SPMI) 3 and sodium N-(4-sulfophenyl)succinimide (SPSI) 13 (Fig. 7) shows that a significant amount of imide was present in the polymers. The PAS-FTIR spectra of the maleimide 3 and the succinimide 13 are so similar, though, that it appears to be difficult to confirm by PAS-FTIR alone whether the polymer samples were actually copolymers, or just polyacrylamide contaminated with the maleimide monomer 3. However, the GPC and ^{13}C NMR data show that copolymerization did occur and that the residual maleimide monomer 3 content was only a fraction of the total imide present.

The weak C=O stretching band observed at 1776 cm^{-1} and the stronger C=O stretching band at 1713 cm^{-1} are characteristic of a five-membered imide ring. The lower frequency imide C=O stretching band appears only as a shoulder in the spectra of PAMSM-1 (7.4% imide) and PAMSM-2 (15% imide), but becomes clearly visible in the spectra of PAMSM-3 (25% imide) through PAMSM-6 (64% imide). Asymmetric S=O stretching contributes to the strong, broad band at 1196 cm^{-1}, while symmetric S=O stretching is responsible for the band at 1038 cm^{-1}. The intensities of the N-H and C=O

stretching bands increase relative to those of the acrylamide N-H and C=O stretching bands as the imide content increases, confirming the results calculated from the elemental analyses. Also, the methylene C-H stretching band at 2930 cm^{-1} becomes weaker as the imide content increases since the imide units contain no methylene groups. The absence of a strong carboxylic acid C=O stretching vibration at about 1735 cm^{-1} shows that little, if any, of the imide monomer that was incorporated into the copolymers was hydrolyzed.

The origin of the band at about 3440 cm^{-1} is uncertain. The band lies at about the same frequency as the N-H stretching band of residual maleamic acid 10 in spectrum of the maleimide 3 monomer (Fig. 5), so residual maleamic acid monomer 10 may be responsible for the band. Another possibililty is that the bulky imide units in the copolymer may interupt intra- or intermolecular hydrogen bonding of the adjacent acrylamide groups, causing the N-H stretching band of those groups to shift to higher frequency. Evidence supporting this suggestion is obtained from the N-H stretching band of sodium N-(4-sulfophenyl)maleamic acid 10, which lies at 3284 cm^{-1} in the spectrum of the neat maleamic acid, but shifts to 3473 cm^{-1} when the maleamic acid is present in low concentrations (i.e. 1 to 5%) as an impurity in SPMI (Fig. 5). The N-H band also shifts to 3425 cm^{-1} when SPMA 10 is run as a KBr pellet (i.e. at low

concentration in KBr).

The ^{13}C NMR spectra of PAMSM-1 to -4 are shown in Figs. 14 to 17. The ^{13}C resonances were assigned by comparison of the spectra of the copolymers with the spectra of polyacrylamide and sodium N-(4-sulfophenyl)succinimide 13 (Fig. 9). The succinimide monomer 13 is similar in structure to the imide units in the copolymer, except that two methylene carbons replace the two methine carbons. This difference would be expected to have little effect on the chemical shifts of the aromatic carbons. Aromatic ^{13}C resonances were observed at about 127.2, 127.6, 133.6, and 143.7 ppm in the copolymer spectra, which are virtually the same as the chemical shifts observed for the succinimide monomer 13 (Fig. 9) and are significantly different from the chemical shifts observed for sodium N-(4-sulfophenyl)-maleimide 3. The absence of an alkene ^{13}C resonance at 134.8 ppm is further evidence that the copolymer samples contained mostly polymerized, not monomeric SPMI 3.

The weak resonance seen at 121.5 ppm in the copolymer NMR spectra lies at about the same chemical shift as the resonances of two of the unsubstituted aromatic carbons of both sodium N-(4-sulfophenyl)maleamic acid 10 and sodium N-(4-sulfophenyl)succinic acid 13. The resonances of the other two unsubstituted aromatic carbons of the maleamic 10 and succinic 13 acids would lie under the signal at 127.2 ppm in the copolymer spectra. GPC showed that the

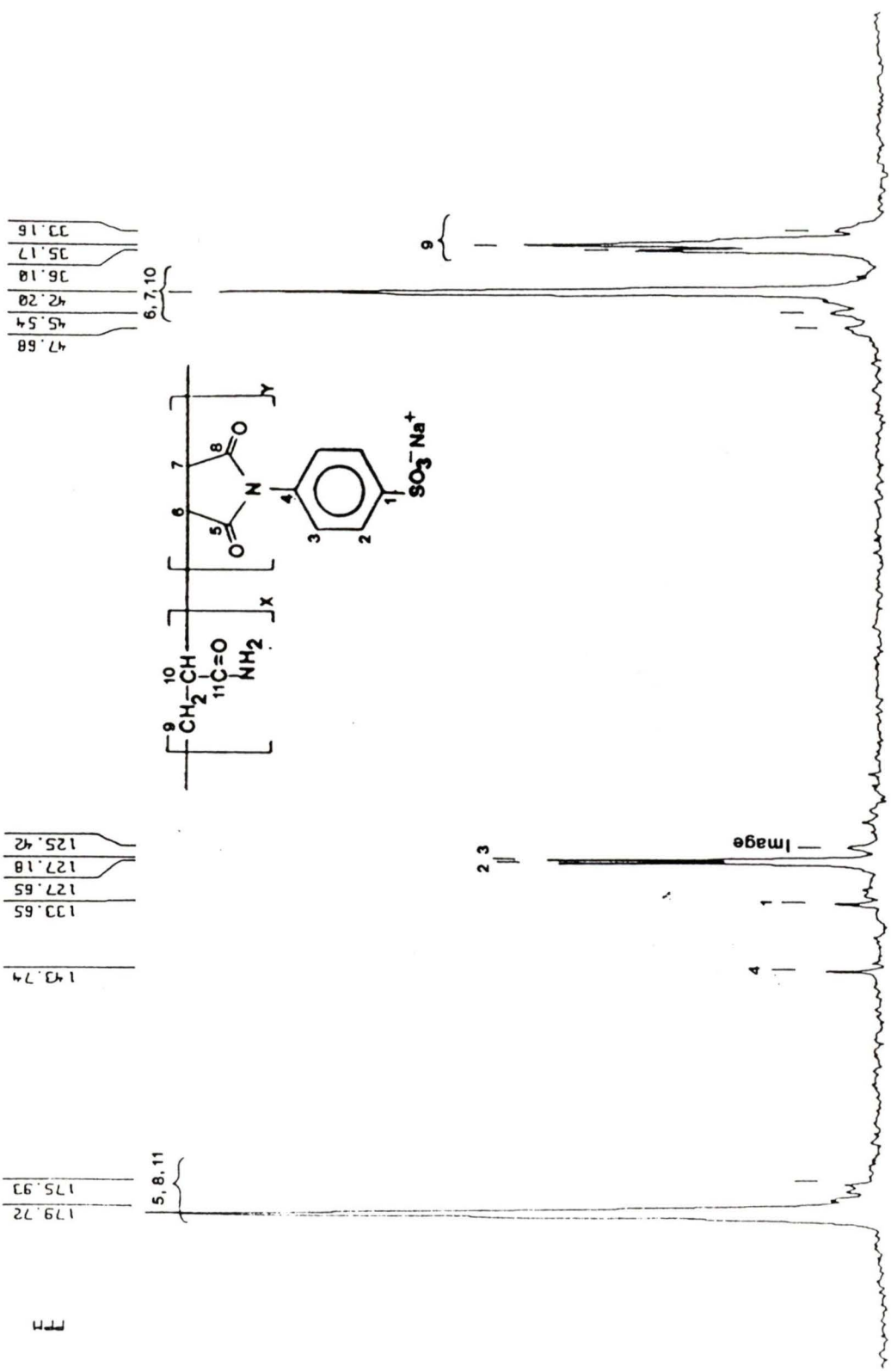


Fig. 14: ^{13}C NMR Spectrum of PAMSM-1

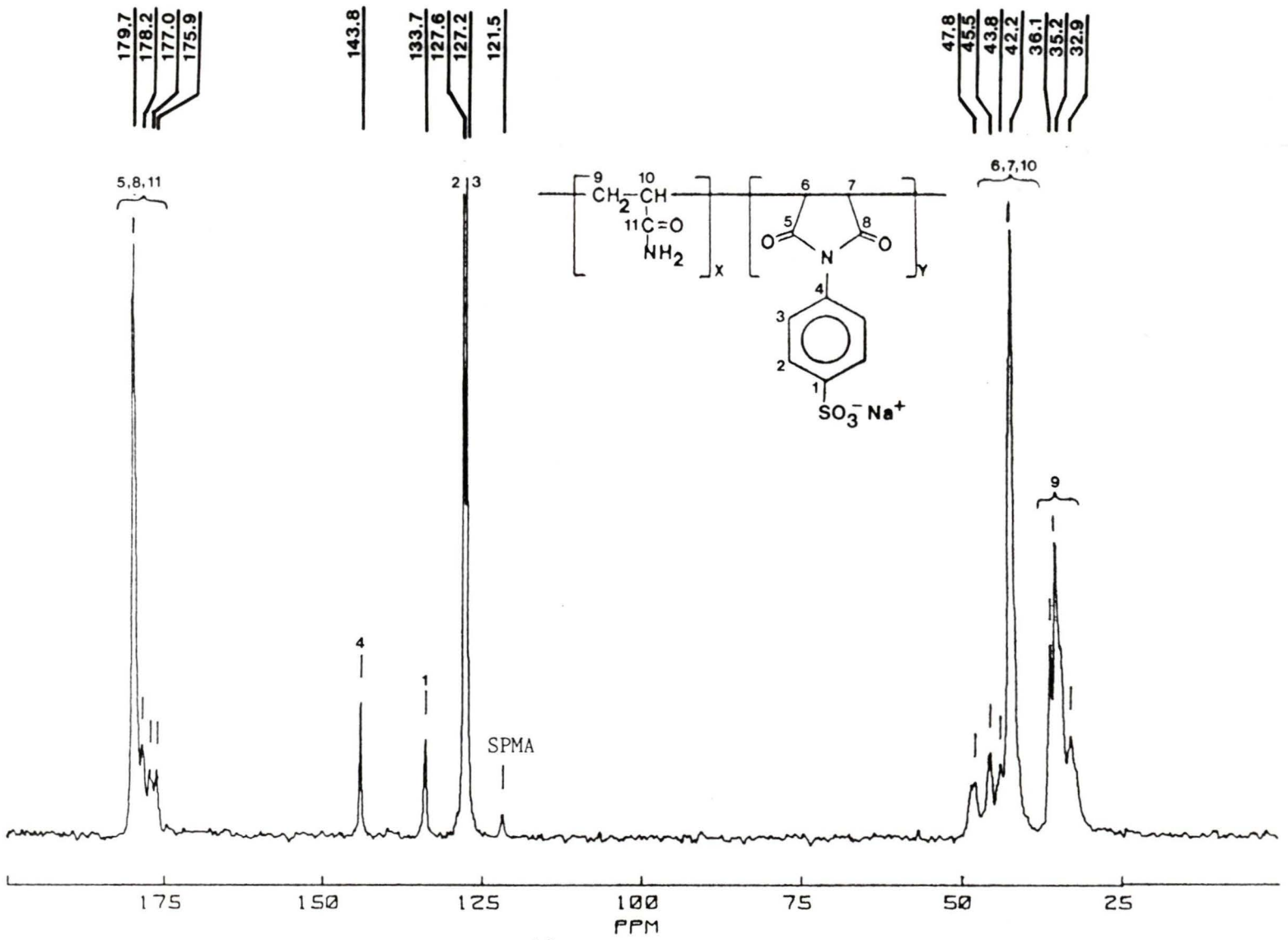


Fig. 15: ^{13}C NMR Spectrum of PAMSM-2

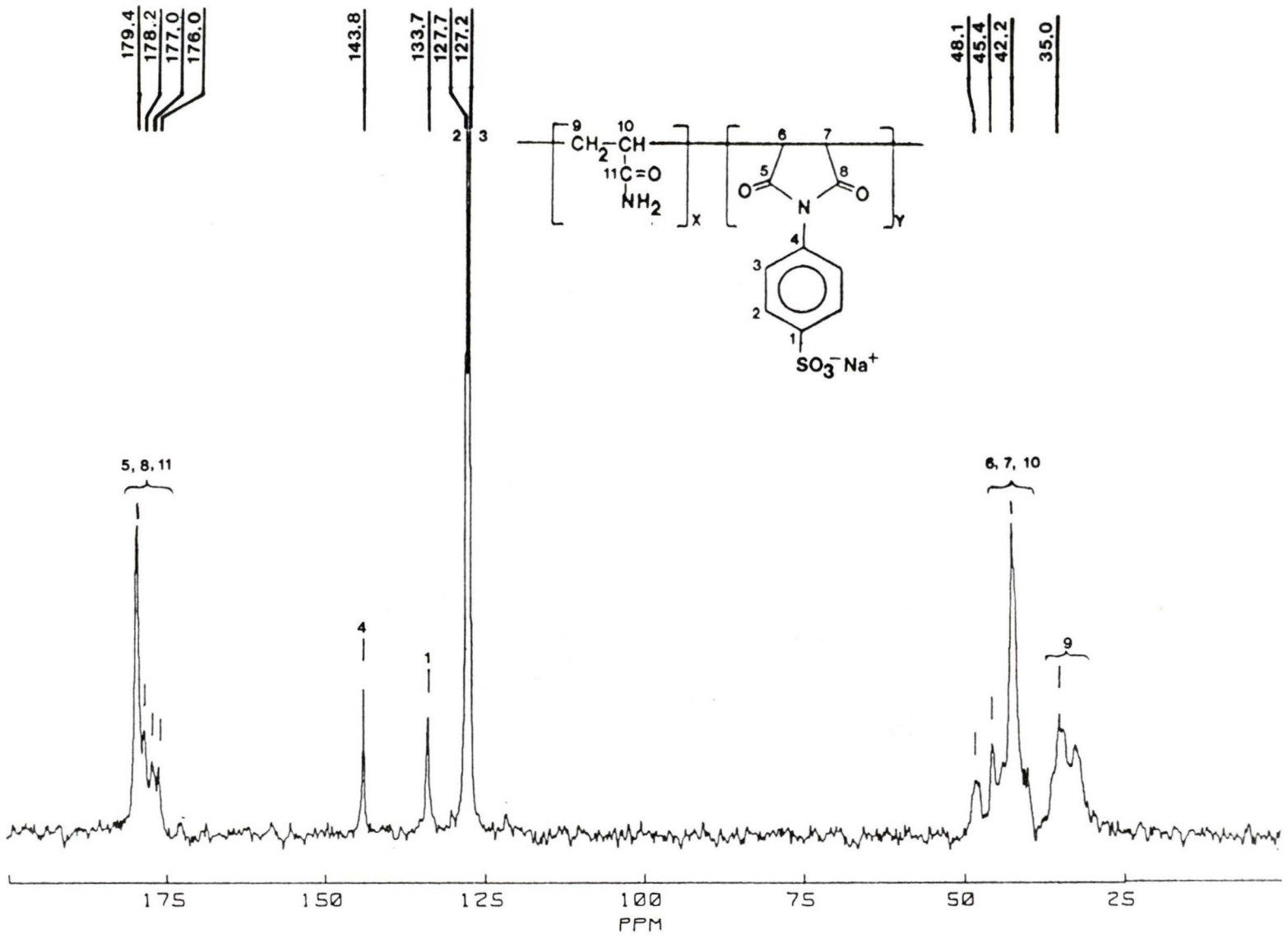


Fig. 16: ^{13}C NMR Spectrum of PAMSM-3

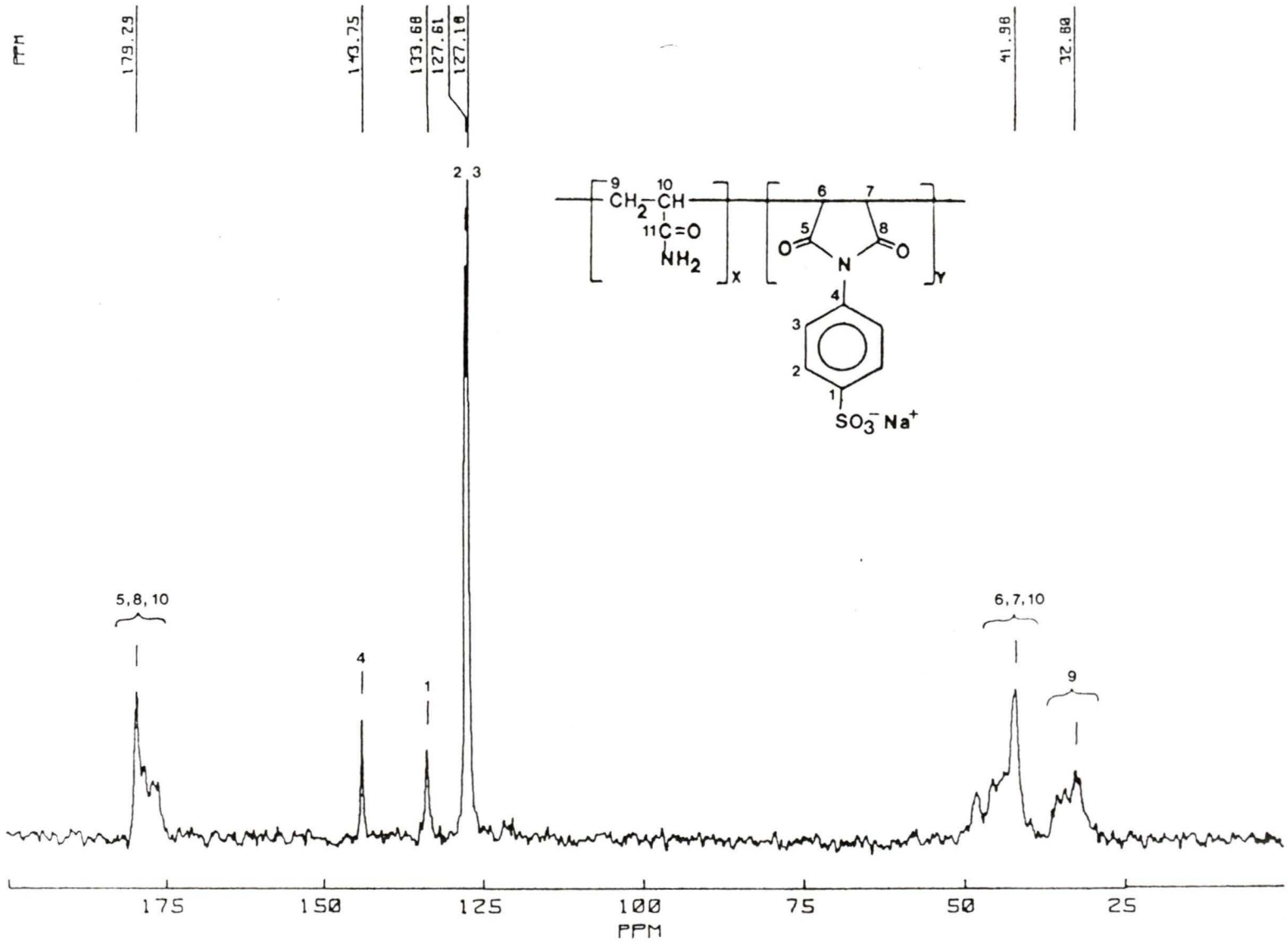


Fig. 17: ^{13}C NMR Spectrum of PAMSM-4

copolymers were contaminated with small amounts of residual maleimide 3 and maleamic acid 10 monomers, so the resonance at 121.5 ppm in the copolymer spectra is probably due to the presence of residual maleamic acid monomer 10 instead of hydrolyzed imide units in the copolymers. The hydrolyzed imide units, if they were present, would resemble the structure of the succinic acid monomer 13.

The multiplets observed between 42 and 47 ppm in the copolymer spectra correspond to the methine carbons while the multiplets from 32 to 37 ppm belong to the methylene carbons. The resonances between 175 and 180 ppm correspond to the carbonyl carbons of both the acrylamide and imide units in the copolymers.

The relative intensities of the aliphatic, aromatic, and carbonyl carbon resonances in the ^{13}C NMR spectra are not quantitative because of differences in the relaxation times of the different types of carbons and nuclear Overhauser effects. However, the spectra do show qualitatively that the imide content of the copolymers increases from PAMSM-1 to PAMSM-4, which is consistent with the PAS-FTIR spectra and the results of the elemental analyses.

Both low angle laser light scattering (LALLS) and viscometry showed that the molecular weights of the copolymers decreased as the SPMI 3 content of the polymers was increased (Table 8). Both techniques indicated that the

Table 8: Molecular Weights of the PAMSM Copolymers

Copolymer	LALLS[a]	Viscometry	
	Weight Average Mol. Wt. (g/mol)	Intrinsic[b] Viscosity (mL/mg)	Viscosity[c] Avg. Mol. Wt. (g/mol)
PAMSM-1 (7.4% imide)	1.8×10^6	184	0.53×10^6
PAMSM-2 (15% imide)	n/m	125	0.32×10^6
PAMSM-3 (25% imide)	0.60×10^6	80	0.18×10^6

[a]Low angle laser light scattering method. Results are averages of two separate determinations taken a few days apart on different subsamples of the copolymers. The separate determinations differed by 0.6% for PAMSM-1 and 7% for PAMSM-3.

[b]Viscosities measured in aqueous 0.5 M NaCl at pH 7.0 ± 0.2 and 25 ± 0.05°C using a Ubbelohde dilution viscometer.

