

Synthesis and Solution Properties of Polymeric Zwitterionic Ammonium Betains

by

Asif Rasheed

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

April, 1998

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COLLEGE OF GRADUATE STUDIES

This thesis, written by Mr. Asif Rasheed under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMISTRY.

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

Dedicated to my Parents

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Praise and thanks to Almighty Allah, for giving me the help and guidance that enabled me to work successfully.

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ABSTRACT

NAME	ASIF RASHEED
TITLE OF STUDY	SYNTHESIS AND SOLUTION PROPERTIES OF POLYMERIC ZWITTERIONIC AMMONIUM BETAINS
MAJOR FIELD	CHEMISTRY
DATE OF DEGREE	APRIL, 1998

The quaternary ammonium salt, *N,N*-diallyl-*N*-carboethoxymethyl-*N*-methylammonium chloride (**8**), has been synthesized in excellent yield. The monomer **8** on polymerization in water solution using ammonium persulfate as initiator afforded the polyelectrolyte **10**. The polyelectrolyte **10** on acidic hydrolysis gave the polyampholyte **11** in excellent yield. The solution properties of these polymers are discussed in detail. The polyampholyte **11** showed "antipolyelectrolyte" behaviour.

The copolymer **12** of quaternary ammonium salt, *N,N*-diallyl-*N*-carboethoxymethyl-*N*-methylammonium chloride (**8**) and sulfur dioxide has been synthesized in excellent yield. The polyelectrolyte **12** on acidic hydrolysis gave the polyampholyte **13** readily in excellent yield. The solution properties of these polymers are discussed in detail. The polyampholyte **13** was found to be insoluble in water but dissolved readily in presence of low molecular weight common salts. The polyampholyte shows "antipolyelectrolyte" behaviour; the viscosity of the polyampholyte increases by increasing the ionic strength of its aqueous solutions.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

DHAHRAN, SAUDI ARABIA.

الخلاصة

اسم الطالب : أصف رشيد
عنوان الرسالة : تركيب بوليمرات ثنائية الشحنة ودراسة خواص محلليها
المجال : الكيمياء
تاريخ الدرجة : أبريل ١٩٩٨ م .

تم تركيب ملح الامونيوم الرباعي ، ثنائي الاثيل كاربو إيثوكسي ميثيل - ميثيل أمونيوم كلوريد ، بمرود ممتاز وتم تحويل هذا المركب إلى بوليمر في محلول مائي بإضافة البادئ أمونيوم بيرسلفات . ثم تم تحويل هذا البوليمر إلى بوليمر ثنائي الشحنة (يحتوي على شحنات سالبة وموجبه) بإضافة حامض في وسط مائي . وتمت دراسته تفصيليه لخواص المحاليل المائية للبوليمر الناتج .

وتم ذلك تركيب بوليمر ثنائي من ملح الامونيوم المذكور مع ثاني اكسيد الكبريت بمرود ممتاز . وتم تحويل البوليمر الثنائي إلى بوليمر ثنائي الشحنة بنفس الطريقة السابقه ، ولكن البوليمر الثنائي ترسب ، ولمنه ذاب عند إضافة ملح من الاملاح الشائعه للمحلول المائي .

وكلا البوليمرين أظهر خاصيه معاكسه لمحاليل البوليمرات المشحونه ، حيث زادت لزوجة المحلول بزيادة تركيز الملح الشائع (مثل ملح الطعام)

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران - المملكة العربية السعودية