[c]Calculated using the Mark-Houwink equation for polyacrylamide in 0.5 M NaCl at 25°C:

$$[\eta] = 7.19 \times 10^{-3} M^{0.77}$$

average molecular weight of PAMSM-3 (25% imide) was about one third that of PAMSM-1 (7.4% imide). The LALLS molecular weights were higher than the viscosity average molecular weights by a factor of 3.4 for each copolymer, which suggests that the copolymers were branched. LALLS gives the weight average molecular weight whereas viscometry gives the intrinsic viscosity, which is related to the viscosity average molecular weight by the Mark-Houwink equation (Eq. 2-1, p. 40). Solutions of branched polymers tend to have lower intrinsic viscosities than solutions of linear polymers of the same molecular weight because intrinsic viscosity depends on the hydrodynamic volume of a polymer rather than the molecular weight.[48]

This series of copolymerizations of acrylamide with sodium N-(4-sulfophenyl)maleimide (SPMI) 3 covered a wide range of acrylamide to maleimide monomer feed ratios and most of the copolymerizations appear to have been kept to below 15% conversion. Therefore, the copolymerization data given in Table 7 were used to calculate reactivity ratios for this monomer pair. Applying the Kelen-Tudos[8] method to the data of all nine copolymerizations gave r values of 0.55 for acrylamide and 0.31 for SPMI 3 (Table 9). Examination of the linear Kelen-Tudos plot of these data showed that the points for copolymerizations PAMSM-7, -8, and -9 deviated the most from the best-fit line. When the reactvity ratio calculations were repeated using only the data for

Table 9: Copolymerization Reactivity Ratios of Acrylamide and SPMI[a]

Polymerization Incorporation Data	r_1, Acrylamide	r_2, SPMI	Correlation Coefficient
PAMSM-1 to -9	0.545	0.308	0.9695
PAMSM-1 to -6	0.577	0.334	0.9936

[a]Calculated from the data of Table 7 using the method of Kelen and Tudos.[17]

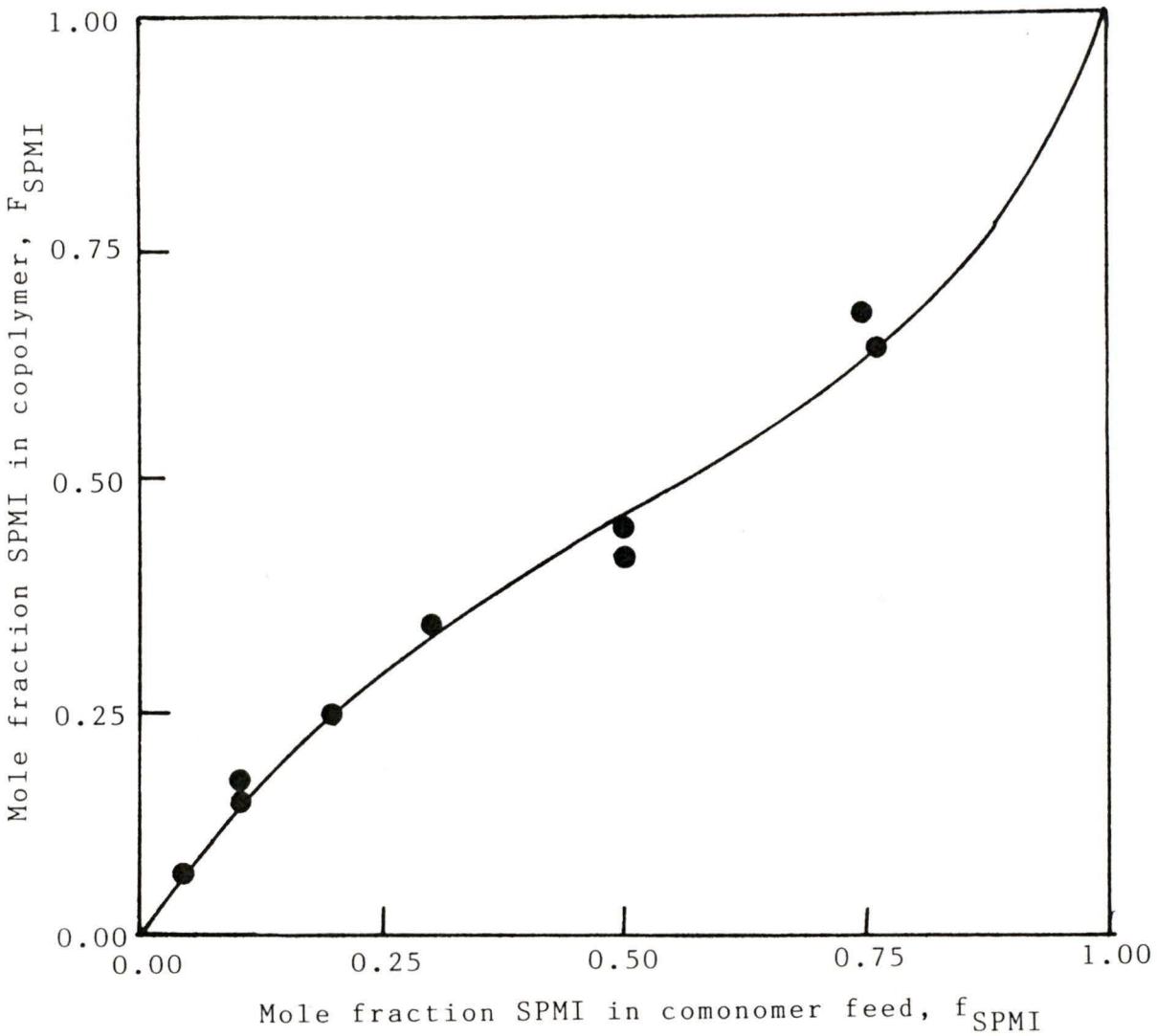


Fig. 18: Dependence of the instantaneous copolymer composition on the comonomer feed composition.

copolymers PAMSM-1 through -6, very similar r values of 0.58 and 0.33 were obtained together with a much improved correlation coefficient. Therefore it appears that the r values for acrylamide and SPMI 3 are about 0.57 ± 0.02 and 0.32 ± 0.02, respectively. The main sources of error appear to be inhomogeneity of the polymer samples (i.e. sampling error), and errors inherent in the elemental and GPC analyses.

A plot of monomer versus copolymer composition data for copolymerizations PAMSM-1 through -9 is shown in Fig. 18. The curve drawn through the data points was generated by computer by substituting the reactivity ratios of the two monomers into the copolymerization equation (Eq. 1-1, p. 5). As stated in the introduction, the copolymerization equation was derived by assuming that the reactivity of a propagating polymer molecule depends only on the monomer unit at the propagating end of the molecule. This assumption appears to be valid for this particular copolymer system since all of the data points lie on or near the curve in Fig. 18, and the Kelen-Tudos plots were linear.[8]

3.1.2. Poly(acrylamide-co-p-maleimidobenzoic acid) (PAMMBA)

Preparation and Characterization of the Monomers

The PAS-FTIR and ^{13}C NMR spectra of the monomers are shown in Figs. 19 to 23. p-Succinimidobenzoic acid 17 and p-carboxysuccinanilic acid 16 were prepared because the monomers are similar in structure to the MBA and partially hydrolyzed MBA units present in the PAMMBA copolymers and hence, could be used to confirm spectral assignments reported for the copolymers in the following section.

Preparation and Characterization of Poly(acrylamide-co-p-maleimidobenzoic acid) (PAMMBA)

Unlike sodium N-(4-sulfophenyl)maleimide 3, p-maleimidobenzoic acid (MBA) 4 is not sufficiently water-soluble to be copolymerized with acrylamide 1 in water. MBA 4 only partially dissolved when 1.0 to 1.5 equivalents of NaOH or $NaHCO_3$ were used to convert the monomer to its sodium salt form. Much of the monomer that did dissolve hydrolyzed to p-carboxymaleanilic acid 15, p-aminobenzoic acid 14 and maleic acid 19.

Copolymerizations were done in acetic acid and DMSO since both the monomers and the copolymers are soluble in these solvents (Tables 2 and 3, Section 2.4.2.). The disadvantage of using organic solvents is that the weight average molecular weights of polyacrylamides prepared in organic solvents tend to be lower than those of polyacryl-

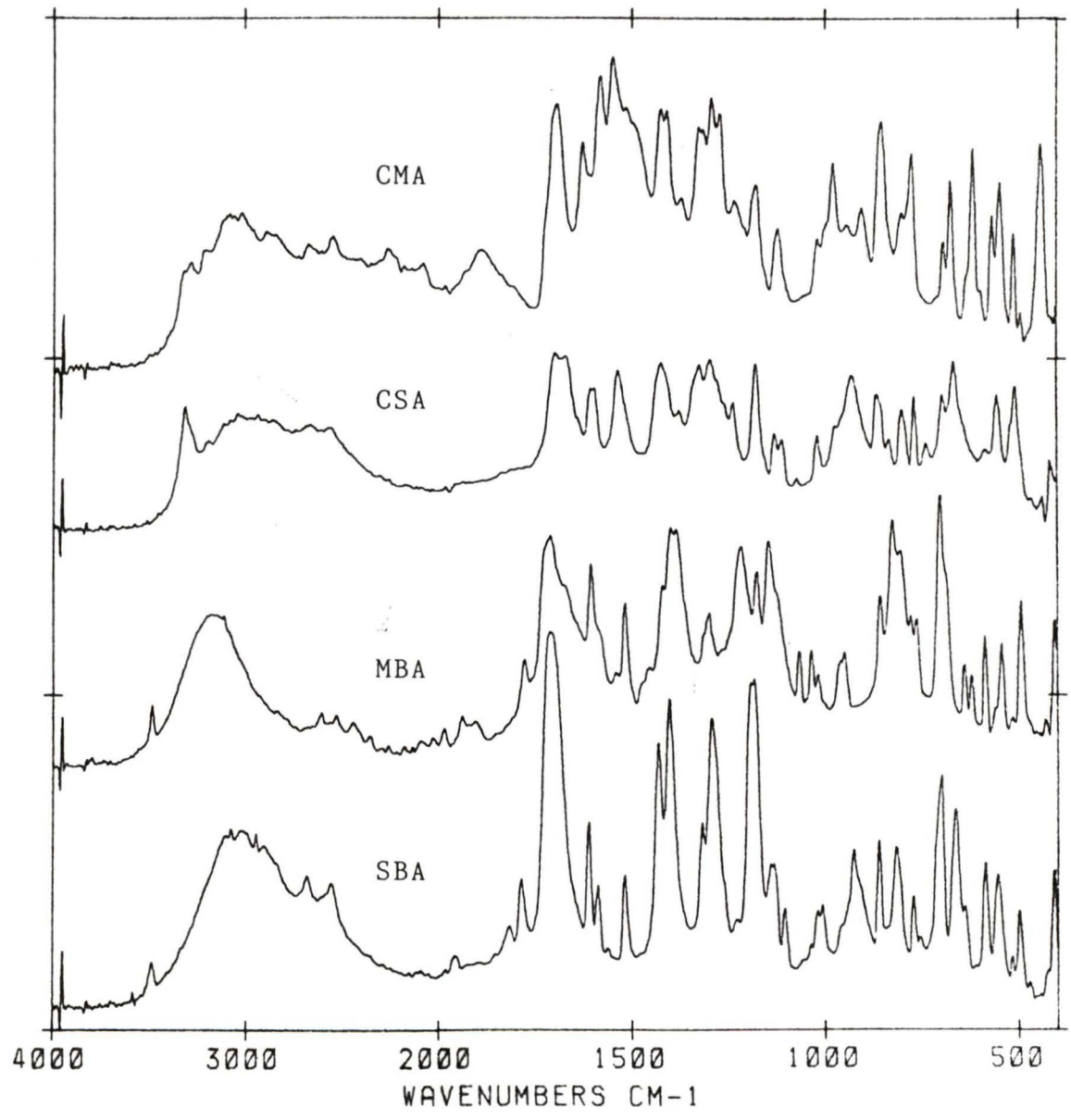
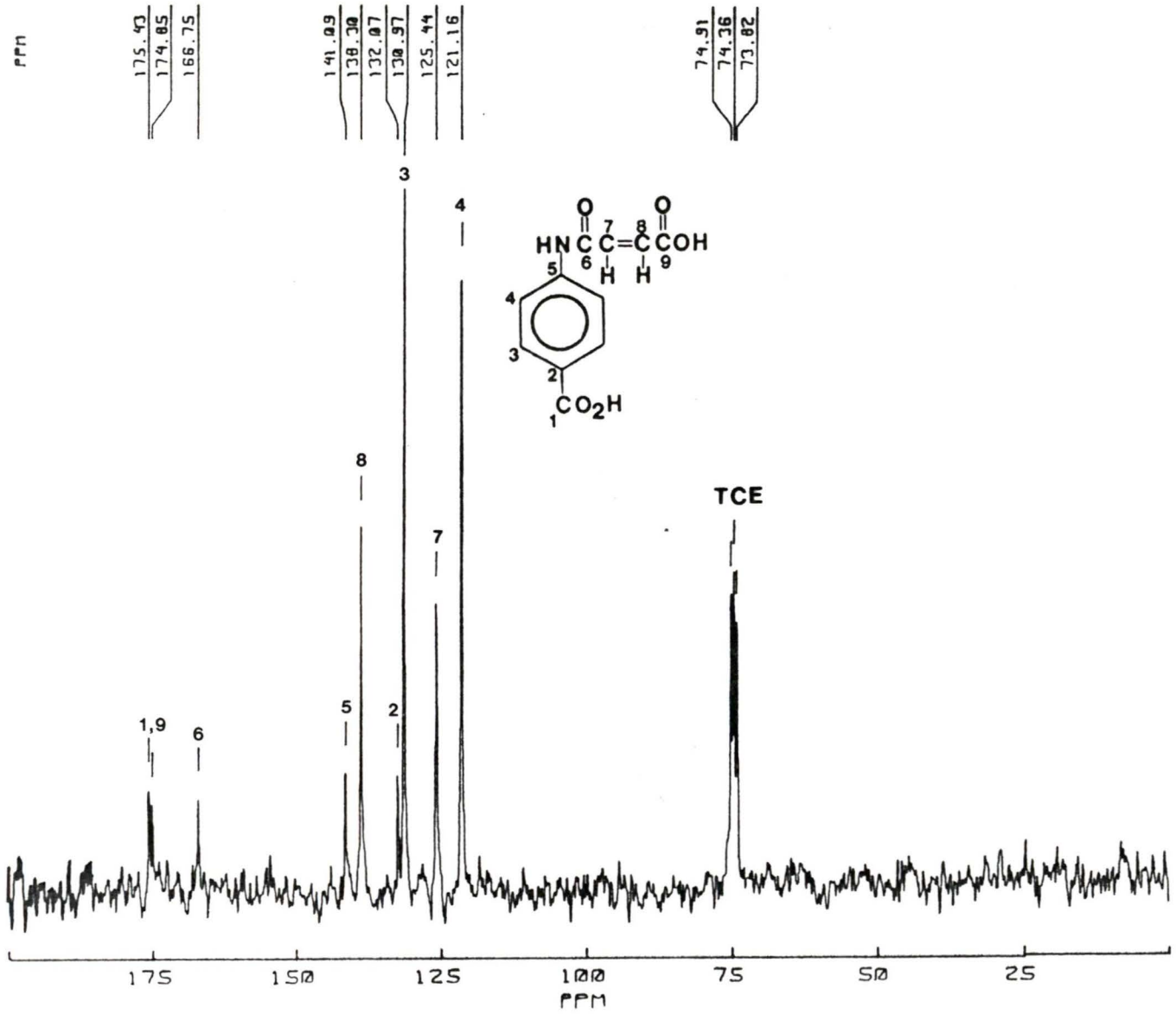


Fig. 19: PAS-FTIR Spectra of the Benzoic Acid Monomers.



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F2	-.009PPM
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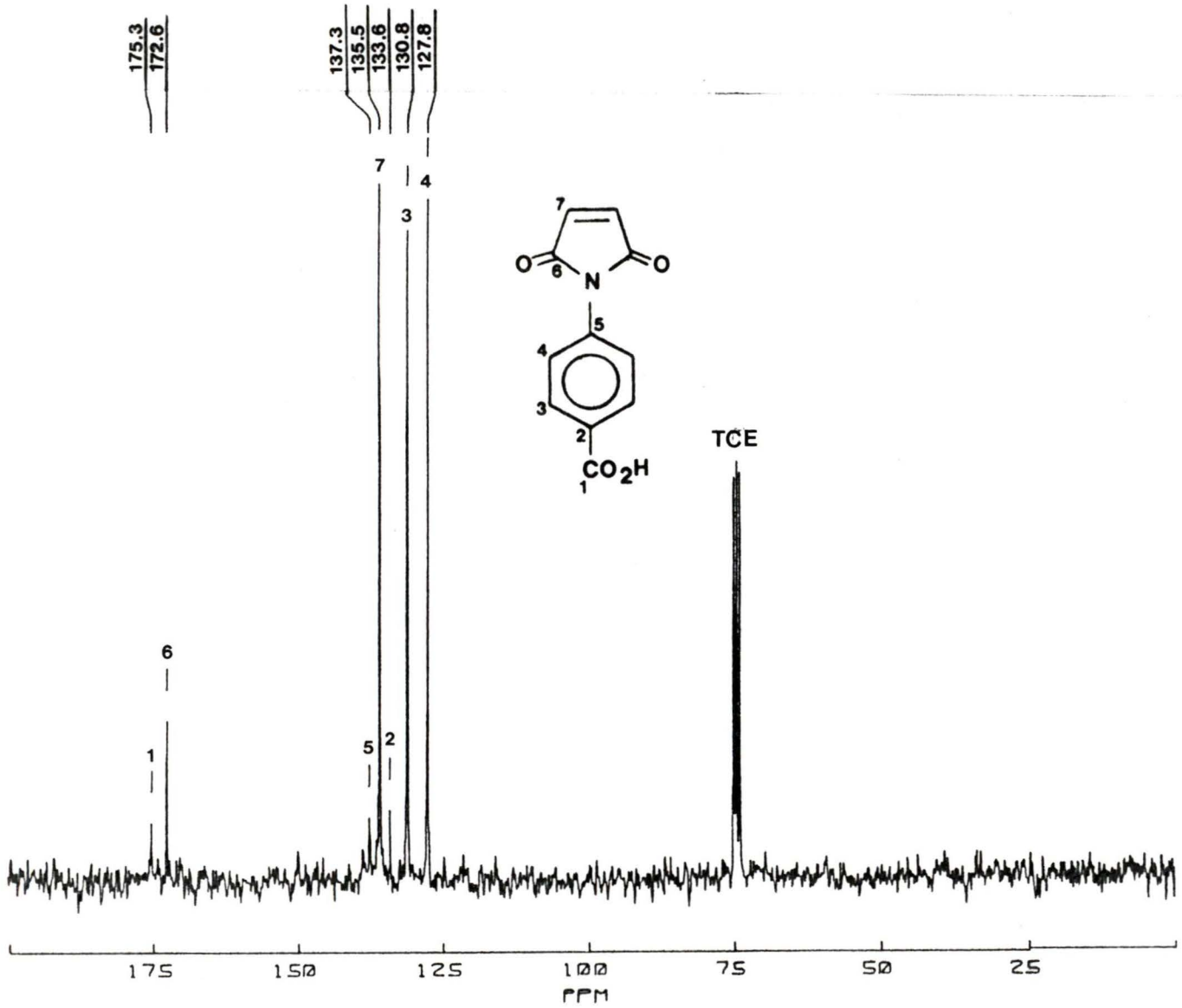
Fig. 20: ^{13}C NMR Spectrum of p-Carboxymaleanilic Acid 15 in pH 6.7 Buffer.



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HZ/PT 1.526

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TE 297

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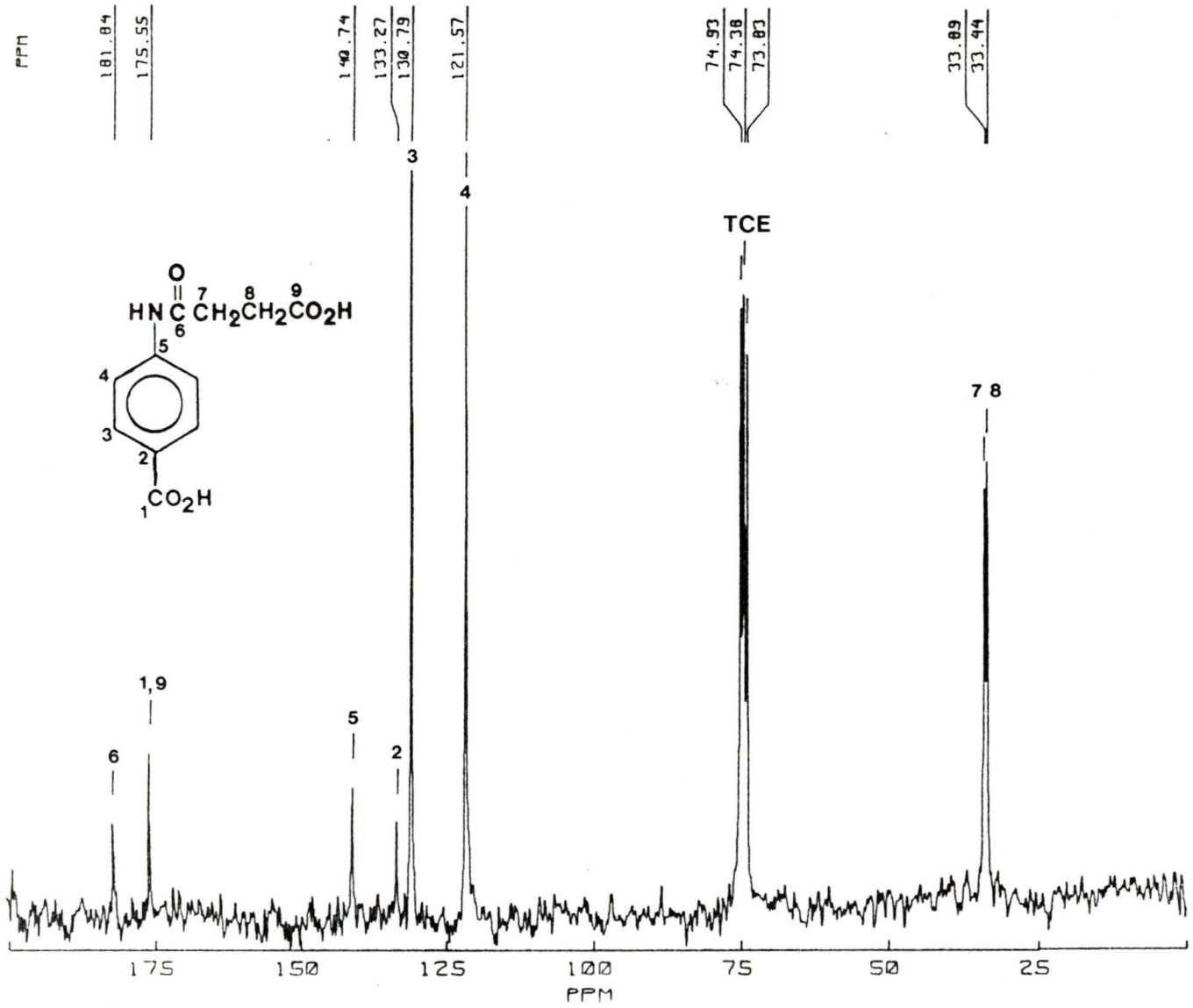
HZ/CM 503.311
PPM/CM 10.000
SR -6638.12

Fig. 21: ^{13}C NMR Spectrum of p-Maleimidobenzoic Acid 4 in pH 6.7 Buffer.



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D1	1.200E-5
D3	6.000E-5
LB	10.000
F1	200.026PPM
F2	-.069PPM
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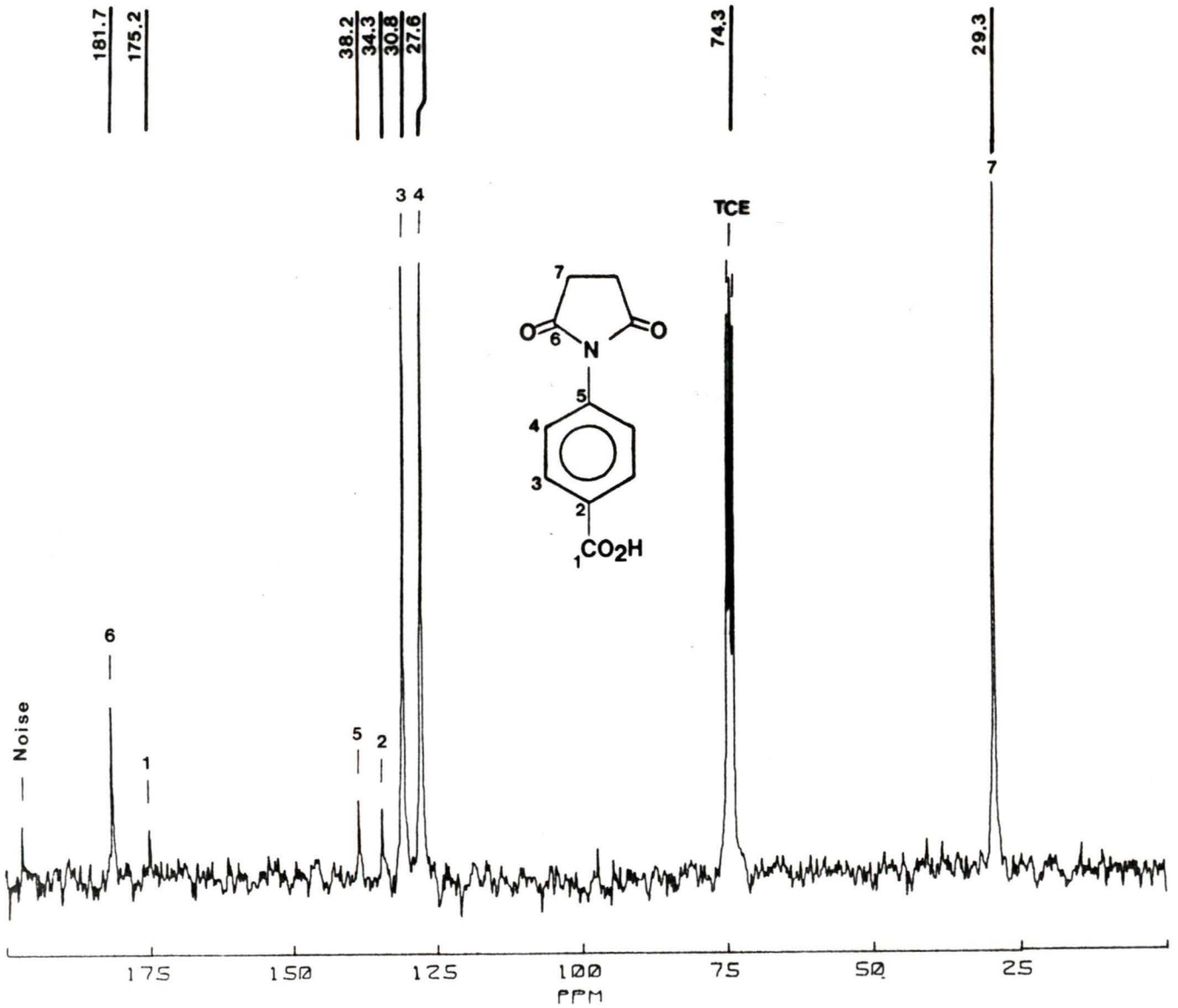
PPM/CM	10.005
SR	-6639.65

Fig. 22: ^{13}C NMR Spectrum of p-Carboxysuccinanilic Acid 16 in pH 6.7 Buffer.



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F1	199.996PPM
F2	-.009PPM
HZ/CM	503.311
PPM/CM	10.000
SR	-6638.12

Fig. 23: ^{13}C NMR Spectrum of p-Succinimidobenzoic Acid 17 in pH 6.7 Buffer.

amides prepared in water.[49,50]

GPC showed that copolymers PAMMBA-1 through -8 were contaminated with less than 1 wt % residual monomer. Much better separation of the PAMMBA copolymers and monomers was achieved using the TSK-GEL TOYOPEARL HW-40S column than was achieved for the PAMSM copolymers and monomers using the TSK-GEL G5000 PW column. The PAMMBA copolymers had a retention time of about 3.4 minutes, acrylamide 1 10.5 minutes, p-maleimidobenzoic acid (MBA) 4 16.5 minutes, and p-carboxymaleanilic acid 15 (partially hydrolyzed MBA) 7.8 minutes.

The weight ratio of acrylamide (AM) to p-maleimidobenzoic acid (MBA) 4 in the copolymers was calculated by substituting the C/N weight percent ratios determined by elemental analysis into Eq. 3-6. No correction was made for residual monomer because gel permeation chromatography indicated that the residual monomer content of all of the samples was less than 1% by weight.

$$\frac{\text{Wt\% AM}}{\text{Wt\% MBA}} = \frac{(C/N)(14.01)(71.08) - (11)(12.01)(71.08)}{(3)(12.01)(217.18) - (C/N)(14.01)(217.18)} \qquad (3\text{-}6)$$

Then Eqs. 3-7 and 3-8 were used to calculate the mole % acrylamide and mole % p-maleimidobenzoic acid in the copolymers.

$$\text{Mole \% AM} = \frac{\dfrac{\text{Wt \% AM}}{\text{Wt \% MBA}}\ \dfrac{(217.18)}{(71.08)}}{1 + \dfrac{\text{Wt \% AM}}{\text{Wt \% MBA}}\ \dfrac{(217.18)}{(71.08)}} \qquad (3\text{-}7)$$

$$\text{Mole \% MBA} = 100 - \text{Mole \% AM} \qquad (3\text{-}8)$$

The calculations showed that copolymers containing 7 to 23 mole % p-maleimidobenzoic acid (MBA) 4 were obtained using initial monomer feed ratios of 5:95 to 20:80 MBA to acrylamide (AM) (Table 10).

The yields and viscosity average molecular weights of the copolymers obtained decreased as the monomer feed ratio was increased, probably because MBA 4, like sodium N-(4-sulfophenyl)maleimide 3, is a 1,2-disubstituted alkene which would be expected to have a lower rate of propagation than acrylamide because of steric hindrance.[51] Propagation is hindered in favour of termination or chain transfer reactions, resulting in lower molecular weights.

Increasing the length of time that nitrogen was bubbled through the solution prior to initiation and reducing the initiator concentration did not greatly increase the molecular weights of the copolymers. (Compare the viscosity average molecular weights of PAMMBA-1 and PAMMBA-4 given in Table 10).

Copolymerizations were tried in 1.5:1 (v/v) DMSO:water

Table 10: Composition of PAMMBA Copolymers Prepared in Glacial Acetic Acid and DMSO at 60°C

Copolymer	Mole Feed Ratio AM:MBA	Wt% C	Wt% H	Wt% N	Wt% MBA[a]	Mole% MBA[a]	Intrinsic[b] Viscosity (mL/g)	Viscosity[c] Avg. M.Wt. (g/mol)
PAMMBA-1	95:5	47.26	6.68	15.60	17.9	7	46	87,000
PAMMBA-2	90:10	47.64	5.88	13.79	31.1	13	33	56,000
PAMMBA-3	80:20	46.98	4.80	11.35	47.5	23	n/m	----
PAMMBA-4	95:5	44.03	6.55	13.82	23.1	9	57	116,000
PAMMBA-5	90:10	46.95	5.62	13.81	29.6	12	n/m	----
PAMMBA-6	80:20	46.74	4.92	11.25	47.8	23	n/m	----
PAMMBA-7	95:5	40.39	5.53	12.89	21.4	8	38	68,000
PAMMBA-8	90:10	46.74	4.97	11.91	42.9	20	15	21,000

[a]The total MBA content was calculated using the C/N ratio and is reported as unhydrolyzed MBA. Unhydrolyzed and hydrolyzed MBA units differ by the equivalent of one water molecule but the C/N ratio is independent of the water content of the copolymers.

[b]Measured in aqueous 0.5 M NaCl at pH 7.0 ± 0.2 and 25 ± 0.05°C using a Ubbelohde dilution viscometer.

[c]Calculated using the Mark-Houwink equation for polyacrylamide in 0.5 M NaCl at 25°C:

$$[\eta] = 7.19 \times 10^{-3} M^{0.77}$$

n/m: Not measured.

at 60°C to try to achieve higher molecular weights than those obtained in DMSO alone. However, ^{13}C NMR showed that the precipitates isolated after 6.0 hours consisted mostly of monomeric p-maleimidobenzoic acid 4, p-carboxymaleanilic acid 18, and p-aminobenzoic acid 17, rather than copolymer.

The PAS-FTIR spectra of three of the copolymers prepared in acetic acid (PAMMBA-1, -2 and -3) are shown in Fig. 24. Acrylamide asymmetric and symmetric N-H stretching bands are observed at 3342 and 3198 cm^{-1}, respectively, and a strong acrylamide C=O stretching band is seen at 1670 cm^{-1}. The strong C=O stretching band at 1709 cm^{-1} and the weaker C-O stretching bands at 1385 and 1190 cm^{-1} belong to the MBA units. The presence of the weak imide C=O band at 1776 cm^{-1} shows that at least some of the imide rings of the p-maleimidobenzoic acid 4 units were still intact. However, it was not possible to determine from the PAS-FTIR spectra alone whether any of the imide rings had hydrolyzed because the C=O and C-O stretching bands of the hydrolyzed MBA units would be expected to lie at about the same frequencies as the bands of the unhydrolyzed MBA units.

The aromatic ^{13}C NMR resonances in the spectra of the PAMMBA copolymers (Figs. 25 to 27) were assigned by comparison with the spectra of p-succinimidobenzoic acid (SBA) 17 (Fig. 23) and p-carboxysuccinanilic acid (CSA) 16 (Fig. 22). These two monomers are similar in structure to the unhydrolyzed and hydrolyzed MBA units, respectively,

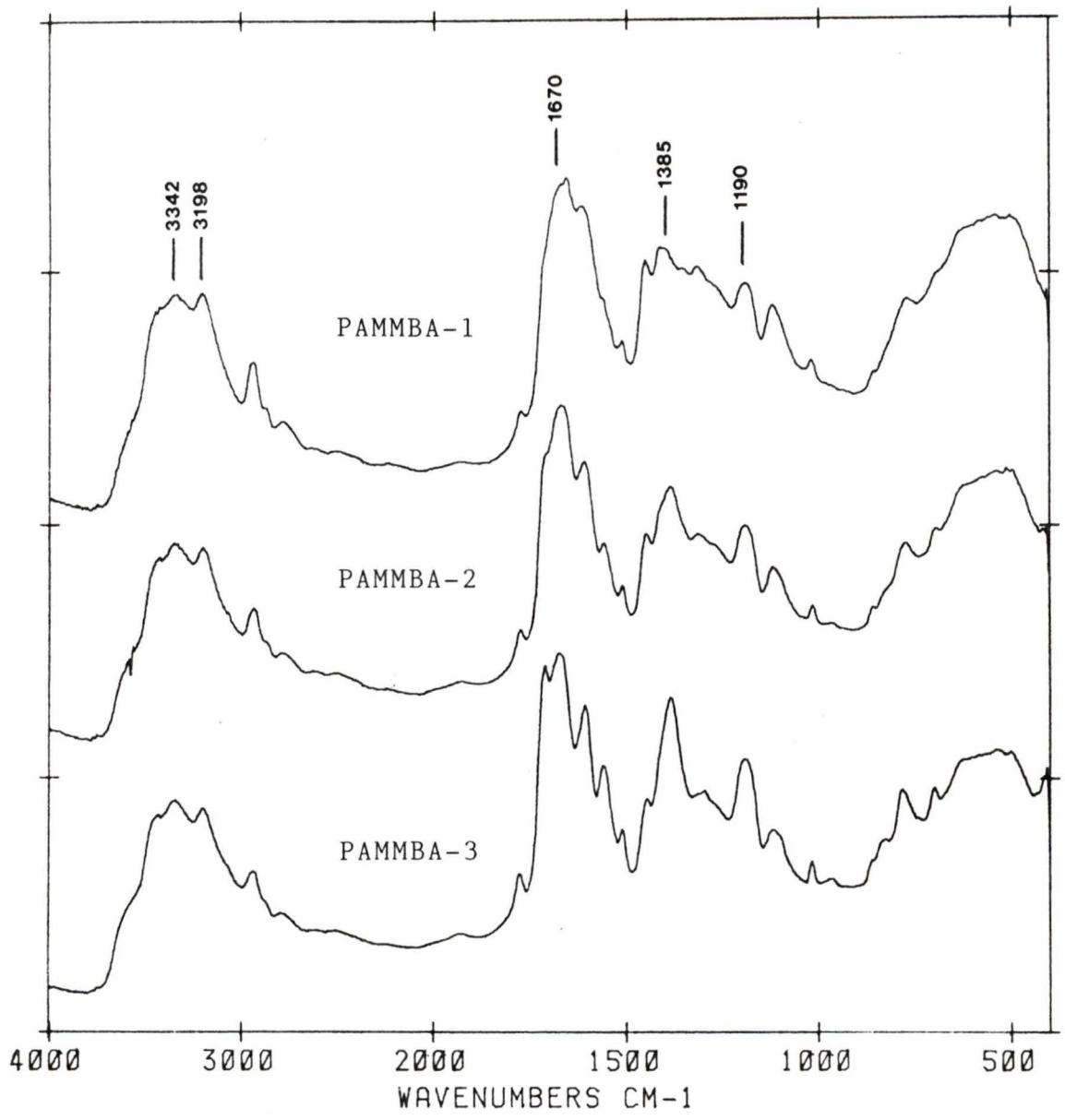
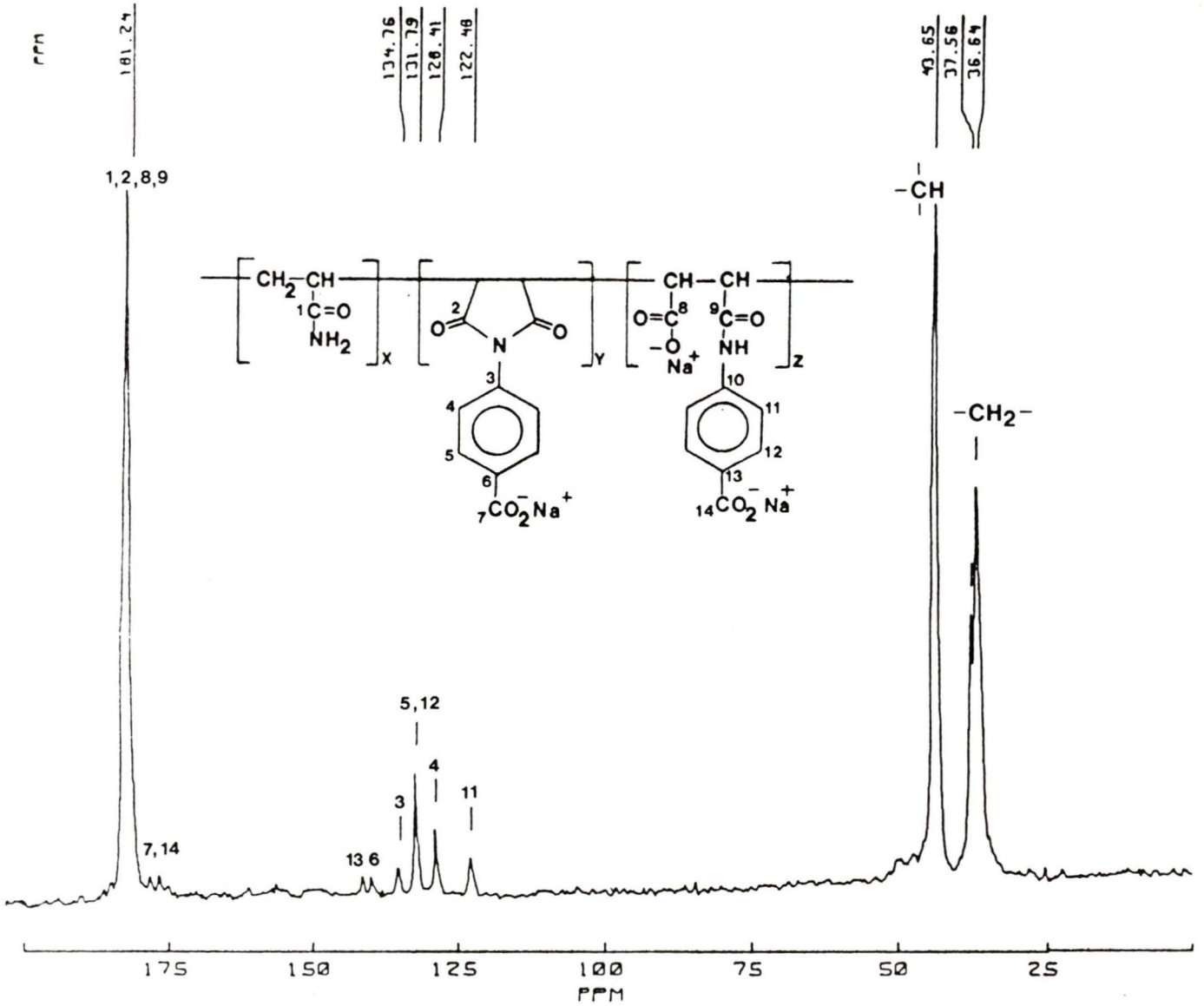


Fig. 24: PAS-FTIR Spectra of PAMMBA-1 (7% MBA), PAMMBA-2 (13% MBA) and PAMMBA-3 (23% MBA)



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F2        -.009PPM
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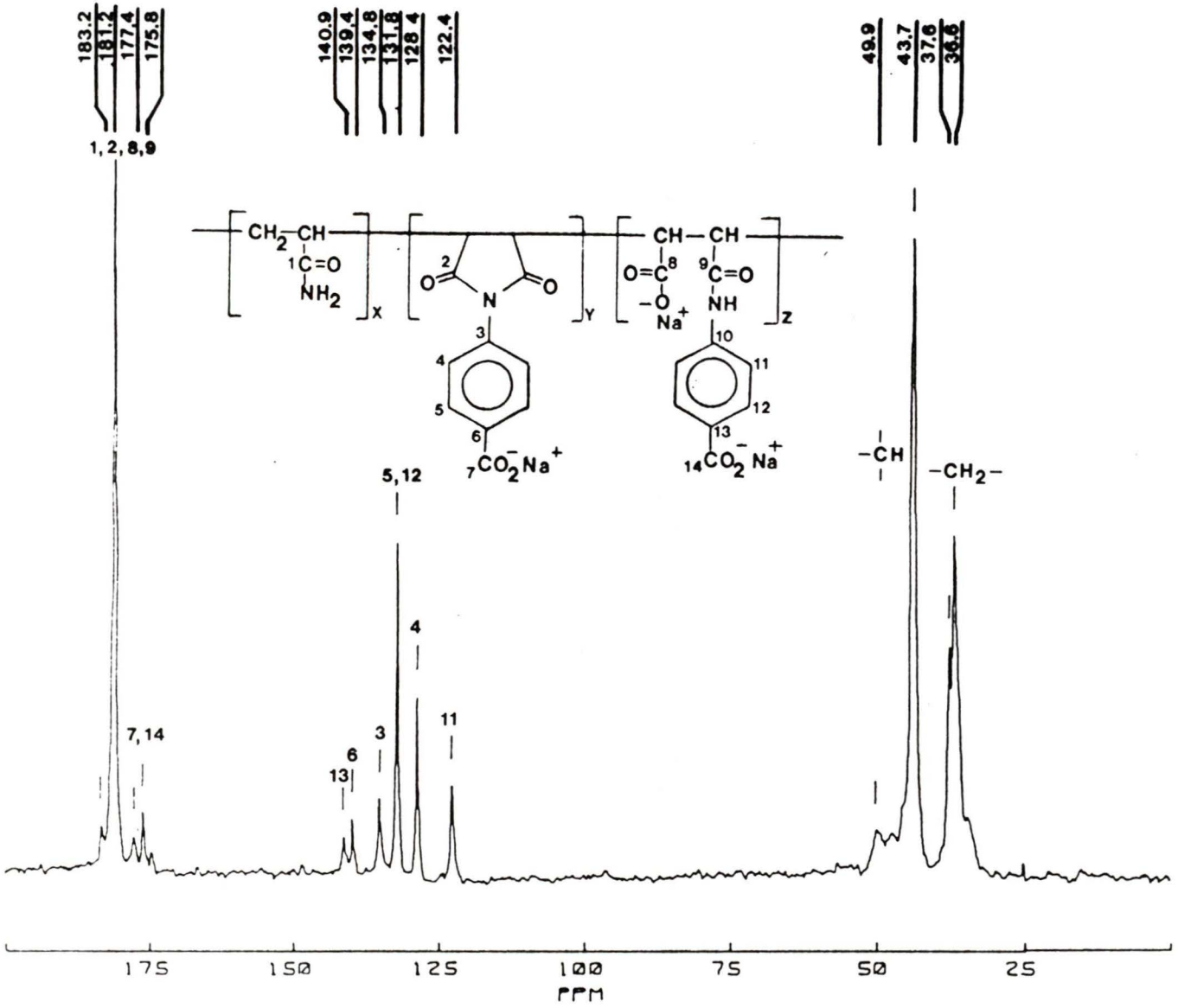
Fig. 25: ^{13}C NMR Spectrum of PAMMBA-1 in pH 6.7 Buffer.



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D3 6.000E-5

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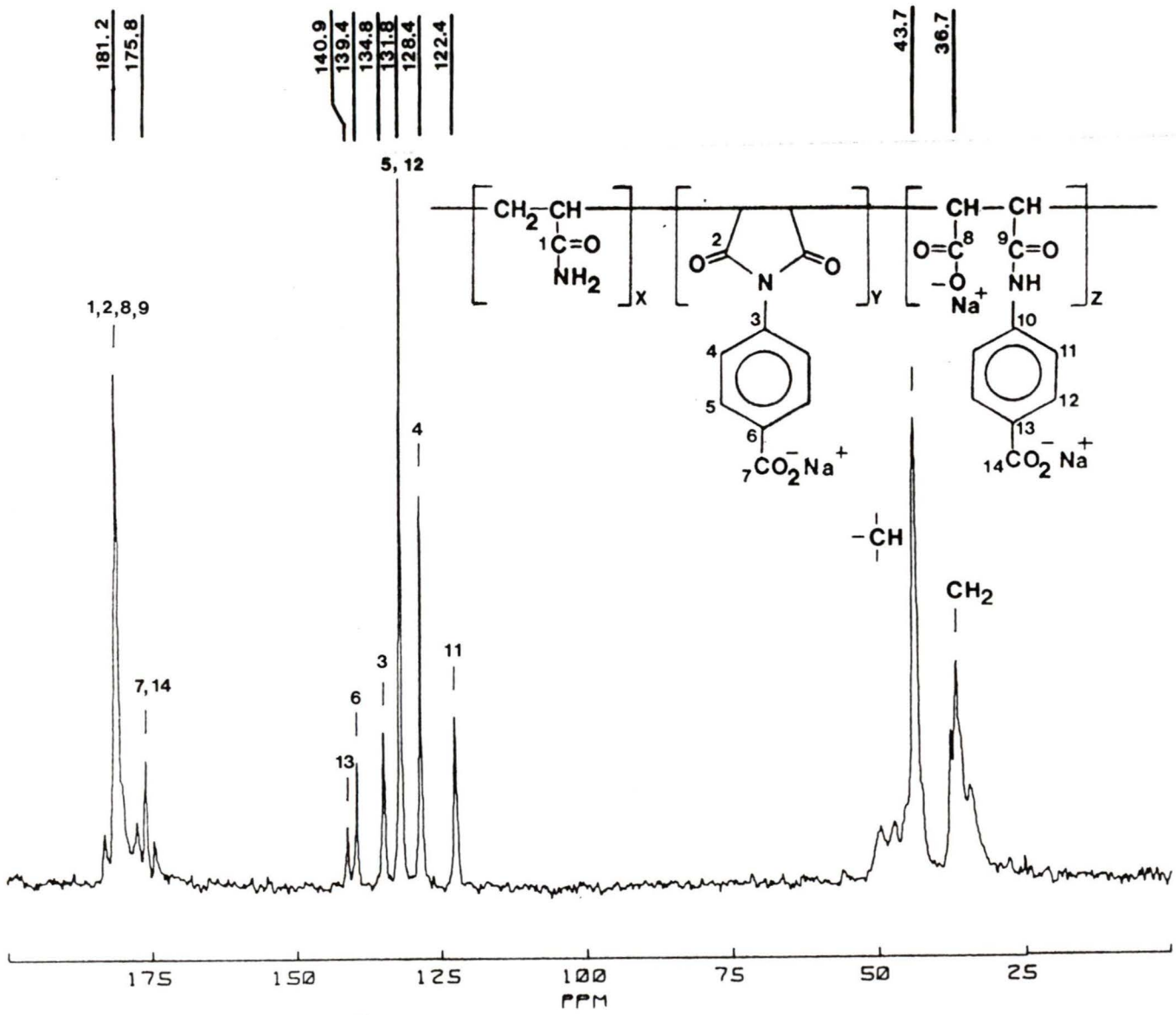
SR -6638.12

Fig. 26: ^{13}C NMR Spectrum of PAMMBA-2 in pH 6.7 Buffer.



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HZ/CM	503.311
PPM/CM	10.000
SR	-6639.65

Fig. 27: ^{13}C NMR Spectrum of PAMMBA-3 in pH 6.7 Buffer.

that should be present in the copolymers. Comparison of the spectra of these monomers with the spectra of the copolymers indicates that about 30 to 40 percent of the MBA units in the copolymers were hydrolyzed during the preparation and purification of the polymers.

The aromatic resonances of p-maleimidobenzoic acid (MBA) 4 and p-carboxymaleanilic acid (CMA) 15 lie at about the same chemical shifts as those of p-succinimidobenzoic acid (SBA) 17 and p-carboxysuccinanilic acid (CSA) 16, respectively. However, the absence of alkene ^{13}C resonances at about 138.3, 135.5 and 125.4 ppm shows that the polymers prepared were copolymers, not acrylamide homopolymers contaminated with a large amount of p-maleimidobenzoic acid (MBA) or p-carboxymaleanilic acid (partially hydrolyzed MBA) monomer.