CHAPTER 1

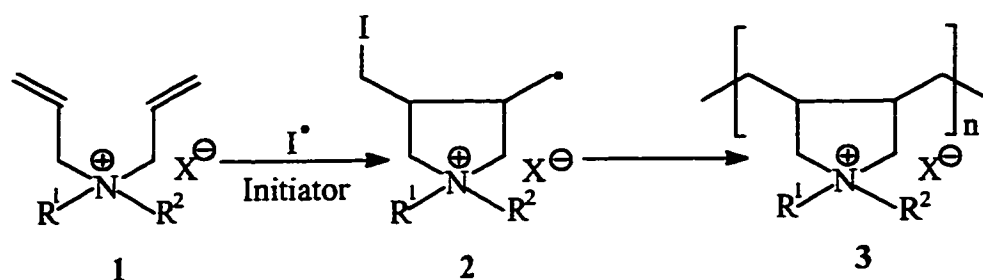
INTRODUCTION

1.1 Introduction

Water-soluble polymers are of significant importance to industry. There are two major classes of water-soluble polymers, nonpoelectrolytes and poeectrolytes. The major contributors to the nonpoelectrolyte group of water-soluble polymers are poly(acrylamide), poly(acrylic acids), poly(vinyl alcohol), poly(ethylene oxides) and the naturally occurring water-soluble polysaccharides.

Quaternary ammonium salts are one of the most significant and extensively used polymers among the cationic poeectrolytes.¹⁻³ The quaternary ammonium functional group is highly hydrophilic. These type of polymers are applied in water treatment, as flocculating agents⁴, in sludge dewatering^{4,5}, in sedimentation of suspended polymers,^{6,7} for electroconductivity in electrophotography,^{8,9} and in enhanced oil recovery (EOR).¹⁰

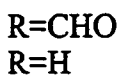
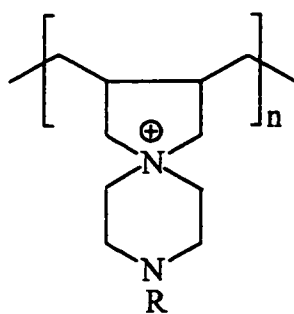
Butler and coworkers have polymerized various diallyl quaternary ammonium salts to yield linear water-soluble polymers with little or no unsaturation.¹¹⁻¹⁴ They carried out polymerization of a variety of diallyl quaternary ammonium salts **1**, which polymerizes *via* an intra- inter-molecular chain propagation (termed cyclopolymerization) through the five-membered cyclic structure **2** to yield linear water-soluble polymers **3** (Scheme 1).



Scheme 1

The copolymers of dialkyldiallyl ammonium salts with sulfur dioxide are manufactured commercially and have various industrial uses.¹⁵ Anion-exchange cross-linked polymers, derived from tri- or tetra- alkyl quaternary ammonium salts have been used in extraction of uranium¹⁶ and also for cheap removal of salinity from brackish water.¹⁷

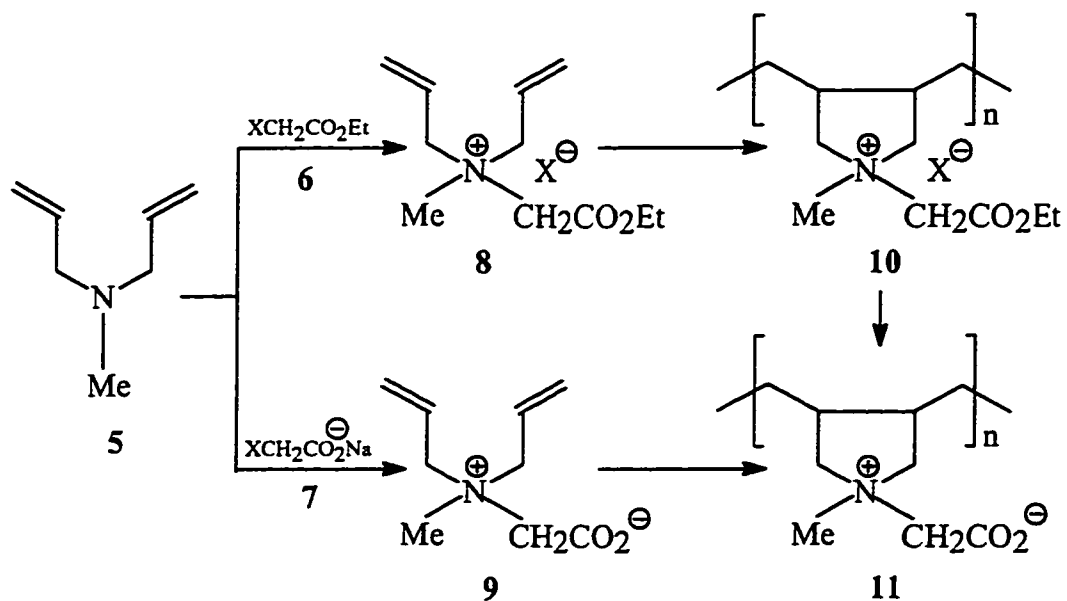
Hydrophobically associating copolymers of the salts 1 may have potential application in Enhanced Oil Recovery and other applications where viscofication of water is of interest.¹⁸ Further inroad into the water-soluble polymers has been reported¹⁹ which describe the synthesis of a novel class of piperazine based homo- and co-polymers containing quaternary as well as trivalent nitrogen in the same polymer.