3.1.3. Poly(N,N-diallylaniline) (PDAA)

A sample of poly(N,N-diallylaniline) was prepared to help in the assignment of adsorption peaks in the PAS-FTIR and ^{13}C NMR spectra of the acrylamide-co-N,N-diallylaniline and acrylamide-co-sodium N,N-diallylsulfanilate polymers. The PAS-FTIR and ^{13}C NMR spectra of poly(N,N-diallylaniline) are shown in Figs. 28 and 29, respectively. The pyrrolidine rings are present in both cis and trans conformations, so two ^{13}C resonances are observed for each of the different

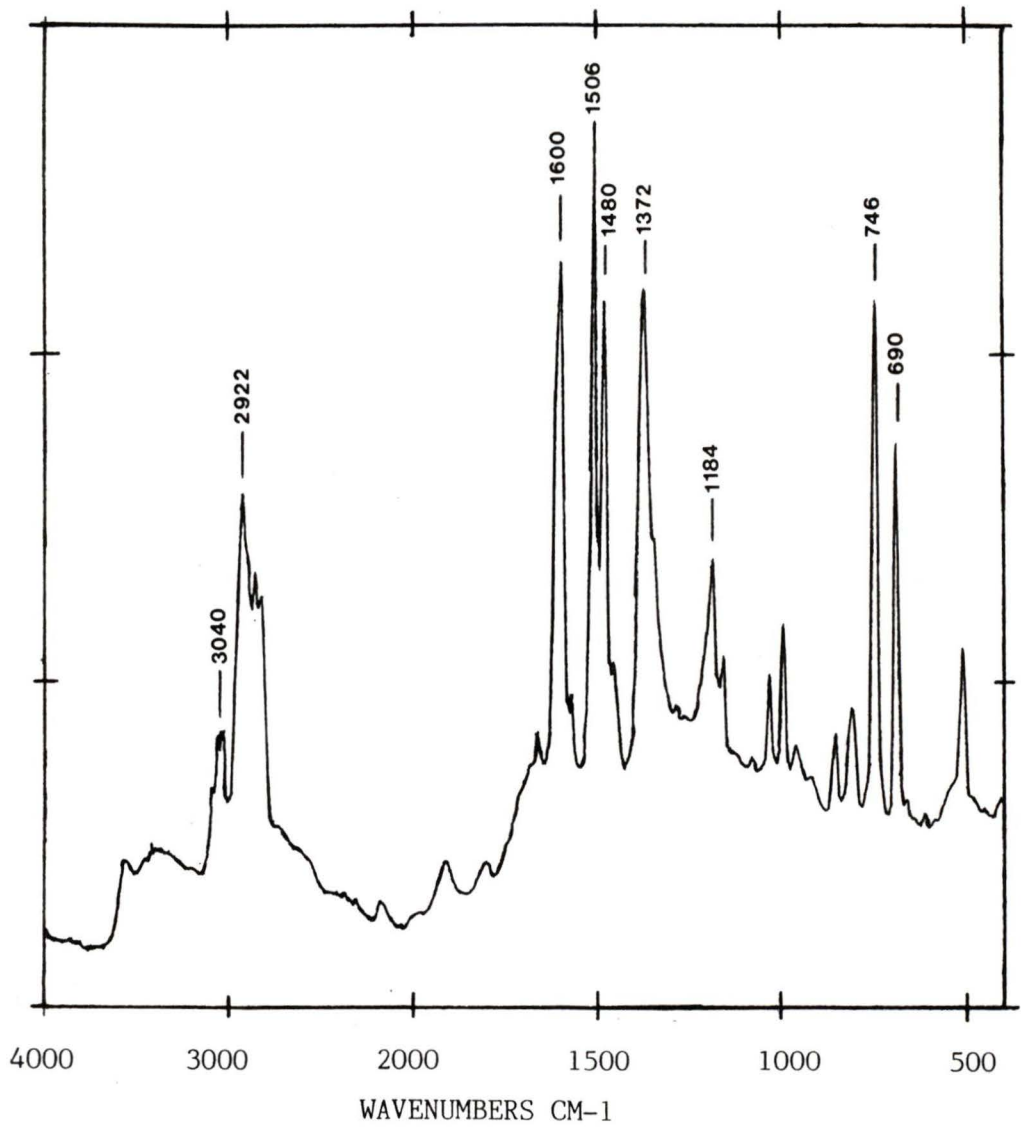


Fig. 28: PAS-FTIR Spectrum of Poly(N,N-diallylaniline).

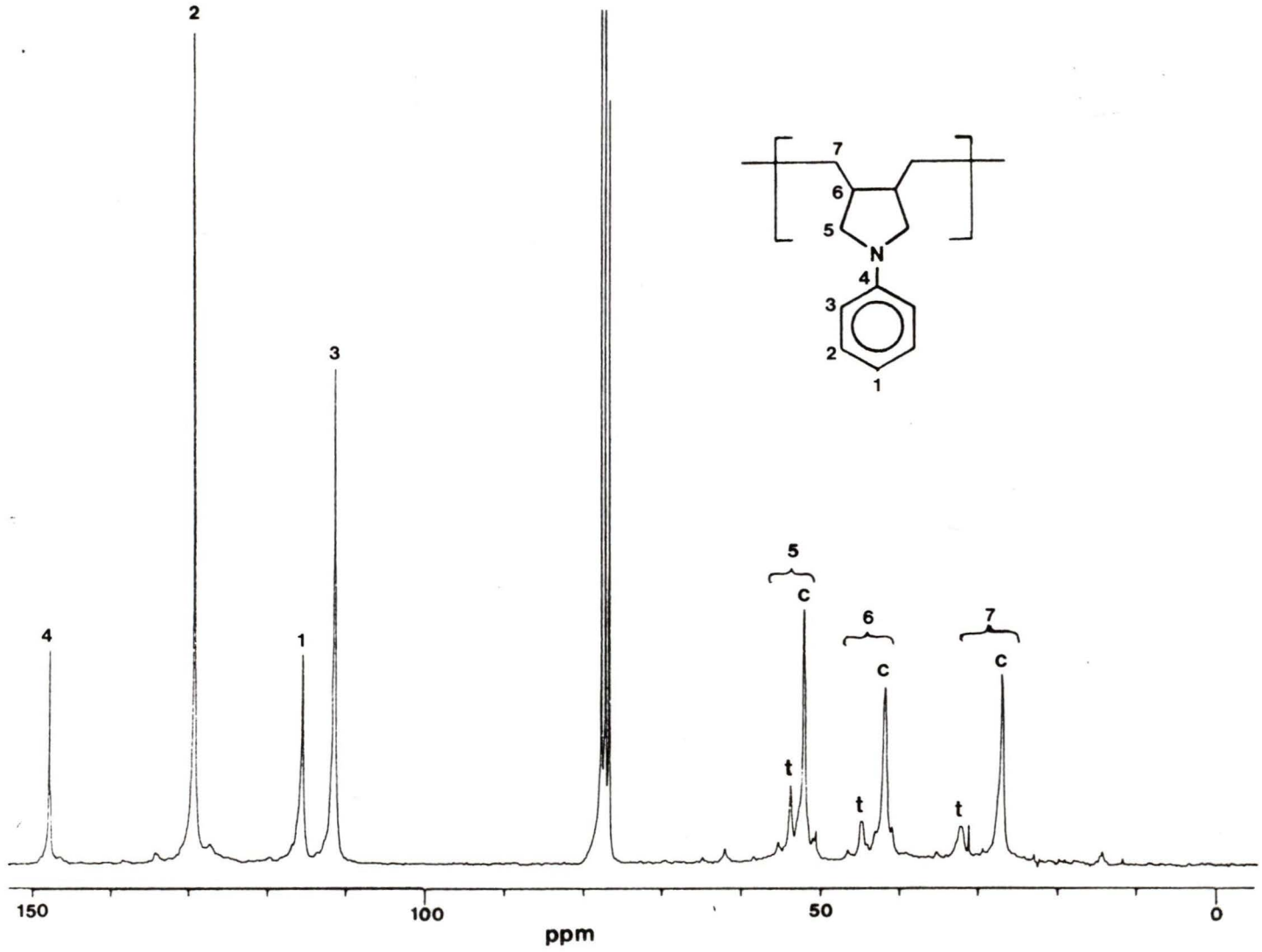


Fig. 29: ^{13}C NMR Spectrum of Poly(N,N-diallylaniline) in $CDCl_3$.

methylene and methine carbons in the NMR spectrum.[42]

3.1.4. Poly(acrylamide-co-N,N-diallylaniline) (PAMDAA)

Copolymers containing 3.5 to 19.2 mole % N,N-diallylaniline 6 were prepared by using initial N,N-diallylaniline (DAA) to acrylamide (AM) monomer feed ratios of 10:90 to 30:70 (PAMDAA-1 to -3, Table 11). The PAMDAA copolymers were only water-soluble below approximately pH 3.0. They precipitated when the pH was raised above 3.0 with NaOH. Therefore, the copolymers are not water-soluble over a wide enough pH range to be useful as flocculants. Slightly-soluble or insoluble PAMDAA gels were obtained if high initiator concentrations were used, presumably because some crosslinking occurred (PAMDAA-4 and -5, Table 5).

The PAS-FTIR spectrum of one of the copolymers, PAMDAA-3 (8.9 mole % DAA), is shown in Fig. 30. Weak aromatic C=C stretching, C-H out-of-plane bending, and C=C out-of-plane ring bending bands of the DAA units are observed at 1507, 750, and 693 cm^{-1}, respectively. The remainder of the spectrum is similar to that of acrylamide homopolymer.

The presence of the N,N-diallylaniline units is much more obvious in the ^{13}C NMR spectrum of PAMDAA-3 (8.9 mole %

Table 11: Composition of the PAMDAA Copolymers

Copolymer	Feed Ratio AM:DAA	Wt% C	Wt% H	Wt% N	Wt% DAA	Mole % DAA
PAMDAA-1	90.0:10.0	48.71	7.13	17.16	8.0	3.5
PAMDAA-2	79.9:20.1	49.83	7.41	15.87	16.2	7.4
PAMDAA-3	69.1:30.1	50.05	6.97	15.36	19.2	8.9

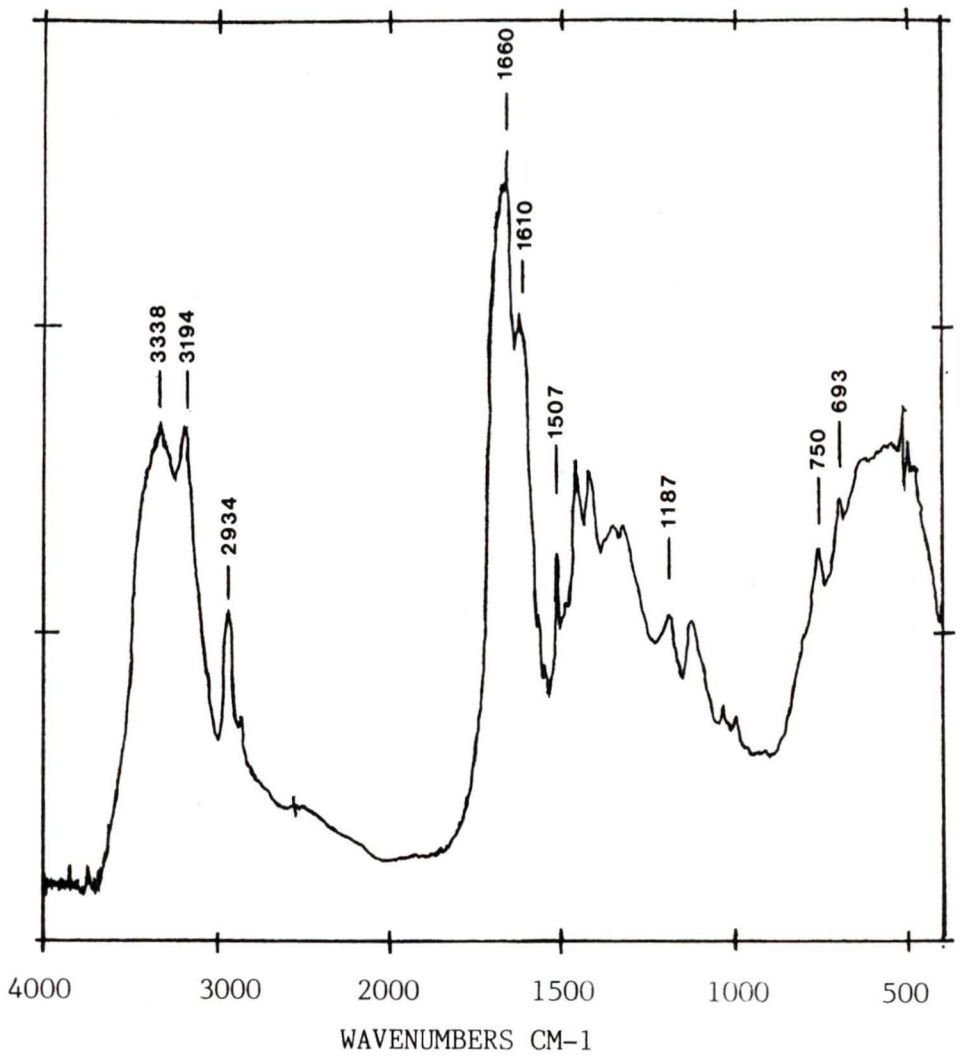


Fig. 30: PAS-FTIR Spectrum of PAMDAA-3

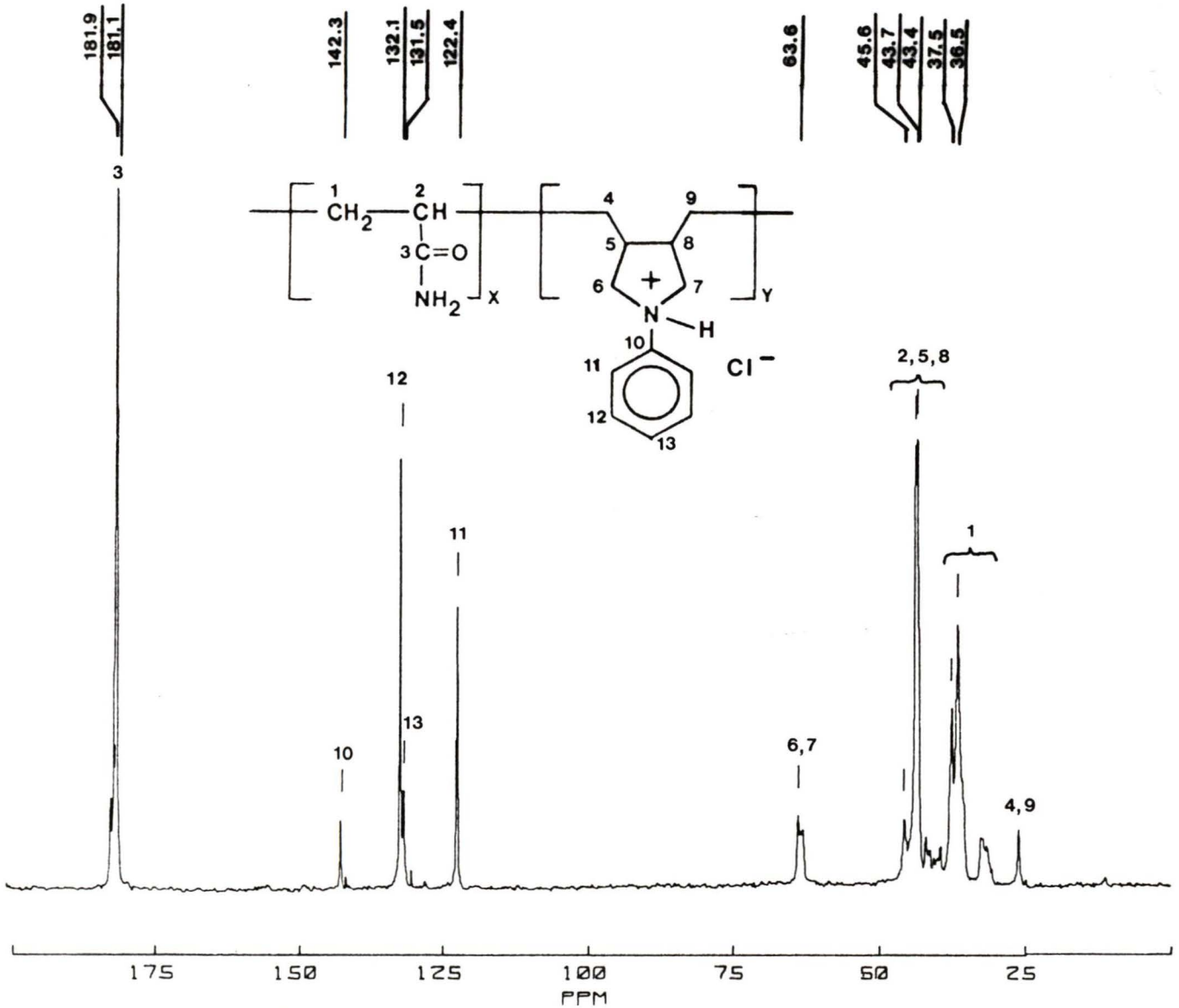


Fig. 31: ^{13}C NMR Spectrum of PAMDAA-3 in Dilute Aqueous HCl (pH 1.5).

DAA) (Fig. 31). All of the ^{13}C resonances of the N,N-diallylaniline units are visible, except for the methine carbons of the pyrrolidine rings. The resonances for those carbons are hidden by the strong methylene and methine ^{13}C resonances of the acrylamide units. The relative intensities of the ^{13}C resonances of the N,N-diallylaniline units are similar to those observed for poly(N,N-diallyl-aniline) (Fig. 29). However, the chemical shifts are somewhat different, primarily because the spectra of the copolymers were run in water at approximately pH 1 (dilute HCl), whereas the spectrum of poly(N,N-diallylaniline) was run in $CDCl_3$.

3.1.5. Poly(acrylamide-co-sodium N,N-diallylsulfanilate) (PAMDAS)

The weight percentage sodium N,N-diallylsulfanilate (DAS) 7 to weight percentage acrylamide (AM) 1 ratio of the copolymers was calculated by substituting the C/N, C/S, and S/N weight ratios determined by elemental analysis into Eqs. 3-9, 3-10, and 3-11, respectively.

$$\frac{\text{wt\% DAS}}{\text{wt\% AM}} = \frac{(253.31)(3)(12.01) - (C/N)(253.31)(14.01)}{(C/N)(71.08)(14.01) - (71.08)(12)(12.01)} \qquad (3\text{-}9)$$

$$\frac{\text{wt\% DAS}}{\text{wt\% AM}} = \frac{(253.31)(3)(12.01)}{(C/S)(71.08)(32.06) - (71.08)(12)(12.01)} \quad (3\text{-}10)$$

$$\frac{\text{wt\% DAS}}{\text{wt\% AM}} = \frac{(S/N)(253.31)(14.01)}{(71.08)(32.06) - (S/N)(71.08)(14.01)} \quad (3\text{-}11)$$

The average of the three values was substituted into Eq. 3-12 to calculate the mole % DAS.

$$\text{mole \% DAS} = \frac{(\text{wt\% DAS/wt\% AM})}{(253.31/71.08) + (\text{wt\% DAS/wt\% AM})} \quad (3\text{-}12)$$

The calculations indicated that copolymers containing 3.8 to 52 mole % sodium N,N-diallylsulfanilate (DAS) 7 were obtained using initial DAS to acrylamide (AM) feed ratios of 10:90 to 80:20. Insufficient data were obtained to be able to calculate reactivity ratios, but the copolymer composition versus initial comonomer feed ratio results (Table 12) show that sodium N,N-diallylsulfanilate 7 was more difficult than sodium N-(4-sulfophenyl)maleimide 3 and p-maleimidobenzoic acid 4 to copolymerize with acrylamide. The yields decreased as the DAS:AM ratio was increased because of the low reactivity of sodium N,N-diallyl-sulfanilate 7 with acrylamide 1.

The PAS-FTIR spectra of PAMDAS-1 (3.9% DAS), PAMDAS-2 (8.4% DAS), PAMDAS-3 (19% DAS), and PAMDAS-4 (52% DAS) are shown in Fig. 32. Acrylamide asymmetric N-H, symmetric N-H,

Table 12: Composition of the PAMDAS Copolymers

Copolymer	Feed Ratio AM:DAS	Wt% C	Wt% N	Wt% S	Wt% DAS[a]	Mole % DAS[b]	Intrinsic[c] Viscosity (mL/g)	Viscosity[d] Avg. M.Wt. (g/mol)
PAMDAS-1	90:10	45.25	15.77	1.40	12.6 ± 0.1	3.9 ± 0.1	34	60,000
PAMDAS-2	70:30	45.57	14.77	3.02	24.5 ± 3.8	8.4 ± 1.5	n/m	----
PAMDAS-3	50:50	46.90	11.26	4.87	45.8 ± 2.2	19.2 ± 1.4	n/m	----
PAMDAS-4	20:80	48.26	6.90	8.28	79.2 ± 3.9	51.8 ± 5.8	n/m	----
PAMDAS-5	90:10	46.44	16.16	1.36	12.2 ± 1.1	3.8 ± 0.2	n/m	----
PAMDAS-6	70:30	46.36	12.37	4.08	37.8 ± 1.1	14.6 ± 0.6	n/m	----
PAMDAS-7	50:50	47.66	8.91	7.18	65.9 ± 0.8	35.2 ± 0.8	n/m	----

[a]Values reported are the averages of the wt% copolymerized sodium N,N-diallylsulfanilate (DAS) in the calculated using the C/N, C/S, and S/N ratios. The error limits are expressed as one standard deviation of the three values calculated for each copolymer.

[b]Mole % of copolymerized DAS in the copolymers.

[c]Measured in aqueous 0.5 M NaCl at pH 6.8 and 25 ± 0.05°C using a Ubbelohde dilution viscometer.

[d]Calculated using the Mark-Houwink equation for polyacrylamide in 0.5 M NaCl at 25°C:

$$[\eta] = 7.19 \times 10^{-3} M^{0.77}$$

n/m: Not measured.

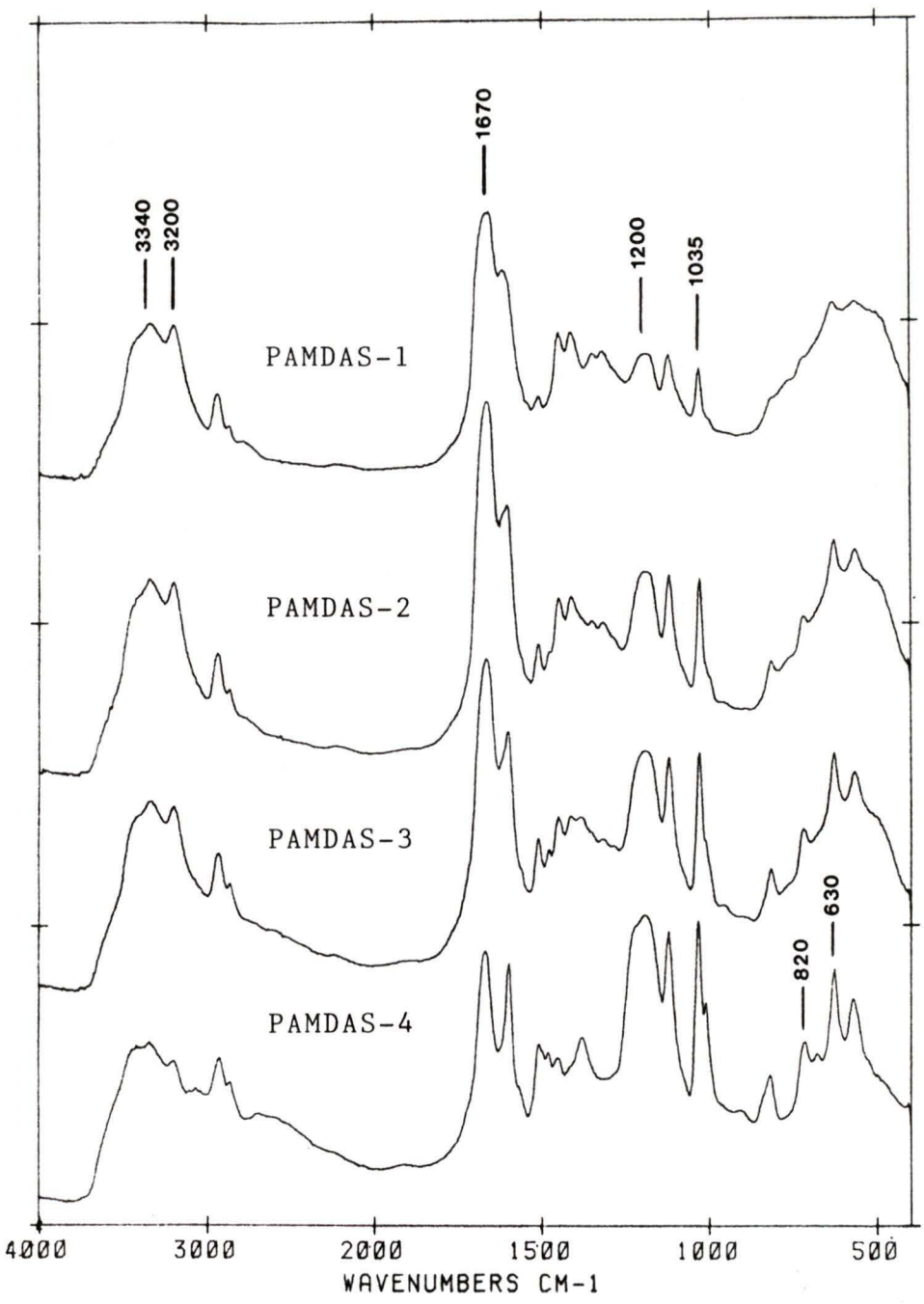


Fig. 32: PAS-FTIR Spectra of the PAMDAS Copolymers

and C=O stretching bands are observed at 3340, 3200, and 1670 cm^{-1}, respectively. Aromatic C=C, asymmetric S=O, and symmetric S=O stretching bands of the sodium N,N-diallylsulfanilate units are observed at 1600, 1200, and 1035 cm^{-1}, respectively.

The ^{13}C NMR spectra of the copolymers PAMDAS-1 (3.9% DAS), PAMDAS-2 (8.4% DAS), and PAMDAS-3 (19% DAS) are shown in Figs. 33 to 35. The ^{13}C resonances of the DAS units were assigned by comparing the spectra of the copolymers with that of poly(N,N-diallylaniline) (Fig. 29). The absence of vinyl ^{13}C resonances at 111.8 and 133.8 ppm shows that the samples contained polymerized, not monomeric sodium N,N-diallylsulfanilate. Although the relative intensities of the ^{13}C resonances in the spectra are not quantitative because of differences in the relaxation times of the different types of carbons, it is clear that the sodium N,N-diallylsulfanilate 7 content of the copolymers is much lower than the initial sodium N,N-diallylsulfanilate to acrylamide comonomer feed ratio.

Gel permeation chromatography confirmed that the samples were copolymers, not polyacrylamide contaminated with sodium N,N-diallylsulfanilate monomer 7, nor a mixture of sodium N,N-diallylsulfanilate and acrylamide homopolymers. Both the sodium N,N-diallylsulfanilate and acrylamide units absorb energy at 208 nm, but only the sodium N,N-diallylsulfanilate units absorb energy at 274 nm.

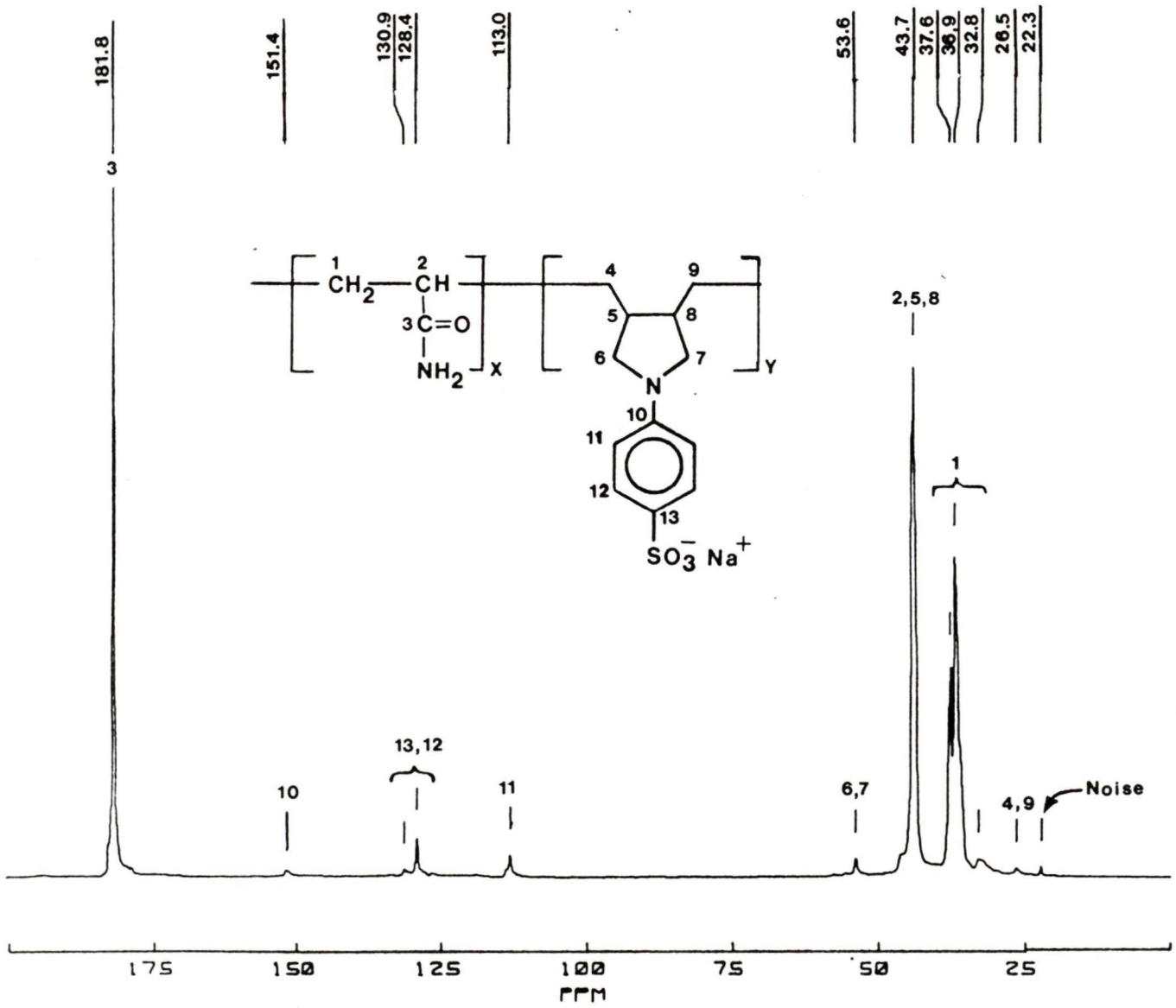
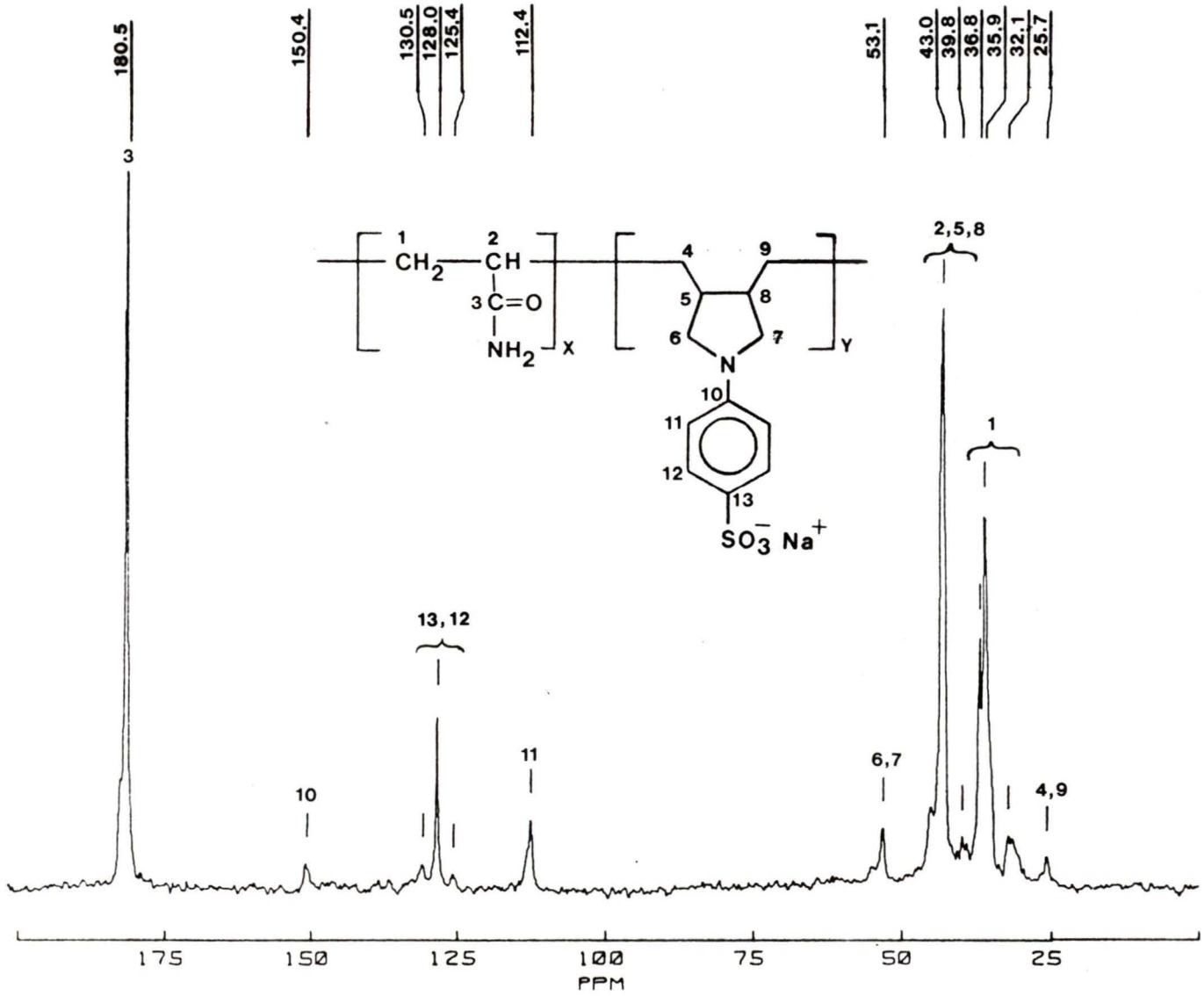


Fig. 33: ^{13}C NMR Spectrum of PAMDAS-1.



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D3 6.000E-5

LB 10.000
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F2 -.071PPM
HZ/CM 503.540
PPM/CM 10.005
SR -6599.07

Fig. 34: ^{13}C NMR Spectrum of PAMDAS-2.

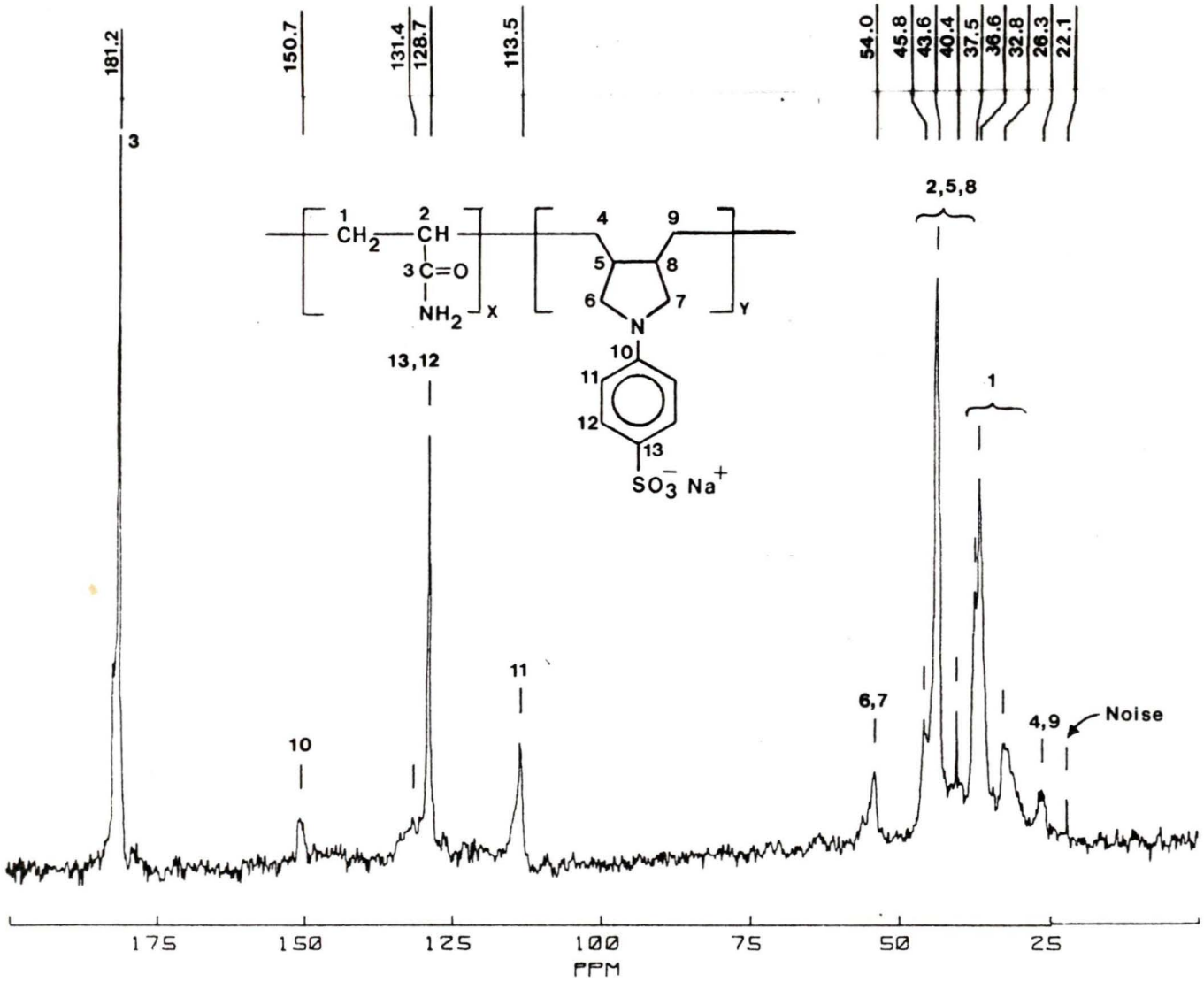

Fig. 35: ^{13}C NMR Spectrum of PAMDAS-3.

Only one peak with a retention time shorter than that of the monomers was observed when the samples were chromatographed with the UV detector set at 208 nm and an identical, but lower intensity peak was observed when the samples were chromatographed with the detector set at 274 nm. It is unlikely that peaks with identical retention times and shapes would be observed at both wavelengths if the sample consisted of two homopolymers. Therefore, the samples must be acrylamide-sodium N,N-diallylsulfanilate copolymers.

The viscosity average molecular weight of PAMDAS-1 (3.9%) was only about 60,000 g/mol (Table 12). Molecular weights of the other PAMDAS copolymers were not measured because of insufficient sample, but appeared to decrease with increasing DAS content.

3.2. Flocculation Tests of PAMSM Copolymers

Montmorillonite and kaolinite consist of platelets that have a pH independent negative charge on the faces and a pH dependent charge on the edges.[52] The edges are positively charged in acidic media and negatively charged in alkaline media because of hydroxylation and ionization of broken Si-O and Al-O bonds. Studies have shown that both polyacrylamide and partially hydrolyzed polyacrylamides adsorb only on the edges, not on the faces of the clay particles. Adsorption

of these polymers involves hydrogen bonding between the carbonyl groups of the polymers and the aluminol or silanol groups on the edges of the particles.[53]

3.2.1. Flocculation of a 3% Ca-Montmorillonite Suspension

Only Percol E24 (10% HPAM) was an effective flocculant at low dosages at pH 7.5, the natural pH of the suspension. An initial settling rate of 27 cm/hr and supernatant turbidity of 83 nephelometric turbidity units (NTU) were observed at a dosage of 134 ppm. An initial settling rate of 28 cm/hr and a turbidity of 25 NTU were achieved when 828 ppm of Percol 351 (nonionic PAM) was used. Percol 351 did not produce flocs at dosages below 300 ppm. Praestol 2935/73 (37% HPAM) produced only very small flocs at a dosage of 200 ppm; the supernatant turbidity was 840 NTU at that dosage. Praestol 2935/73 was not tested at higher dosages. PAMSM-1a (7.4% imide, freeze dried) and PAMSM-1b (7.4% imide, non-freeze dried) started to produce very small flocs at a dosage of about 220 ppm, but did not reduce the turbidity below 400 NTU, even at a dosage of 850 ppm. Neither PAMSM-2 (15% imide) nor PAMSM-3 (25% imide) produced flocs.

At pH 7.5, the faces of the Ca-montmorillonite particles have a negative charge while the edges probably have little or no charge. Therefore, only nonionic and low charge density anionic polymers, such as Percol 351 and

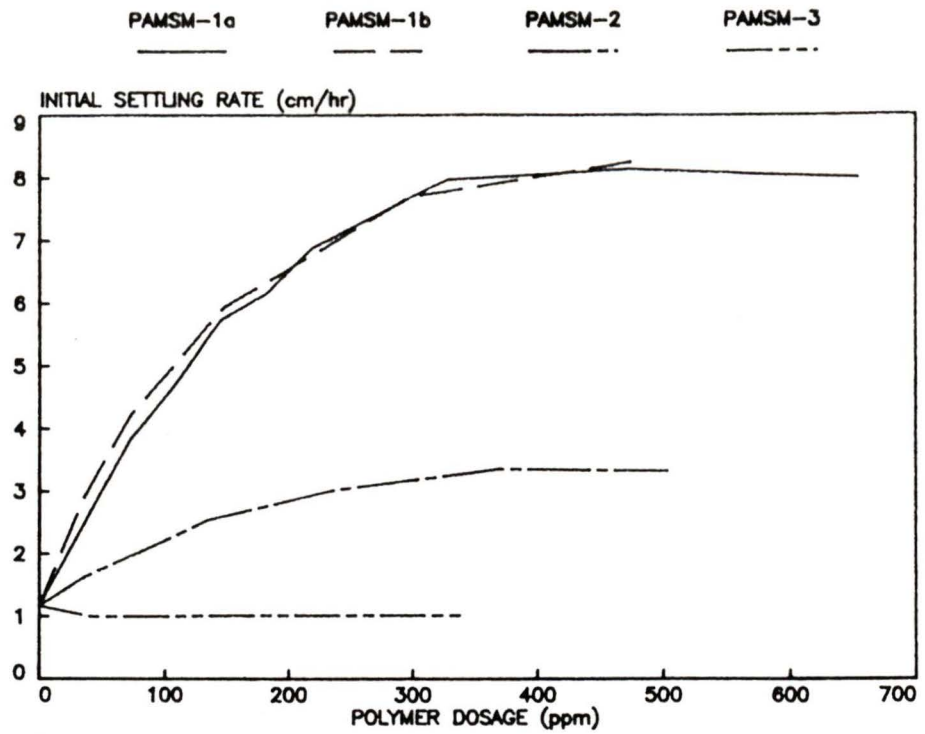

Fig. 36: Effect of polymer dosage on the initial settling rate of a 3% Ca-montmorillonite suspension at pH 4.0.

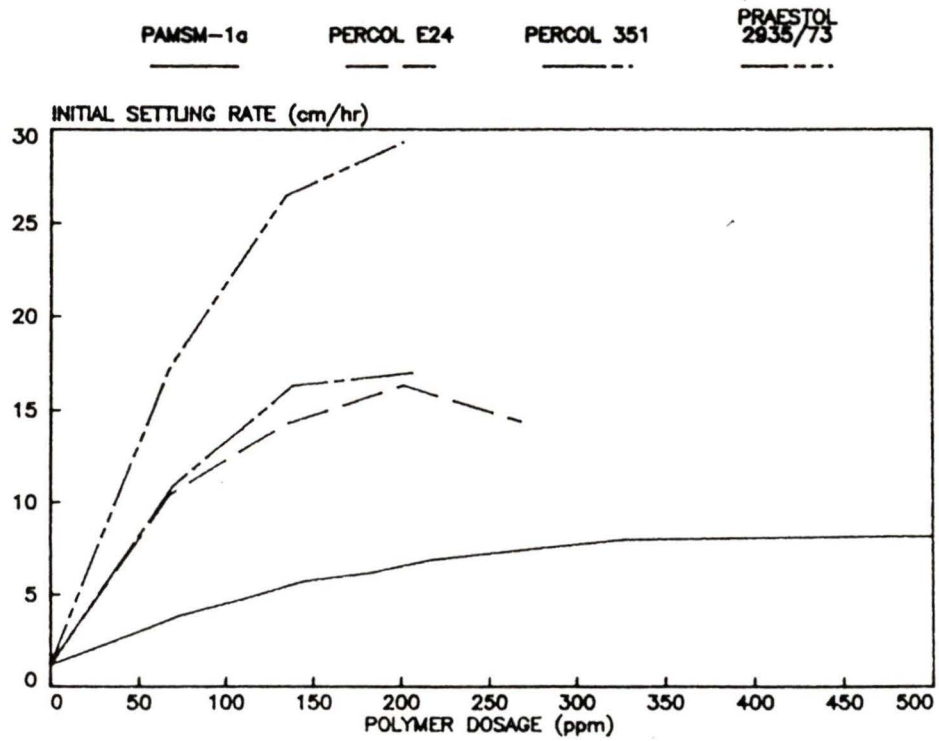

Fig. 37: Effect of polymer dosage on the initial settling rate of a 3% Ca-montmorillonite suspension at pH 4.0.

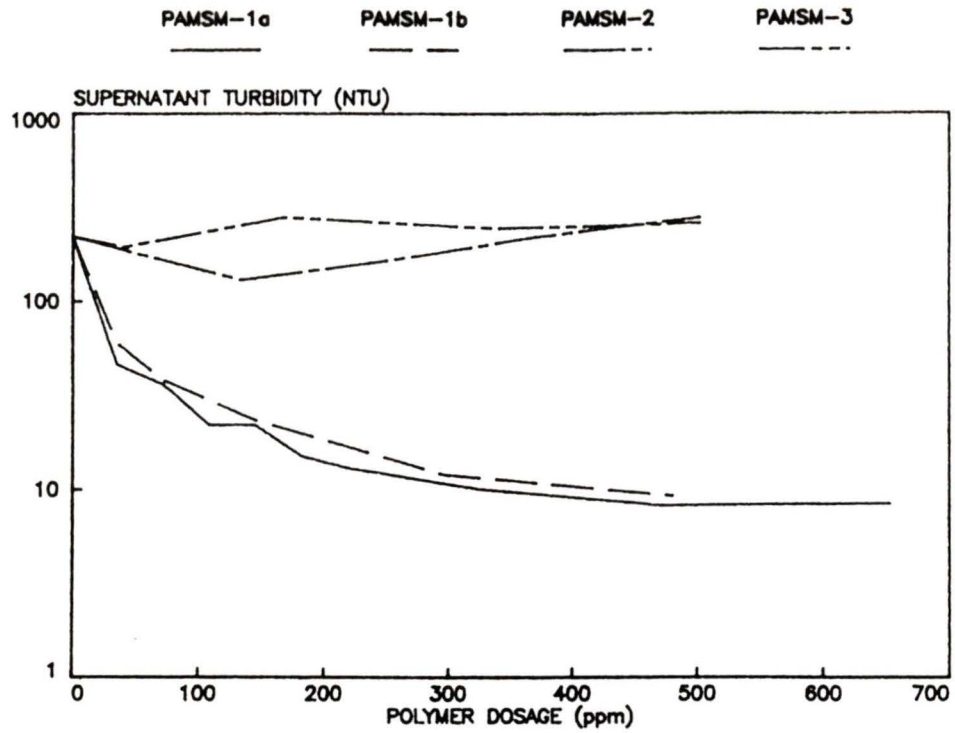

Fig. 38: Effect of polymer dosage on the turbidity of a 3% Ca-montmorillonite suspension at pH 4.0.