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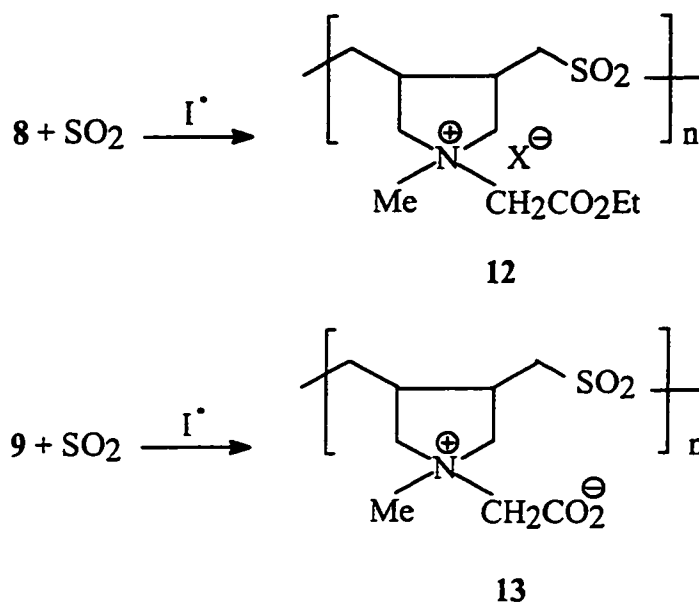
1.2 Aim of the Work

Viscosity curves for the polyquaternary ammonium salts **3** are typical of polyelectrolytes in general, unlike the behavior of uncharged linear polymers. The plot of reduced viscosity *versus* concentration of the polymers are strongly concave upwards thus resulting in very large intrinsic viscosities. This is attributed to the increase in hydrodynamic volume of the polymers in dilute solution where large repulsive forces between positively charged nitrogen leads to the expansion of the polymeric backbone. The presence of strong electrolyte like sodium chloride suppresses the ionization of the polymer and the viscosity behavior becomes normal. The objective of this research is to synthesize the monomers **8** (diallyl methyl carboethoxymethylammonium salt) and **9** (diallyl methyl carboxymethylammonium betaine) as shown in the Scheme 2.



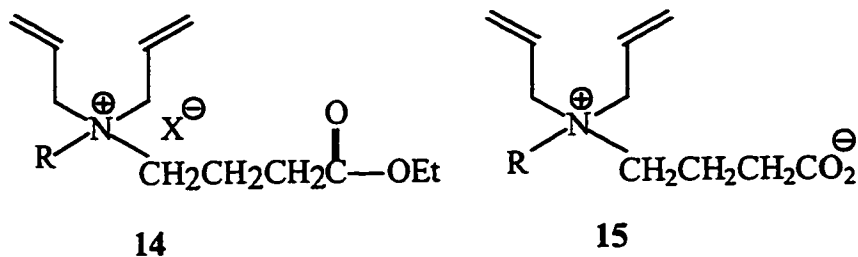
Scheme 2

The monomers **8** and **9** (a zwitterionic monomer) would then be subjected to polymerization reaction using different radical initiators in different solvents at different temperatures in order to optimize the yield of the polymers **10** and **11** and their rheological properties. The polymer **10** could be converted to the polymeric zwitterions **11** by acid or base hydrolysis. The effect of the structure of the monomers **8** and **9** may indeed influence the degree of their polymerization. The copolymerization of the monomers **8** and **9** with sulfur dioxide would also be studied (*scheme 3*) to synthesize copolymers **12** and **13**, respectively.