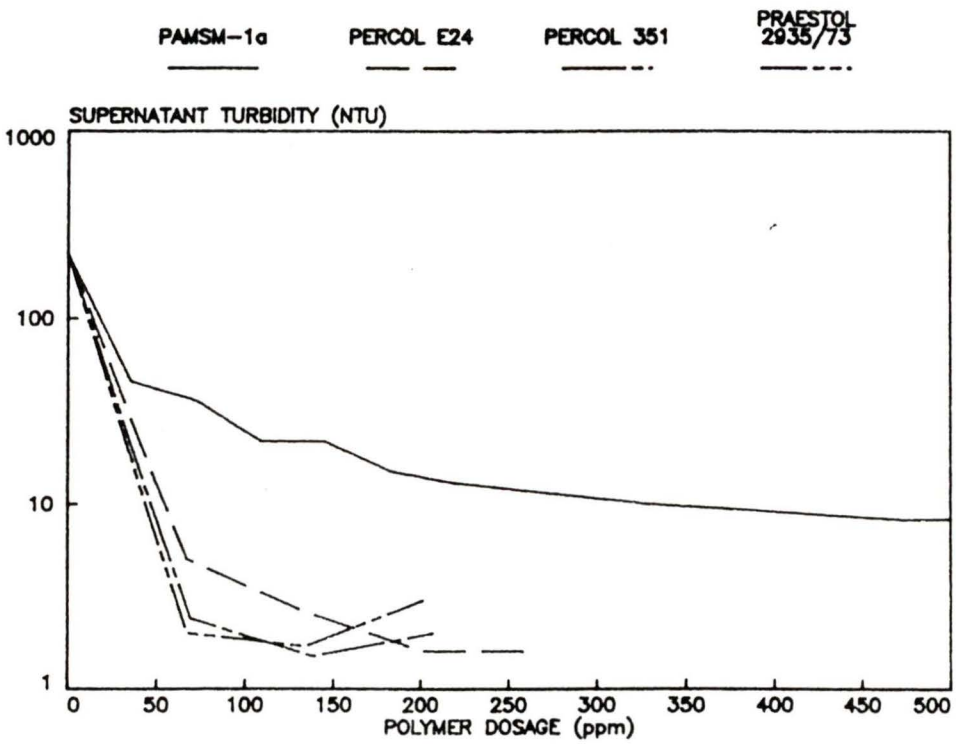

Fig. 39: Effect of polymer dosage on the turbidity of a 3% Ca-montmorillonite suspension at pH 4.0.

Percol E24, would be expected to flocculate the particles. PAMSM-1a (7.4% imide) and PAMSM-1b (7.4% imide) have charge densities similar to that of Percol E24 (10% HPAM), so these experimental copolymers would be expected to be effective flocculants as well. However, the two PAMSM copolymers produced only small flocs. This suggests that their molecular weights were too low to enable effective polymer bridging between clay particles.

At pH 4.0, a maximum initial settling rate of only 8.1 cm/hr was achieved using 350 ppm of copolymers PAMSM-1a (7.4% imide) and PAMSM-1b (7.4% imide), and a rate of only 3.3 cm/hr was observed when 350 ppm of PAMSM-2 (15% imide) was used (Fig. 36). PAMSM-1a and PAMSM-1b lowered the supernatant turbidity from 220 NTU to about 9 NTU while PAMSM-2 and PAMSM-3 had no effect on the supernatant turbidity (Fig. 38).

Initial settling rates of 29 cm/hr, 17 cm/hr, and 16 cm/hr were achieved using 200 ppm of Praestol 2935/73 (37% HPAM), Percol 351 (nonionic PAM) and Percol E24 (10% HPAM), respectively, at pH 4.0 (Fig. 37). All three commercial flocculants reduced the supernatant turbidity to less than 5 NTU (Fig. 39). The flocs formed by the commercial polymers were larger and stronger than those produced by the PAMSM copolymers, with the 37% hydrolyzed Praestol 2935/73 (4 to 6 million mol. wt.) being the most effective flocculant at low pH.

Again, these results suggest that the molecular weights of the PAMSM copolymers were too low to achieve good bridging between clay particles.

3.2.2. Flocculation Tests on a 3% Kaolinite Suspension

The copolymers PAMSM-1a (7.4% imide), PAMSM-1b (7.4% imide), PAMSM-2 (15% imide), and PAMSM-3 (25% imide) were tested at dosages ranging from 30 to 900 ppm on a 3% by weight kaolinite suspension at pH 4.5, the natural pH of the suspension. The copolymers had little effect on the settling rate of the suspension (Fig. 40). However, the turbidity of the supernatant increased markedly with increasing dosage and imide content (Fig. 42). At pH 4.5, the untreated kaolinite settled at a rate of about 0.25 cm/hr and the turbidity of the supernatant was about 60 NTU after 23 minutes. The turbidity was unaffected by the addition of PAMSM-1a and PAMSM-1b, but increased to 200 NTU when 131 ppm of PAMSM-2 was added and to over 1000 NTU when 138 ppm of PAMSM-3 was added. The turbidity increased to 840 NTU after 854 ppm of PAMSM-2 was added. The increase in turbidity of the supernatants demonstrated that the copolymers behaved as dispersants instead of flocculants.

The commercial flocculants Percol 351 (nonionic PAM), Percol E24 (10% HPAM) and Praestol 2935/73 (37% HPAM), on the other hand, were effective flocculating agents (Fig. 41). An initial settling rate of about 26 cm/hr was

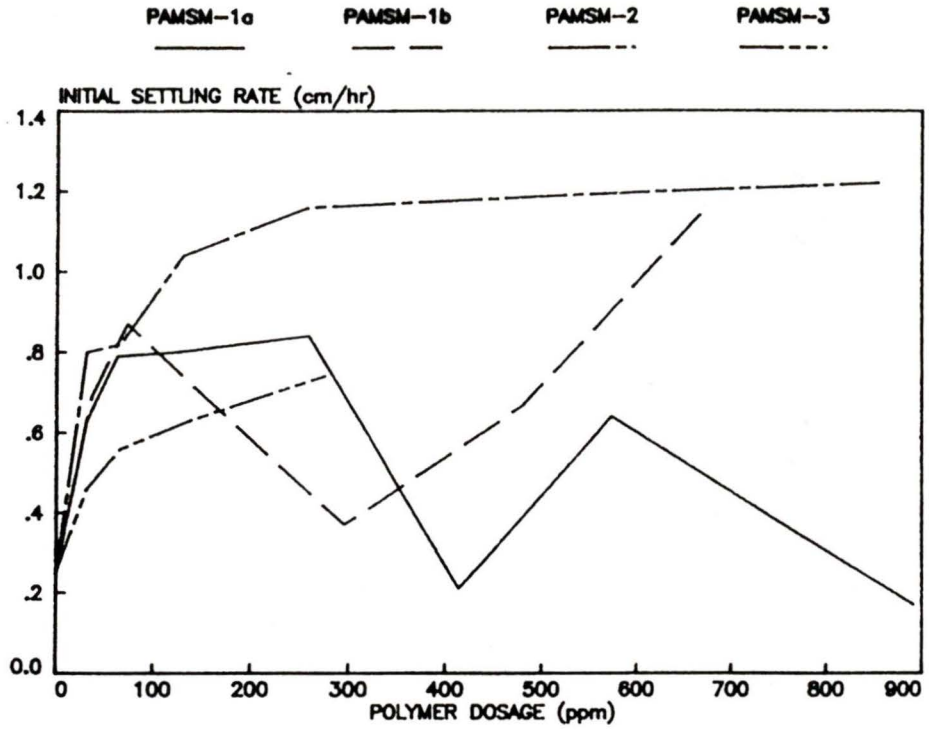

Fig. 40: Effect of polymer dosage on the initial settling rate of a 3% kaolinite suspension at pH 4.5.

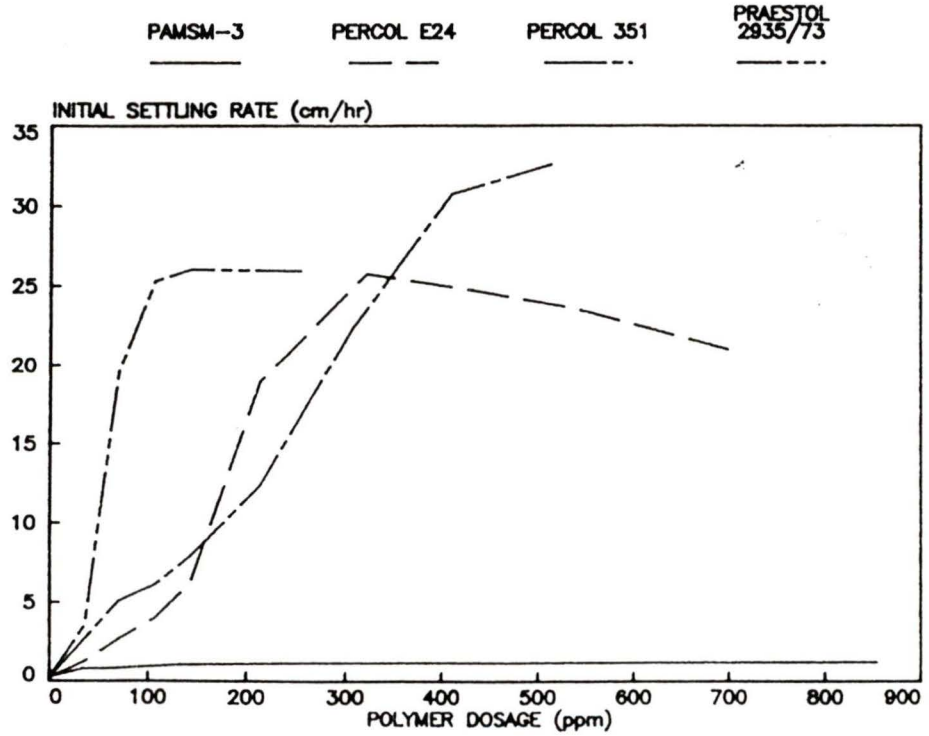

Fig. 41: Effect of polymer dosage on the initial settling rate of a 3% kaolinite suspension at pH 4.5.

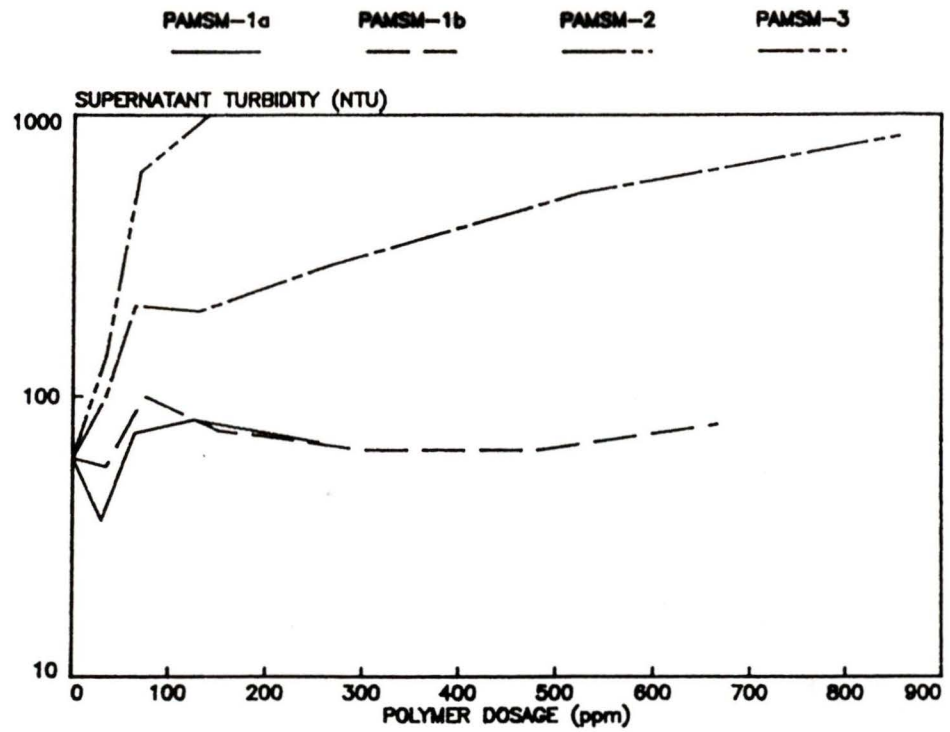

Fig. 42: Effect of polymer dosage on the turbidity of a 3% kaolinite suspension at pH 4.5.

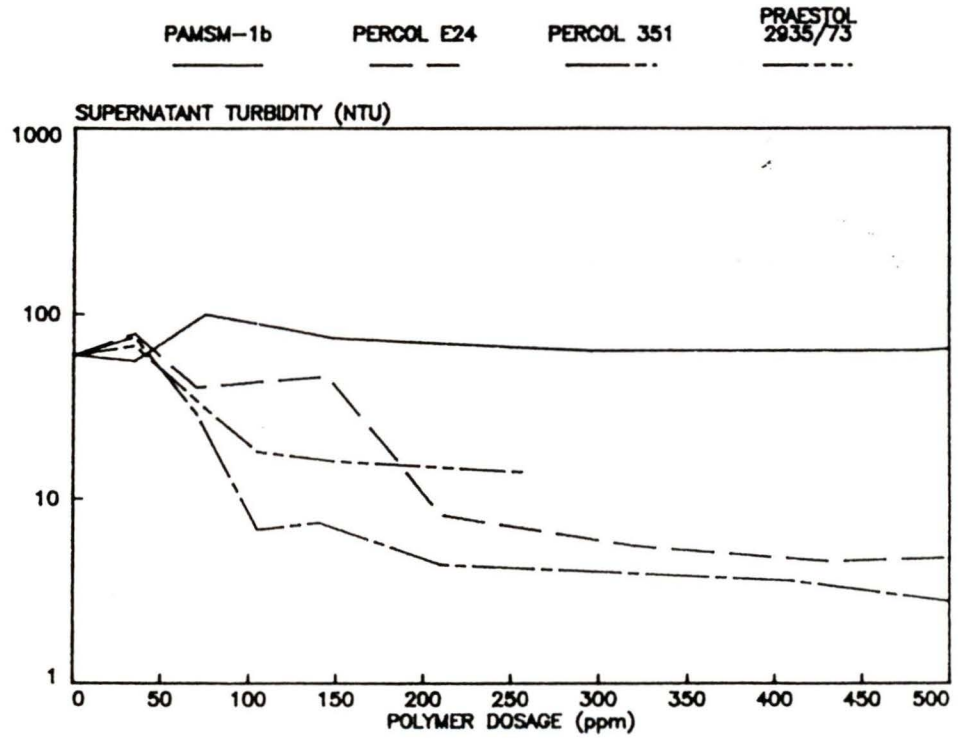

Fig. 43: Effect of polymer dosage on the turbidity of a 3% kaolinite suspension at pH 4.5.

observed using about 150 ppm of Praestol 2935/73. Approximately 300 ppm of Percol 351 and Percol E24 were required to achieve the same initial settling rate. All three of the commercial polymers were effective at improving the settling rate and in reducing the turbidity of the supernatant (Fig. 43).

At pH 4.5, about half of the carboxylate groups of Praestol 2935/73 (37% HPAM) would be in the dissociated anionic carboxylate form[54], i.e. about 18% available acrylate anion, whereas all of the sulfonate groups of the PAMSM copolymers would be in their ionized form.[3] The charge density of Praestol 2935/73 would be approximately double that of PAMSM-1a (7.4% imide) and PAMSM-1b (imide), and about equal to that of PAMSM-2 (15% imide). Therefore, the three PAMSM copolymers would be expected to perform as well as Praestol 2935/73. The fact that the PAMSM copolymers behaved as dispersants instead of flocculants suggests that their molecular weights were too low to enable bridging between clay particles.[3,44] PAMSM that was adsorbed on the positive charged edges of the clay particles probably stabilized the suspension because of electrostatic repulsion between the anionic polymer and the negative charged faces of the particles, or between the dangling segments of the adsorbed polymer.[17a,52]

Some flocculation was observed when the PAMSM copolymers were tested on the Ca-montmorillonite suspension,

though, because polyvalent cations such as Ca^{2+} reduce electrostatic repulsion between clay particles by compression of the diffuse double layer surrounding the particles. Reduction of the repulsive forces decreases the minimum distance of approach between the particles so that polymer bridging is possible.

3.2.3. Flocculation of a 3% Hematite Suspension

PAMSM-1a (7.4% imide), PAMSM-3 (25% imide) and polystyrene sulfonate (500,000 mol. wt.) did not flocculate the hematite suspension when tested at pH 4.5, 6.0, and 8.7 at dosages ranging from 30 ppm to 1000 ppm. Instead, they stabilized the very fine hematite particles. Most of the coarse particles settled within a few minutes.

Praestol 2935/73 (37% HPAM) flocculated the suspension at a dosage of only 30 ppm. The settling rate was not determined because the solids content was too low for a sharp supernatant-pulp interface to form, but most of the particles settled within 30 seconds.

3.3. Dispersion Experiments

3.3.1. Effect of the Copolymer Composition on the Effectiveness of PAMMBA and PAMDAS as Dispersants

Viscosity measurements indicated that the weight average molecular weights of the PAMMBA and PAMDAS copolymers obtained were all less than 100,000. Unlike high molecular weight polymers, low molecular weight anionic polyacrylamides tend to behave as dispersants instead of flocculants.[5] Consequently, it was not surprising that the PAMMBA and PAMDAS copolymers acted as dispersants when tested on a 3% kaolinite (Hydrite R) suspension at pH 4.8.

The effectiveness of these copolymers as dispersants was determined by measuring the turbidity of the supernatant as a function of time.[55] Turbidity depends on both particle size and concentration, so it is difficult to compare quantitatively the results of tests done on different suspensions. However, since the tests involving the PAMMBA and PAMDAS copolymers were done using the same stock suspension, the results should be semi-quantitative and should correctly show the relative effectiveness of these copolymers as dispersants.

The turbidity of most of the samples was greater than 1000 NTU, which was the upper limit of detection of the turbimeter. Therefore, the equivalent turbidity of the undiluted suspensions was calculated by assuming that

$$\text{turbidity of 2.0 mL aliquot} = \text{turbidity after dilution} \times \frac{\text{volume of diluted aliquot}}{2.0\ \text{mL}} \qquad (3\text{-}13)$$

The effect of the MBA content of the PAMMBA copolymers on the turbidity of the supernatant is shown in Fig. 44. The higher the concentration of suspended solids, the greater the turbidity of the suspension. When no polymer was added, the kaolinite settled rapidly and the turbidity was less than 50 NTU after one hour. However, the turbidity was much higher when the suspension was treated with 2000 ppm of a copolymer (i.e. 2000 mg polymer/kg of clay), presumably because the anionic copolymer increased the stability of the suspension by increasing the negative surface charge of the particles.[52] The greater the electrostatic repulsive forces between particles, the more stable the suspension. PAMMBA-3 was the best dispersant, probably because it had the highest charge density (23% MBA) of the three copolymer samples tested.

The effect of each of the copolymers on the stability of the dispersion was also determined by monitoring the level of the interface between the settled or rapidly settling particles, and the turbid supernatant (Fig. 45). When no polymer was added, the level of the interface decreased rapidly at first and then started to stabilize at

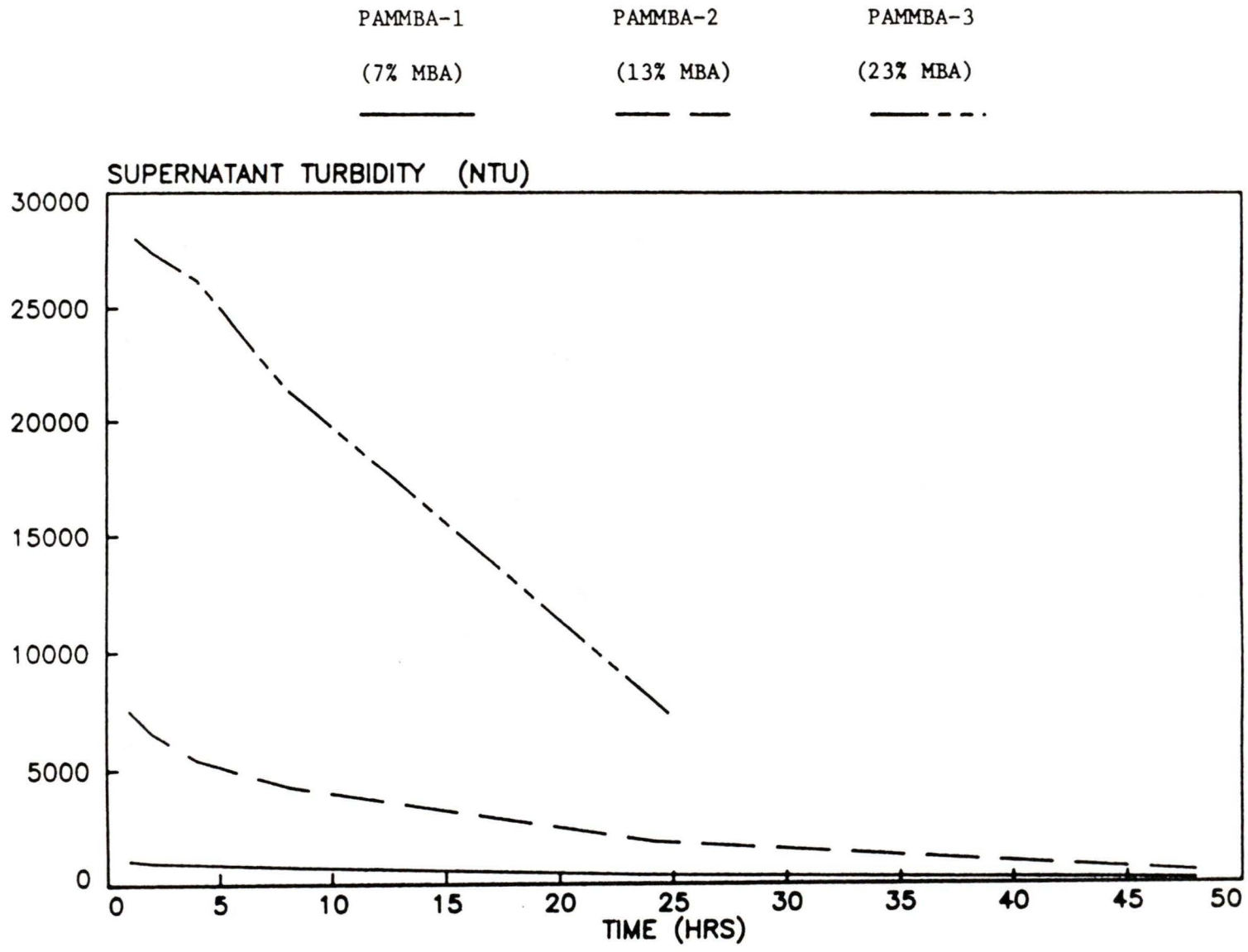

Fig. 44: Turbidity of a 3% kaolinite suspension after addition of 2000 ppm of PAMMBA-1, PAMMBA-2, and PAMMBA-3.