Scheme 3

The effect of salt (NaCl) concentration on the solubility and viscosity of the polymers (**10** - **13**) would be studied. The results of this investigation would indeed pave the way to study the polymerization of the monomers **14** and **15**, with long chain hydrocarbon residue (R), which could have potential application in Enhanced Oil Recovery.²⁰



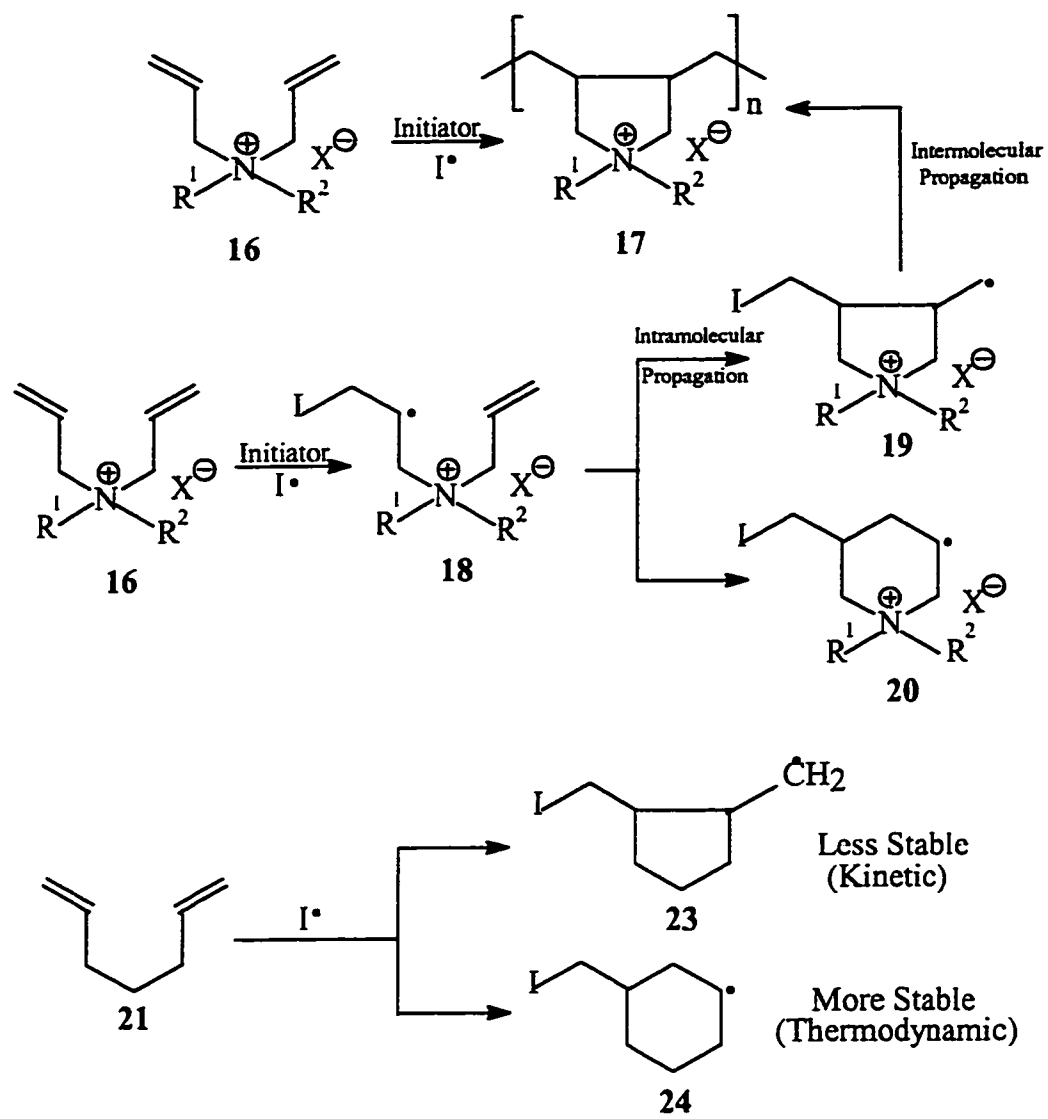
To the best of our knowledge cyclopolymerization of the zwitterionic monomer (amphoteric monomer) of the type **9** and even of **8** (containing a relatively strong acidic hydrogen in the middle of anion stabilizing positive nitrogen and carbonyl group) with sulfur dioxide is not reported to date. As the dissociation of the ionic groups in polyelectrolytes like **3** varies with concentration, meaningful concentration dependent studies in water become difficult. However this complication can be avoided in fully zwitterionic polymers (also called polyampholytes) like **13** and **15** for they are expected to behave as uncharged polymers and show antipolyelectrolyte effects²⁰. It would indeed be interesting to find out their solubility and viscosity behavior especially in presence of added salt (NaCl).

CHAPTER 2

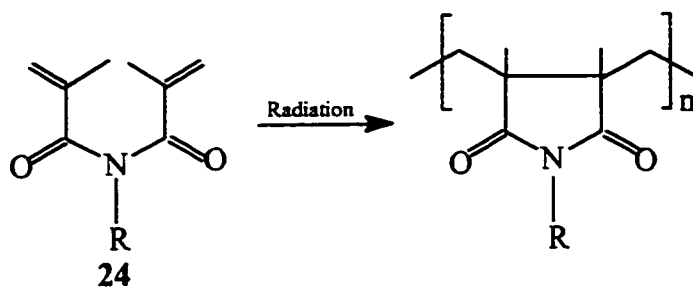
HISTORICAL DEVELOPMENTS

2.1 History of Polymerization of Non-conjugated Dienes

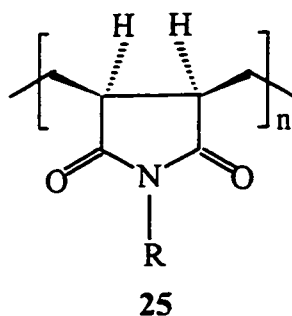
In the early history of polymer science, Staudinger²¹ established a general principle that polymerization of non-conjugated dienes leads to cross-linked, hence insoluble, non-linear polymers or copolymers. However, an exception to this widely accepted principle was observed by Butler² and his coworkers. They found that a variety of diallyl quaternary ammonium salts polymerized to yield soluble, and therefore linear, polymers containing little or no residual unsaturation. To account for these results an alternating intramolecular-intermolecular chain propagation mechanism was proposed. Though, it was evident from the degradation study²² of these polymers that they possess cyclic structure, the size of the ring formed during the intramolecular step was not established. Flory²³ proposed that six-membered structure for radical-initiated cyclopolymerization of 1,6-dienes (symmetrical or unsymmetrical) where predominance of more stable intervening radicals **24** controls vinyl polymerization. However, there are numerous exceptions, especially in the case of diallyl quaternary ammonium salts, where cyclopolymerization do not follow the Flory's theory, but lead to five-membered cyclic structure (17) *via* propagation through less stable intermediate (19) under the conditions of kinetic control.²⁴



Predominant or exclusive formation of five-membered ring is observed in the radiation-induced cyclopolymerization of *N*-substituted dimethacrylamides²⁵⁻²⁷ (24) in the liquid, super liquid and crystalline states.