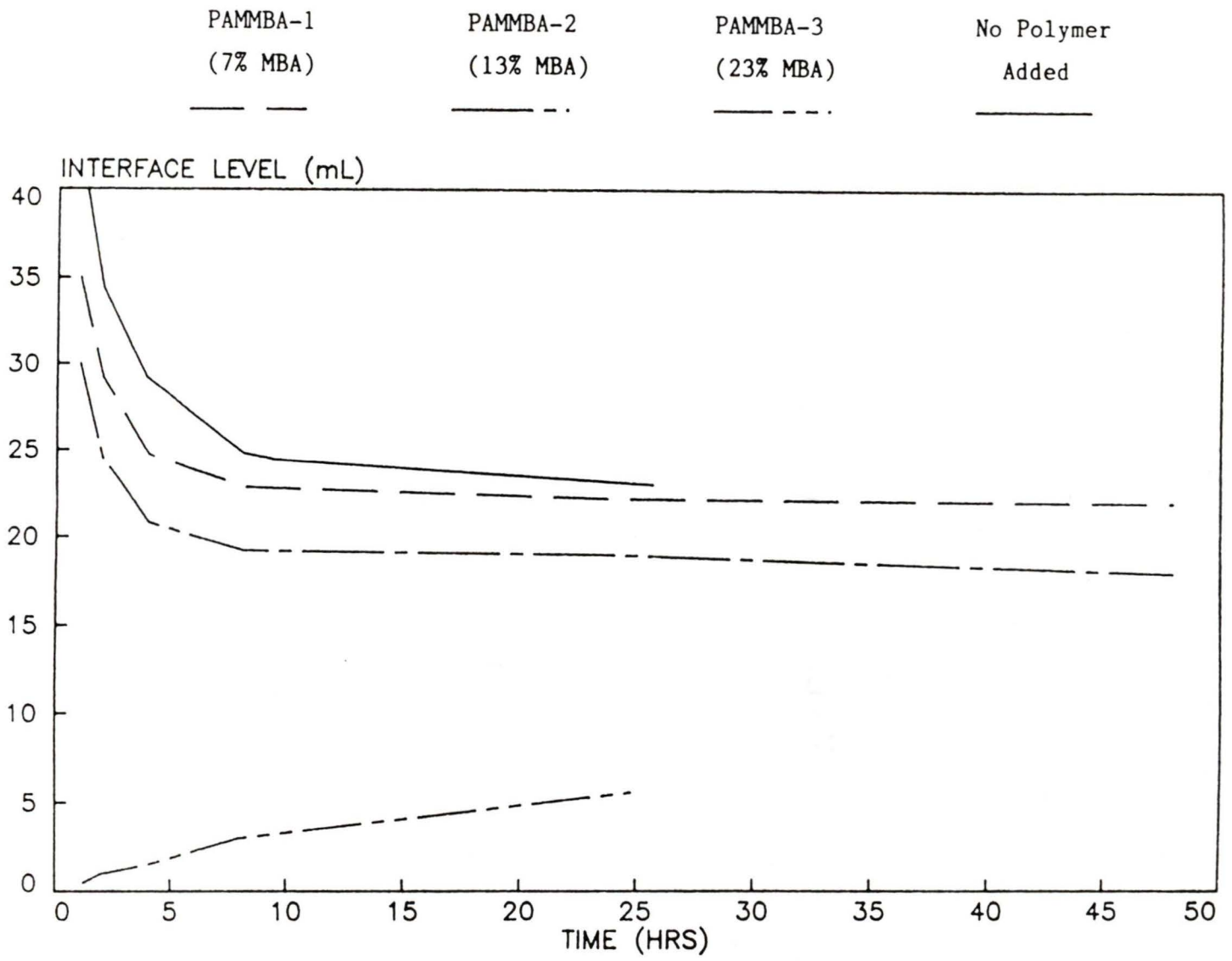

Fig. 45: Interface level of a 3% kaolinite suspension after addition of 2000 ppm of PAMMBA-1, PAMMBA-2, and PAMMBA-3.

about 25 mL after 8 hours. The interface level curves for the samples treated with PAMMBA-1 (7% MBA) and PAMMBA-2 (13% MBA) were similar but the final level of the interface was lower because some of the kaolinite particles still remained suspended in the supernatant after 48 hours. The interface level for the sample treated with PAMMBA-3 (23% MBA) increased, rather than decreased with time because most of the kaolinite particles were still dispersed throughout the solution after 1 hour and only some of the particles settled out during the next 24 hours. The level of the interface after 24 hours, relative to that of the untreated sample, indicated that about 75% of the kaolinite was still in suspension. It is important to note that these results are only semi-quantitative because some kaolinite was removed each time that the turbidity was measured, and the kaolinite that settled appeared to be more densely packed than that of the untreated sample. Nevertheless, they do demonstrate that the effectiveness of the PAMMBA as a dispersant increased as the MBA content of the copolymer increased, which is consistent with the results of the turbidity measurements.

The results for the dispersion tests with the PAMDAS copolymers are shown in Figs. 46 and 47. Again, the effectiveness of the copolymers as dispersants increased as the anionic charge density of the copolymers increased. PAMDAS-1 (3.9% DAS) was a poor dispersant while PAMDAS-3

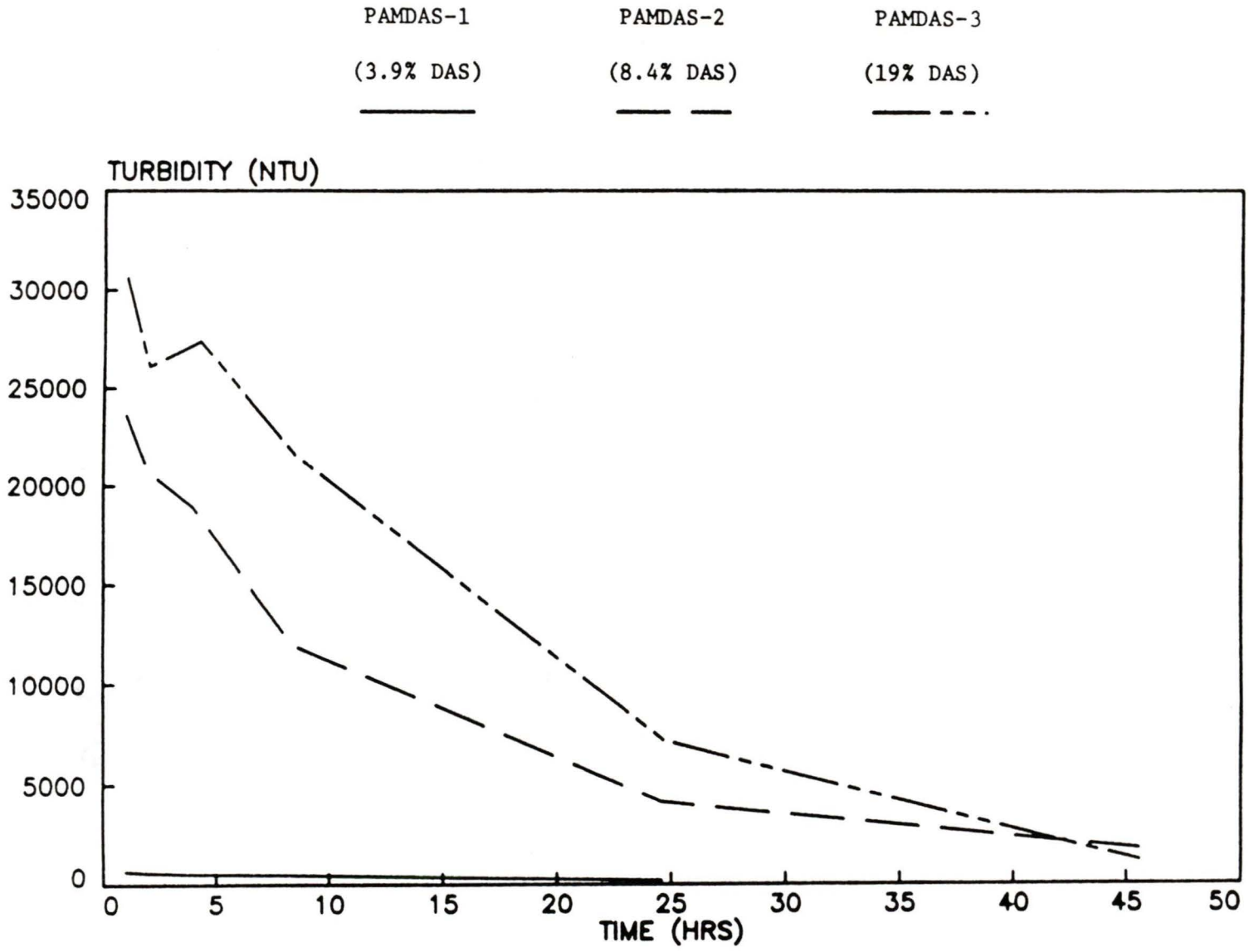

Fig. 46: Turbidity of a 3% kaolinite suspension after addition of 2000 ppm of PAMDAS-1, PAMDAS-2, and PAMDAS-3.

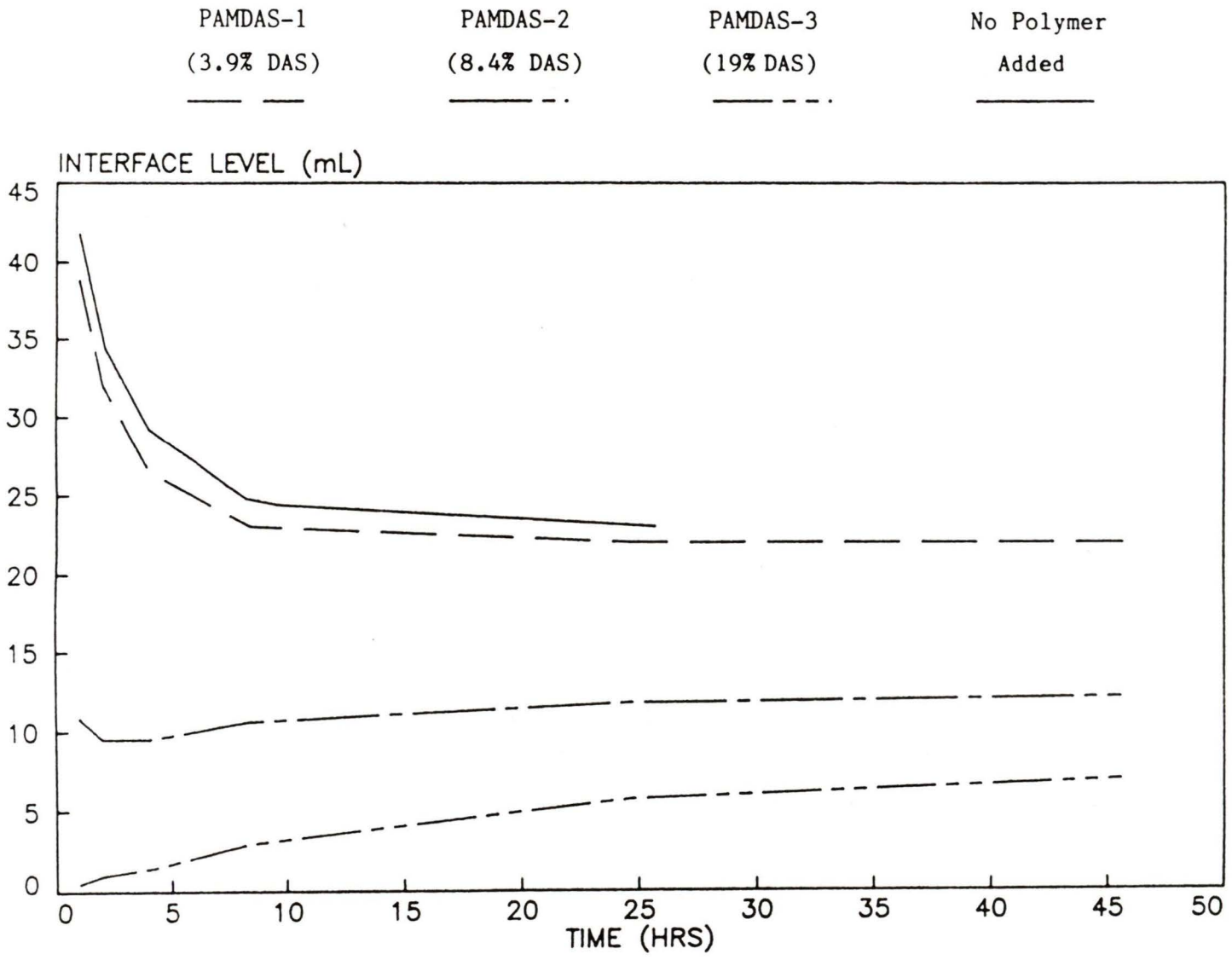

Fig. 47: Interface level of a 3% kaolinite suspension after addition of 2000 ppm of PAMDAS-1, PAMDAS-2, and PAMDAS-3.

(19% DAS) was a relatively effective dispersant. Comparison of the results for the PAMDAS copolymers with those for the PAMMBA copolymers (Figs. 44 and 45) shows that PAMDAS-1 (3.9% DAS) was about as effective as PAMMBA-1 (7% MBA), PAMDAS-2 (8.4% DAS) was more effective than PAMMBA-2 (13% MBA), and PAMDAS-3 (19.2% DAS) was about as effective as PAMMBA-3 (23% MBA).

3.3.2. Effect of Polymer Dosage on the Stability of a Kaolinite Supsension

Both turbidity and interface level measurements (Figs. 48 to 55) showed that the stability of the kaolinite suspension increased as the dosage of PAMMBA-3 (23% MBA) was increased from 250 to 2000 ppm. PAMMBA-3 was not as effective as DISPEX N-40. A dosage of 1000 to 2000 ppm of PAMMBA-3 was needed to achieve the same effect as achieved with only 250 ppm of DISPEX N-40 (100% polyacrylate), presumably because PAMMBA-3 has a lower charge density. A PAMMBA copolymer with a higher MBA content would probably be more effective than PAMMBA-3 as a dispersant, but would not be practical to prepare using the procedures given in Section 2.4.2 because of poor copolymerization yields (Table 2). Better yields could probably be obtained by ensuring that the copolymerization was driven to near 100% conversion, and then isolating the copolymer by evaporating the solvent instead of trying to precipitate the copolymer

in acetone or methanol. This was not done because the objective of this project was to prepare monomer-free, high molecular weight anionic copolymers for flocculation tests, rather than low molecular weight anionic copolymers for dispersion tests.

The turbidity and interface level measurements (Figs. 48 to 55) also showed that the stability of the kaolinite suspension increased as the dosage of PAMDAS-2 (8.4% DAS) was increased from 250 to 2000 ppm. PAMDAS-2 was not as effective as either PAMMBA or DISPEX N-40, though, because of its lower charge density. Again, PAMDAS copolymers with a higher sodium N,N-diallylsulfanilate (DAS) 7 content would be more effective than PAMDAS-2 as dispersants, but would not be practical to prepare by the methods in Section 2.5.2. Again it would be better to drive the polymerization to near 100% conversion and then use the solutions directly without trying to isolate the copolymers from unreacted monomer. This would avoid the loss of the low molecular weight fractions of copolymer.

Another problem with the preparation of PAMDAS copolymers was with NaBr removal from the sodium N,N-diallylsulfanilate monomer 7. NaBr was difficult to remove from the monomer because the two compounds tended to have similar solubility properties in different solvents. It was found that the NaBr content could be reduced from about 63 wt % to about 20 wt % by extracting the monomer into hot

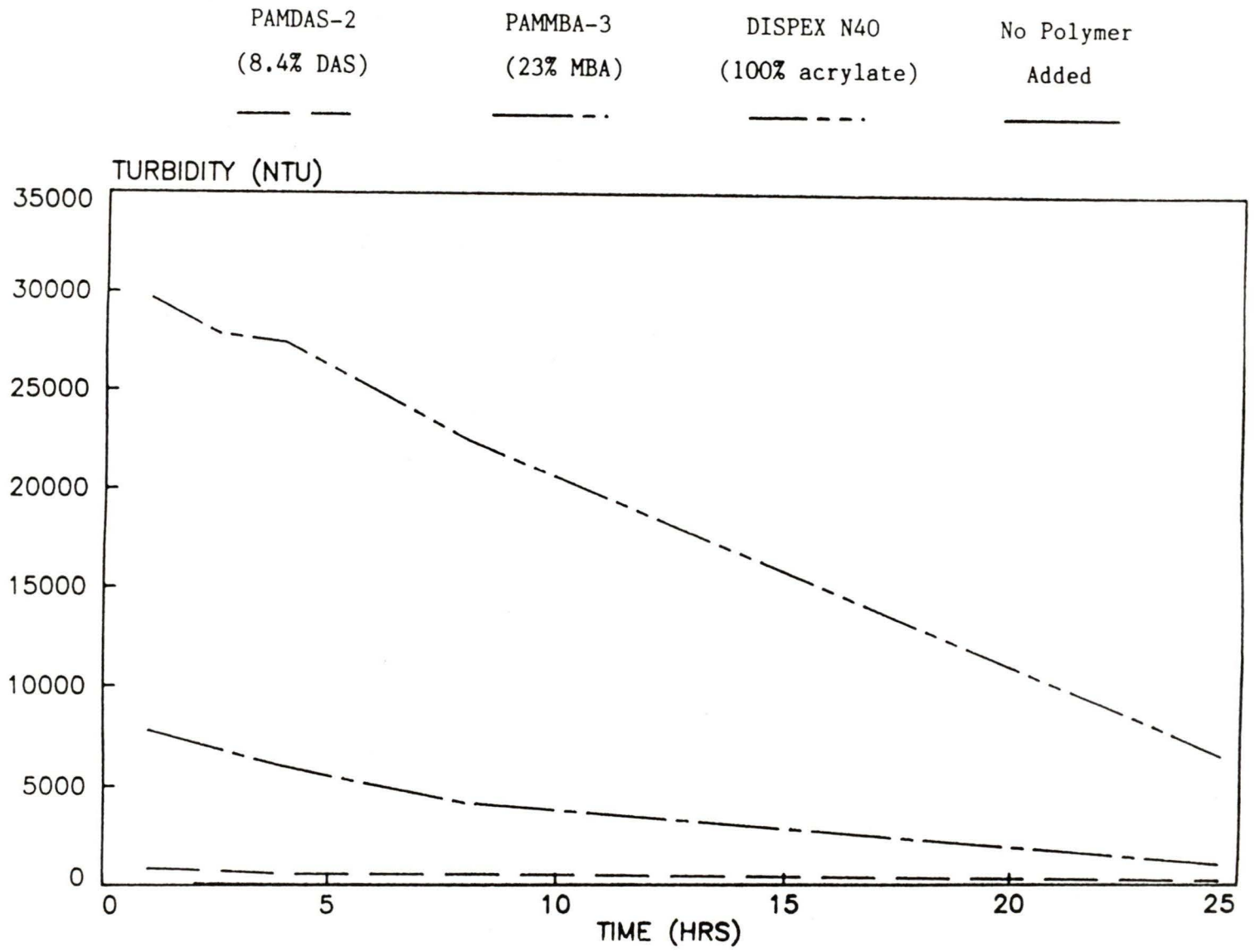

Fig. 48: Turbidity of a 3% kaolinite suspension after addition of 250 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

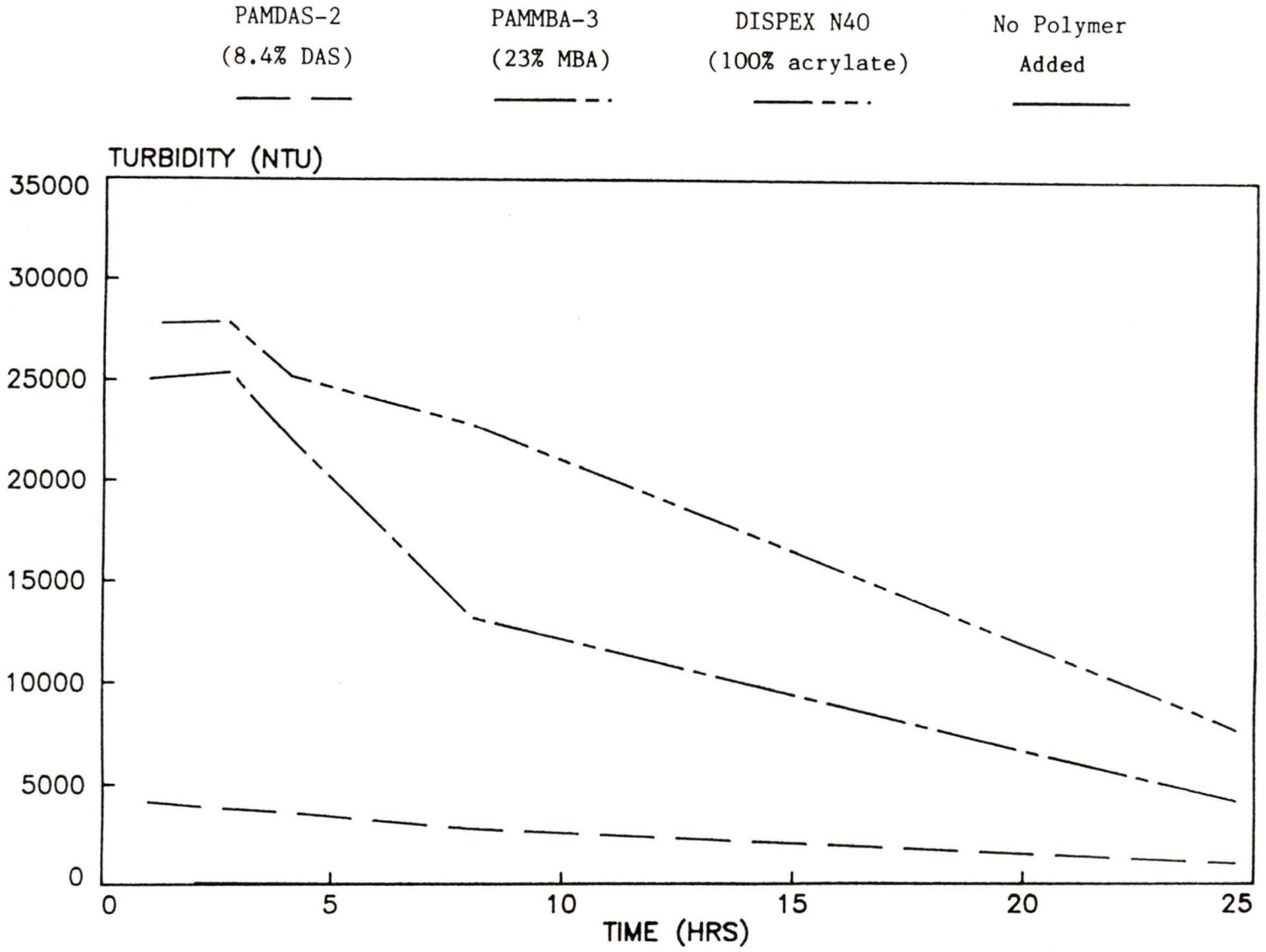

Fig. 49: Turbidity of a 3% kaolinite suspension after addition of 500 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

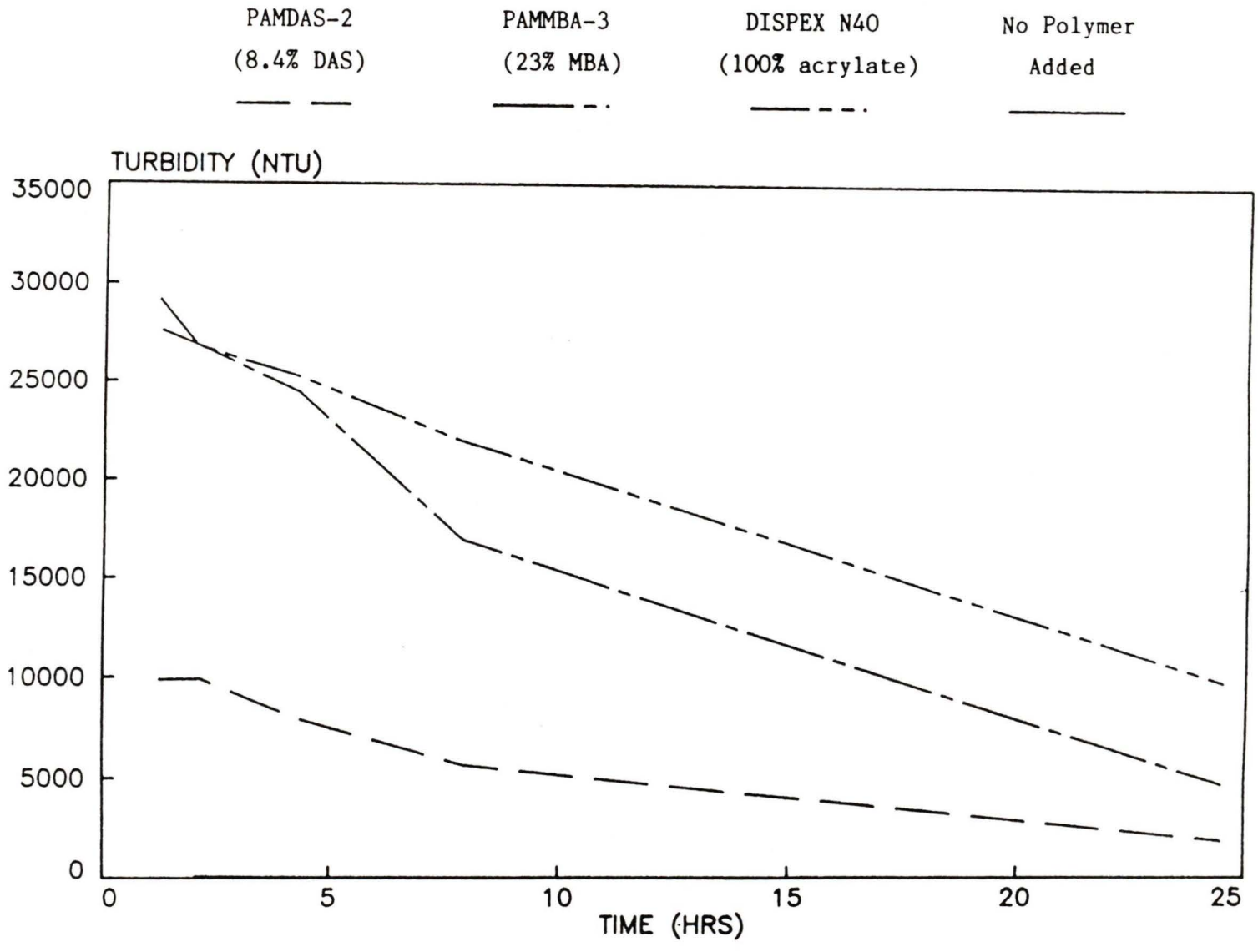

Fig. 50: Turbidity of a 3% kaolinite suspension after addition of 1000 ppm of PAMDAS-2, and PAMMBA-3, and DISPEX N40.