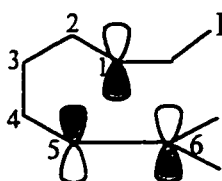
Five-membered rings are also obtained by copolymerization of certain diallylamines and quaternary ammonium salts²⁸, which corresponds to a head-to-head polymerization process. However, when the allyl groups are substituted in the position 2, mixture of both five- and six-membered rings were formed. The polymer 25 has been shown²⁹ by ¹³C NMR study to consist predominantly of five membered ring linked largely in a 3,4-*cis* configuration.



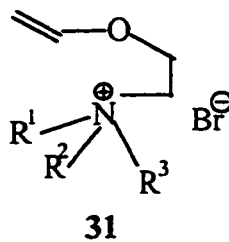
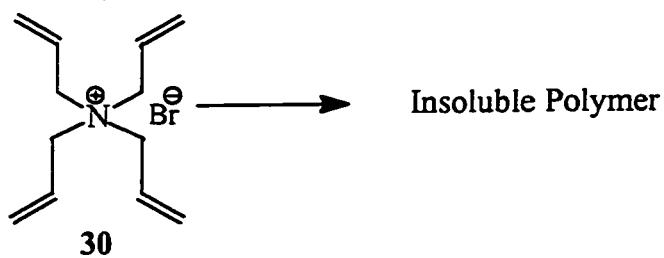
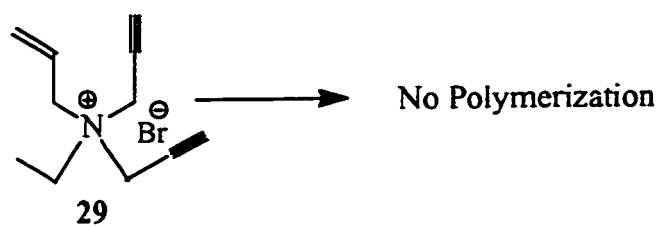
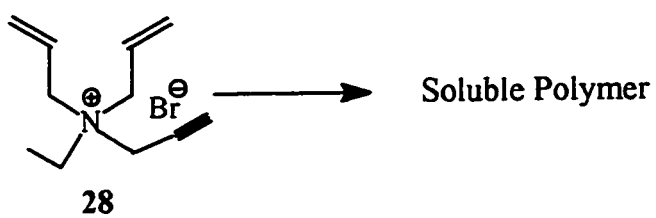
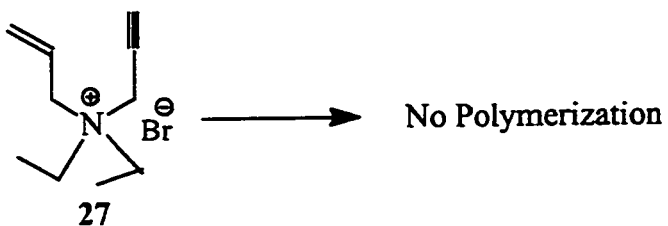
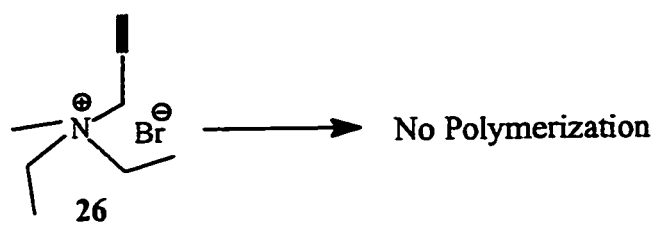
Almost all non-conjugated dienes and other similar structures prefer to undergo cyclopolymerization rather than cross-linking or other modes of propagation². These type of dienes exhibit higher rate of polymerization than their respective monoene counterparts. The cyclization step often leads to less stable ring structure *via* less stable

radical. The high tendency for cyclization has been attributed to a smaller decrease in entropy compared to intermolecular addition.

The explanation for the kinetic preference for the formation of the five-membered ring products is given in terms of stereoelectronic requirements of the transition state for the radical addition reactions³⁰. Maximum overlap of the p orbital with the vacant π^* orbital of the double bond demands the approach of the radical along a vertical line from one of the double bonds. This requirement is met in the 1,5 cyclization but not in 1,6 cyclization. However introducing bulky 5-substituents leads to increasing preference for cyclopolymers with six-membered rings.

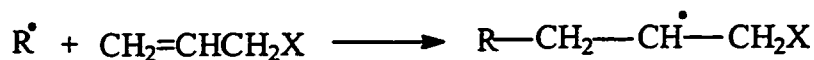
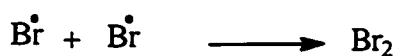


Polymerization studies of unsaturated quaternary ammonium compounds containing propargyl substituents showed that only those compounds **28**, **30** containing two or more allyl groups produced polymer and that the propargyl groups did not enter into the polymerization process. The unsaturated quaternary ammonium bromides **31** yield¹² water soluble polymers, from those compounds containing only two allyl groups in addition to the β -vinyloxyethyl group and water insoluble cross-linked polymers from those compounds having three allyl groups in addition to a β -vinyloxyethyl group. It was found that the β -vinyloxyethyl group did not enter into the polymerization under the conditions used.

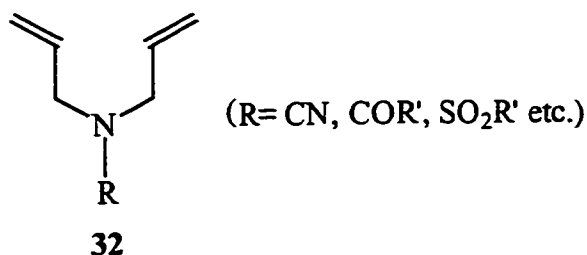


Butler's work showed that the chloride anion form of diallyl quaternary ammonium monomers gave polymers of significantly higher intrinsic viscosity than the bromide salts. The effects of some of the experimental variables such as catalyst ratio, monomer concentration and impurities were summarized by Booth et al⁴. Polymers with better rheological properties were obtained using ammonium persulfate as catalyst in water containing 200 ppm of Na₄EDTA (tetra-sodium ethylenediaminetetraacetate). It is assumed that Na₄EDTA acts as a chelator in removing trace metals which may otherwise act as chain transfer agent. Ammonium persulfate was found to be a much better initiator than azobisisobutyronitrile and t-butylhydroperoxide. Diallyl quaternary ammonium chlorides, bromides and *N*-alkyldiallylamine hydrochlorides were polymerized³¹ with using ammonium persulfate in dimethyl sulfoxide.

It is known that allyl compounds do not yield high molecular weight polymers due to depropagation and chain transfer reactions involving hydrogen abstraction from allylic position. Limiting viscosity numbers in aqueous NaCl demonstrated the high molecular weights of these polymers. Bromide ion is probably oxidized more easily by persulfate to generate bromine which can then inhibit polymerization both by the consumption of starting radical and by termination of growing chain.

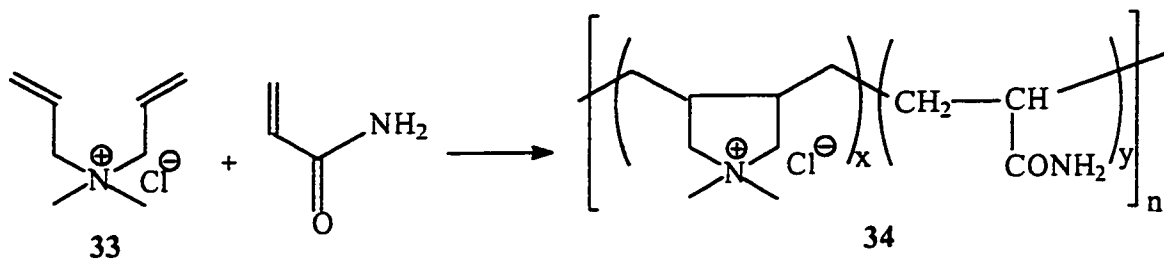


Generally diallylamines do not polymerize readily on free-radical initiation, their corresponding protonated or quaternary salts undergo polymerization. Electrophilic N-substituents in diallylamines **32** are known to activate the monomers towards radical attack³².