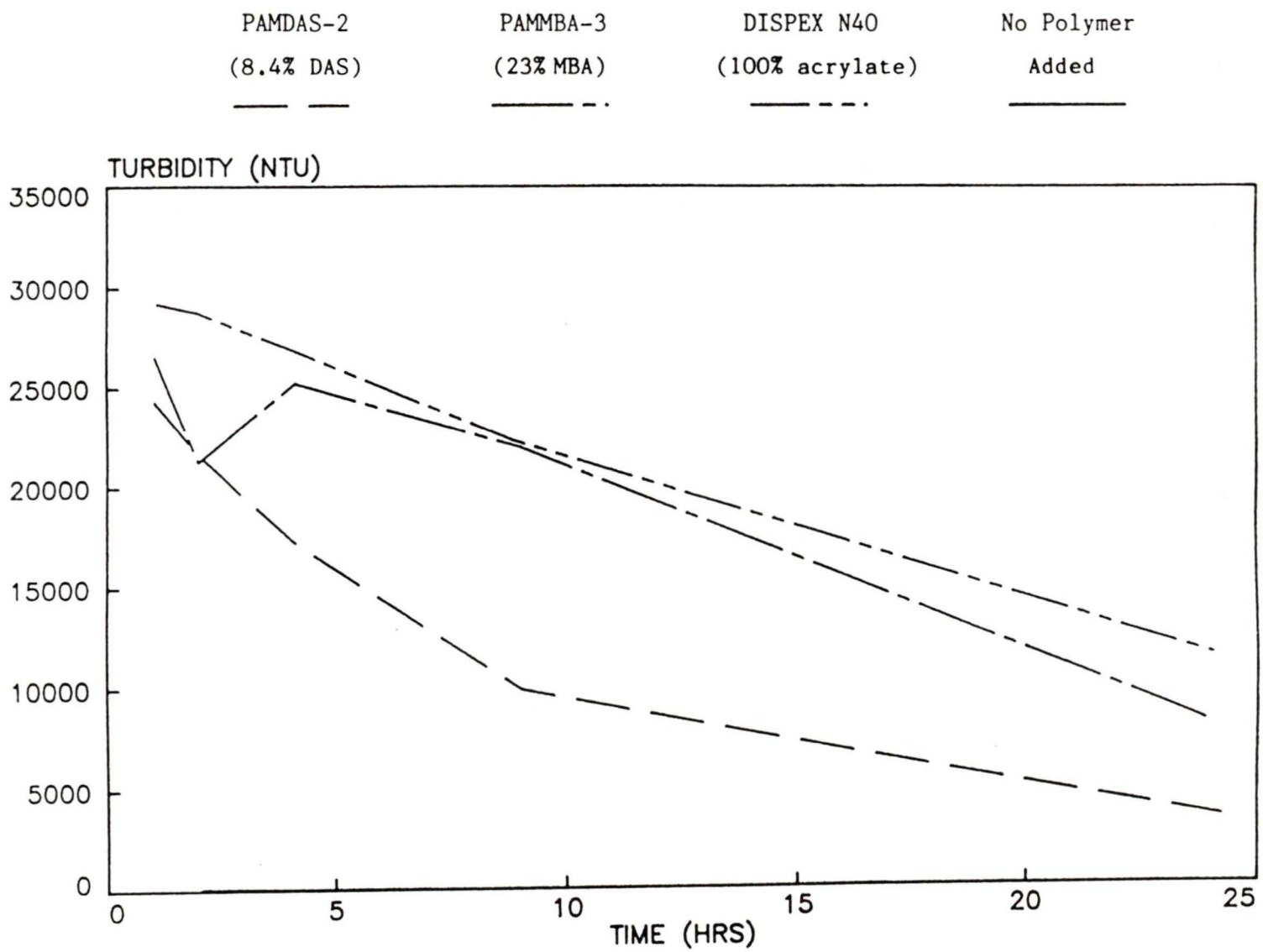

Fig. 51: Turbidity of a 3% kaolinite suspension after addition of 2000 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

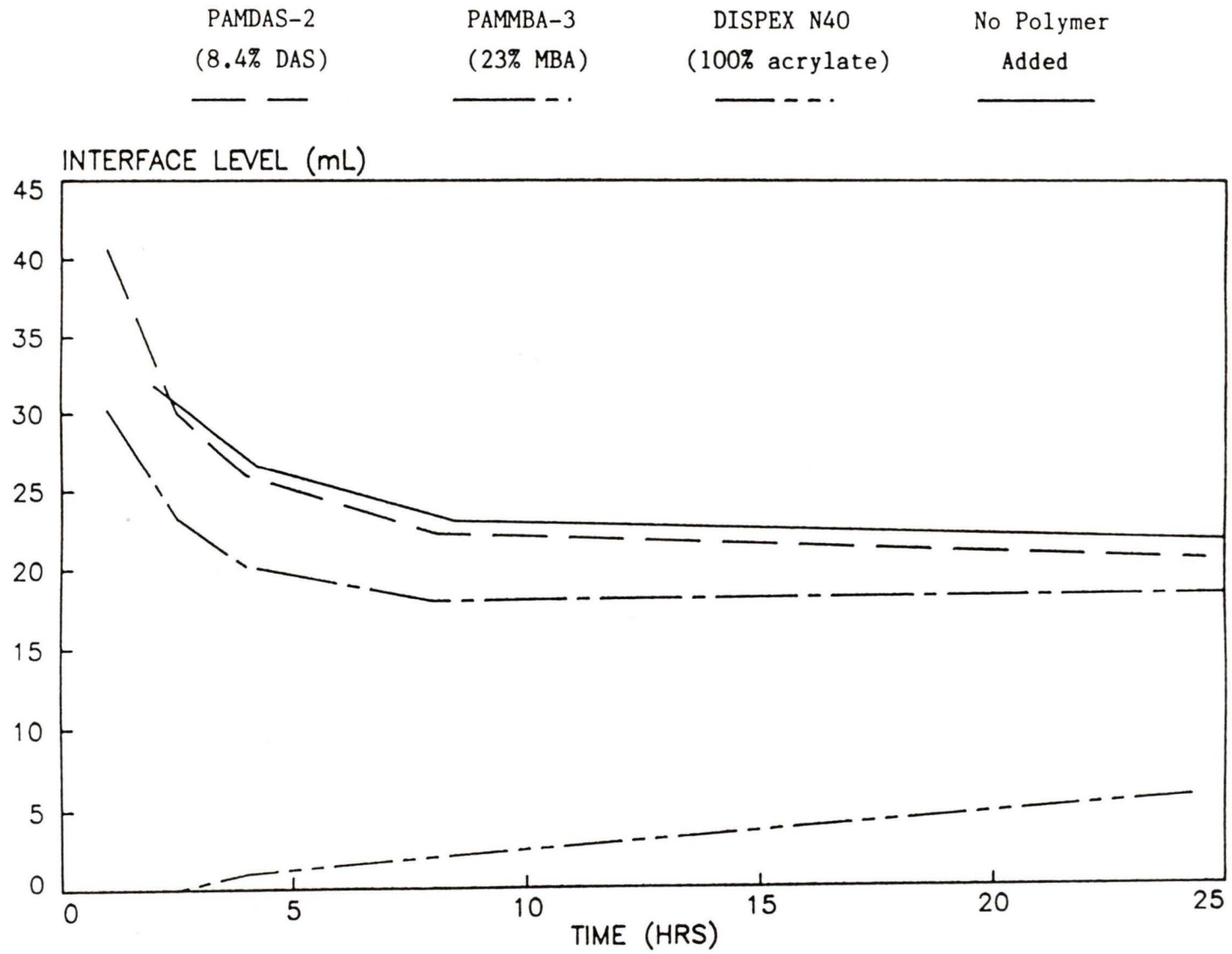

Fig. 52: Interface level of a 3% kaolinite suspension after addition of 250 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

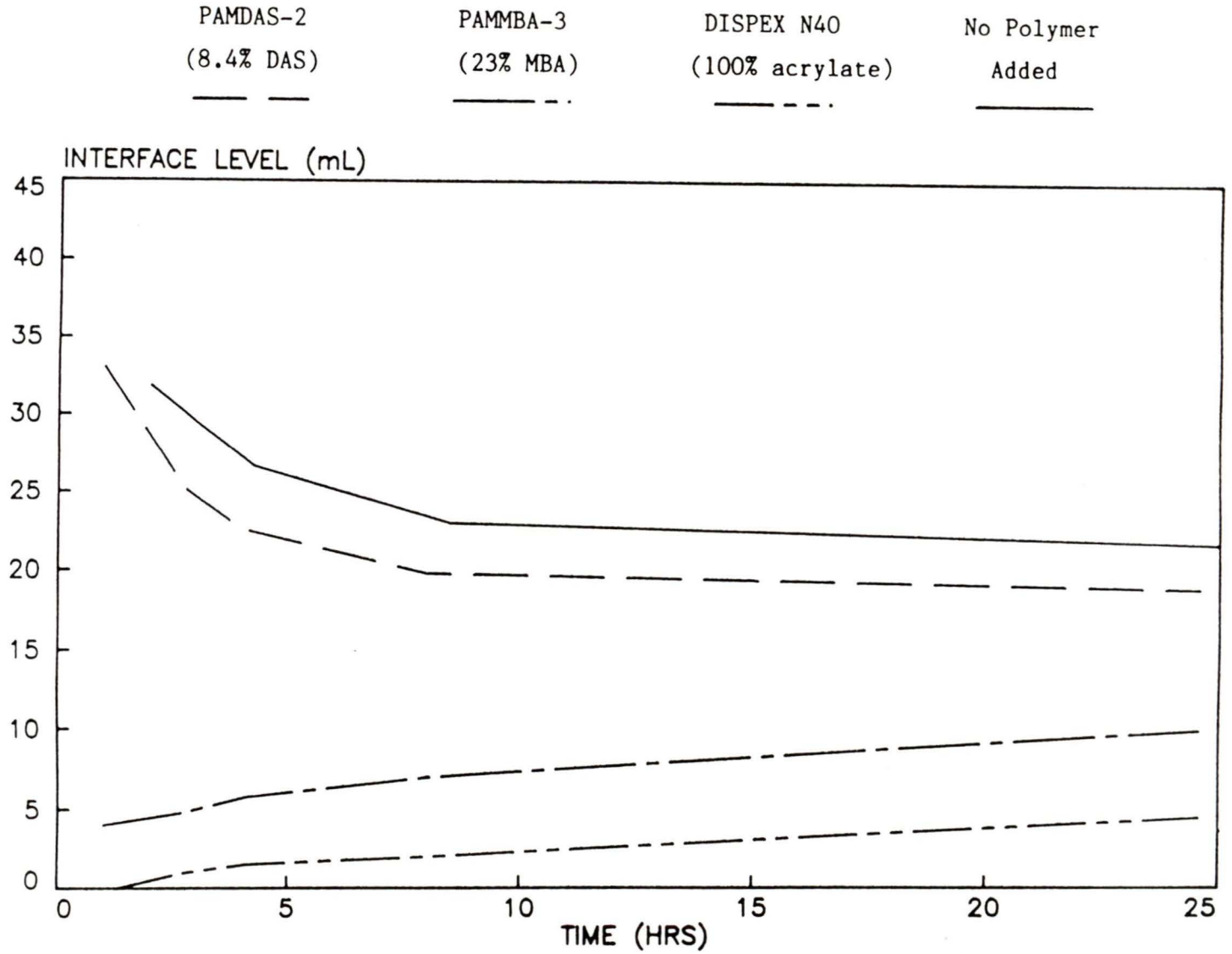

Fig. 53: Interface level of a 3% kaolinite suspension after addition of 500 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

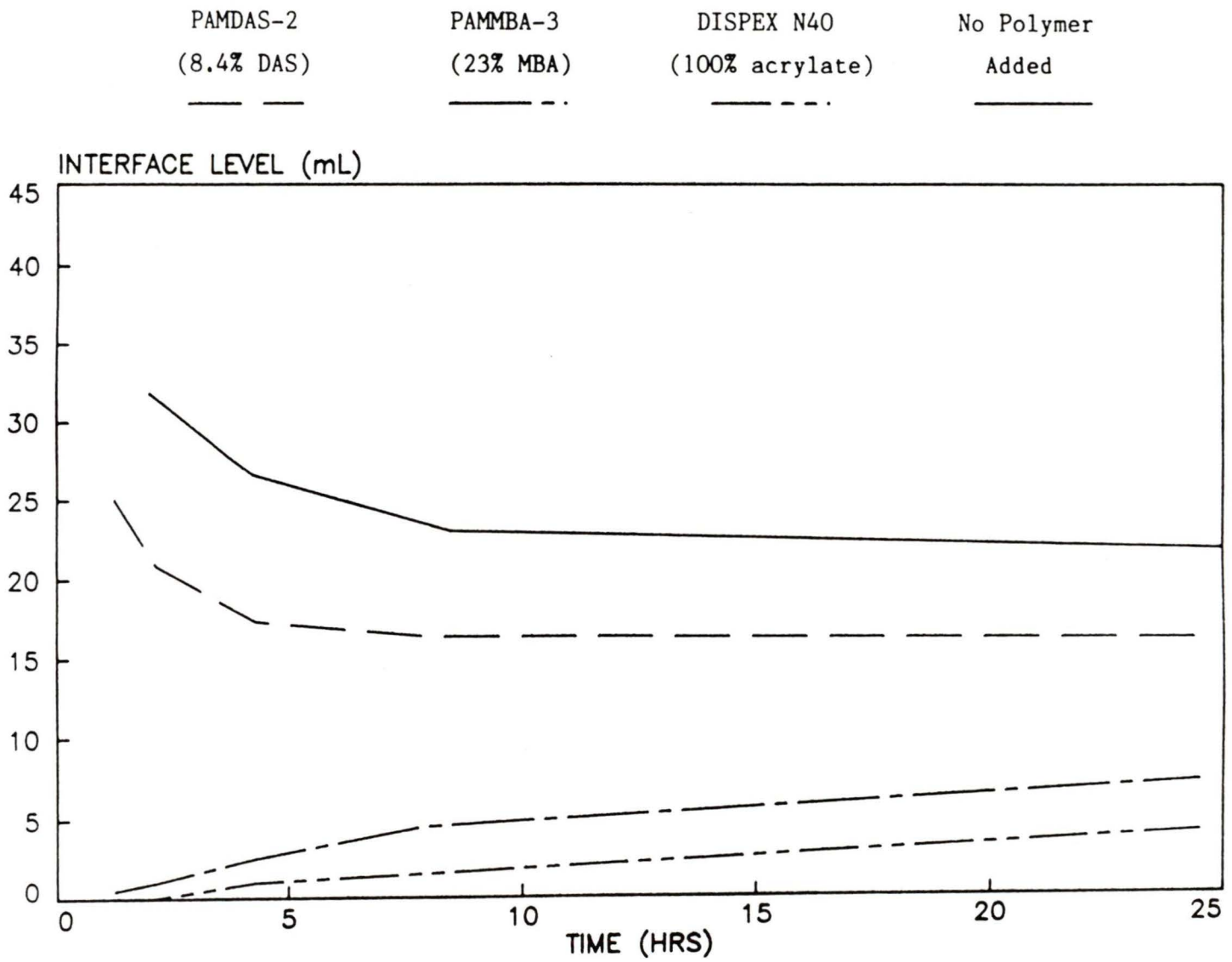

Fig. 54: Interface level of a 3% kaolinite suspension after addition of 1000 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

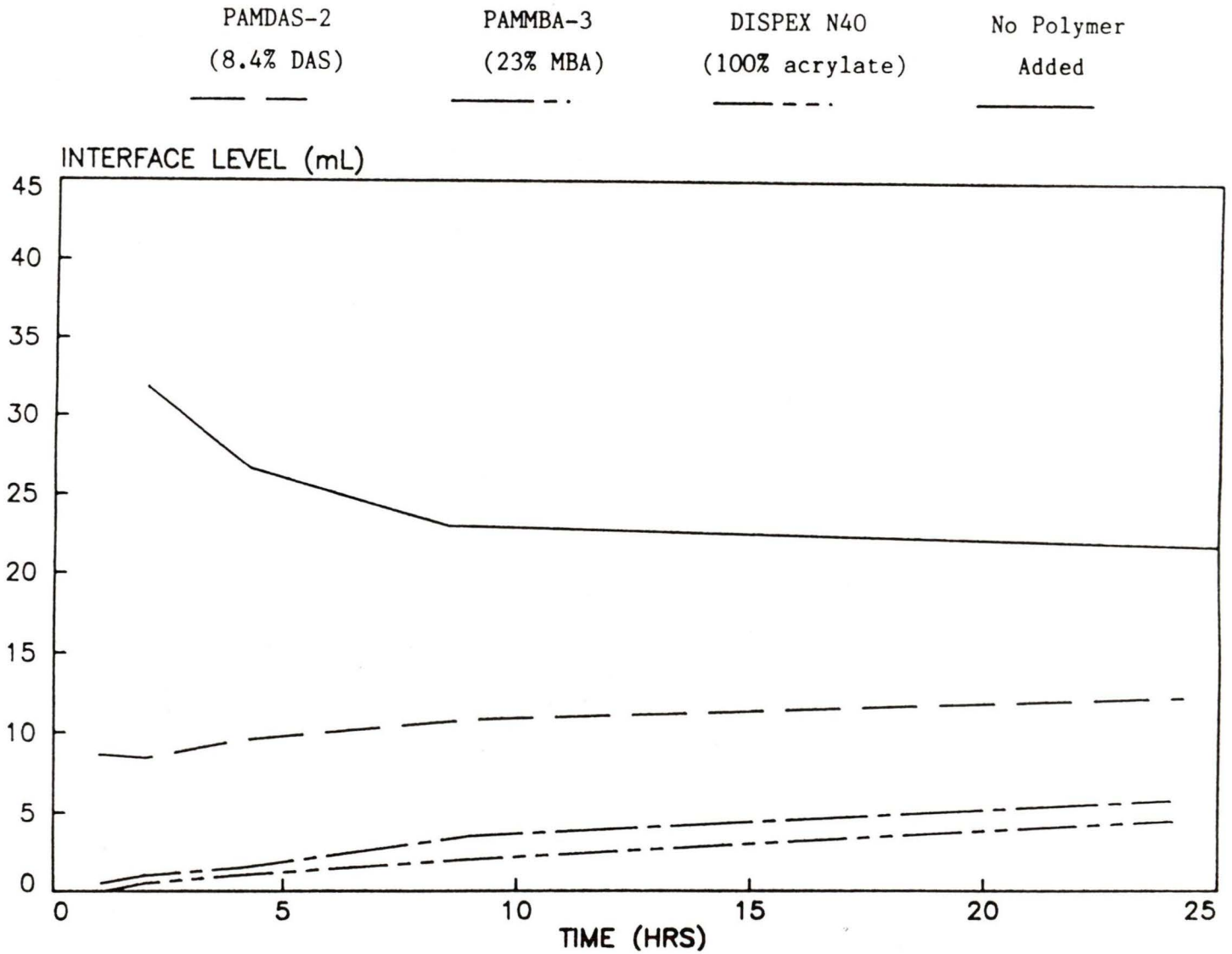

Fig. 55: Interface level of a 3% kaolinite suspension after addition of 2000 ppm of PAMDAS-2, PAMMBA-3, and DISPEX N40.

denatured ethanol or isopropanol, but large quantities of alcohol were required. To try to avoid this problem, attempts were made to prepare sodium N,N-diallylsulfanilate 7 by reacting sodium sulfanilate 8 with allyl chloride instead of allyl bromide. NaCl, which is the byproduct of the reaction with allyl chloride, would have been easier to remove than NaBr. However, allyl chloride was found to be too volatile and unreactive to permit preparation of sodium N,N-diallylsulfanilate 7 by this method.

4. Conclusions

Sodium N-(4-sulfophenyl)maleimide (SPMI) 3 was copolymerized with acrylamide 1 in de-oxygenated de-ionized water at 30°C without cleavage of the imide ring. PAMSM copolymers containing 7.4 to 68 mole % SPMI 3 were prepared using initial monomer feed ratios of 5:95 to 76:24 SPMI to acrylamide. The yields and molecular weights decreased as the SPMI to acrylamide feed ratio was increased because SPMI was less reactive than acrylamide. Copolymerization reactivity ratios of SPMI and acrylamide were determined to be 0.32 ± 0.02 and 0.58 ± 0.02, respectively, using the Kelen-Tudos linear graphic method of analysis.

p-Maleimidobenzoic acid (MBA) 4 was copolymerized with acrylamide 1 in de-oxygenated glacial acetic acid at 60°C. PAMMBA copolymers containing 7 to 23 mole % MBA were prepared using initial monomer feed ratios of 5:95 to 20:80 MBA to acrylamide. Both the yields and molecular weights of these copolymers also decreased as the MBA to acrylamide monomer feed ratio was increased. ^{13}C NMR showed that about 40 to 60% of the MBA units were hydrolyzed when the polymers were converted to their water-soluble sodium salt form using dilute aqueous $NaHCO_3$.

Sodium N,N-diallylsulfanilate (DAS) 7 was copolymerized with acrylamide at pH 1.9 and 60°C in HCl acidified de-ionized water to give PAMDAS copolymers containing

pyrrolidine rings. The diallyl monomer was more difficult to copolymerize with acrylamide than either of the two maleimide monomers. Copolymers containing only 3.9 to 52 mole % DAS were obtained using initial DAS to acrylamide feed ratios of 10:90 to 80:20. Again, the yields and molecular weights decreased as the DAS content increased because of the relatively low reactivity of the monomer with acrylamide.

N,N-diallylaniline 6 was copolymerized with acrylamide at pH 0.65 and 60^{o}C in HCl de-ionized water to give copolymers that also contained pyrrolidine rings. Initial N,N-diallylaniline to acrylamide feed ratios of 10:90 to 31:69 yielded copolymers containing 3.5 to 8.9 mole % N,N-diallylaniline. The copolymers were unsuitable for use as flocculants because they precipitated when the pH was raised above about 3.0 with aqueous NaOH.

PAMSM copolymers containing 7.4, 15, and 25 mole % polymerized SPMI 3 performed poorly compared to commercial partially hydrolyzed polyacrylamides when tested as flocculants on a 3% Ca-montmorillonite suspension. The flocculation performance of the PAMSM copolymers decreased with increasing imide content. They acted as dispersants instead of flocculants when tested on kaolinite and hematite suspensions. Therefore, it was concluded that the molecular weights of these anionic copolymers were too low for effective bridging to occur between the clay or hematite

particles.

PAMMBA copolymers containing 7 to 23 mole % polymerized MBA and PAMDAS copolymers containing 3.9 to 19 mole % polymerized DAS both acted as dispersants when tested on a 3% kaolinite suspensions in water. The effectiveness of the copolymers as dispersants increased with increasing MBA or DAS content. Although the copolymers were reasonably effective dispersants, they did not perform as well as a commercial 100% polyacrylate dispersant (DISPEX N-40) unless dosages about four times that of the commercial dispersant were used. The copolymers would probably be more effective if the MBA or DAS content was increased. The fact that the copolymers acted as dispersants, whereas higher molecular weight partially hydrolyzed polyacrylamides behaved as flocculants, suggested that the molecular weights of the copolymers were too low.

In conclusion, the results reported here indicate that high molecular weight anionic flocculants can not be prepared by copolymerization of acrylamide with maleimide or diallyl monomers. The copolymerization reactivities of the maleimide and diallyl monomers tested here appear to be too low relative that of acrylamide to make it possible to obtain sufficiently high molecular weights. Any increase in polymer hydrodynamic volume resulting from the presence of the succinimide or pyrrolidine rings in the polymer backbone is outweighed by the low molecular weights.

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