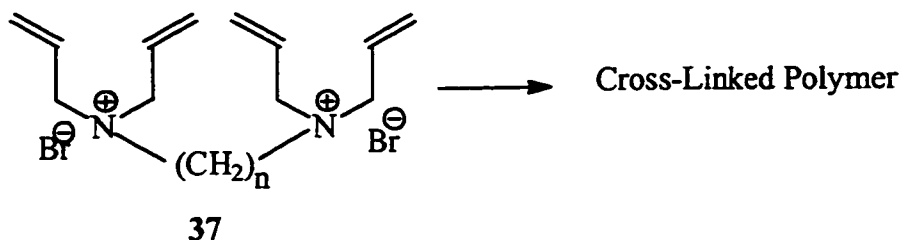
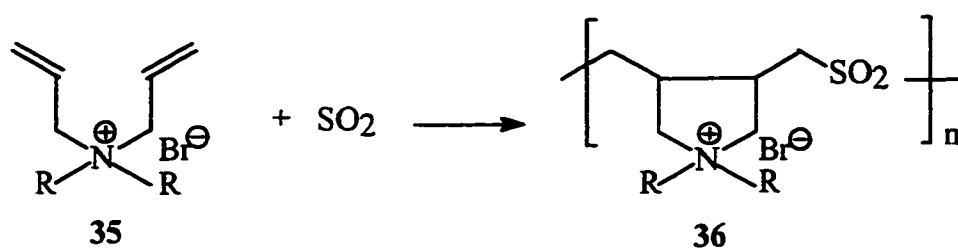


2.2 Copolymerization in Non-conjugated Dienes

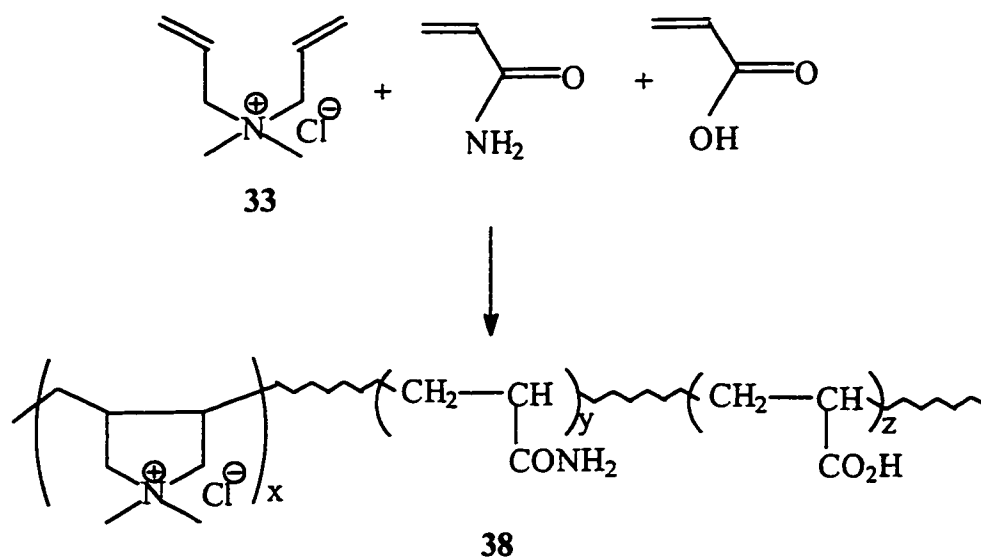
It is reported³³ that dimethyldiallylammonium chloride **33** undergoes copolymerization with acrylamide to give the polymer **34**.



Alternating copolymers (**36**) are obtained on cyclopolymerization of diallyl compounds **35** with sulfur dioxide^{34,15} in different solvents with free radical initiators as ammonium persulfate, ammonium nitrate, azobisisobutyronitrile, t-butylhydroperoxide, dilauroyl peroxide.

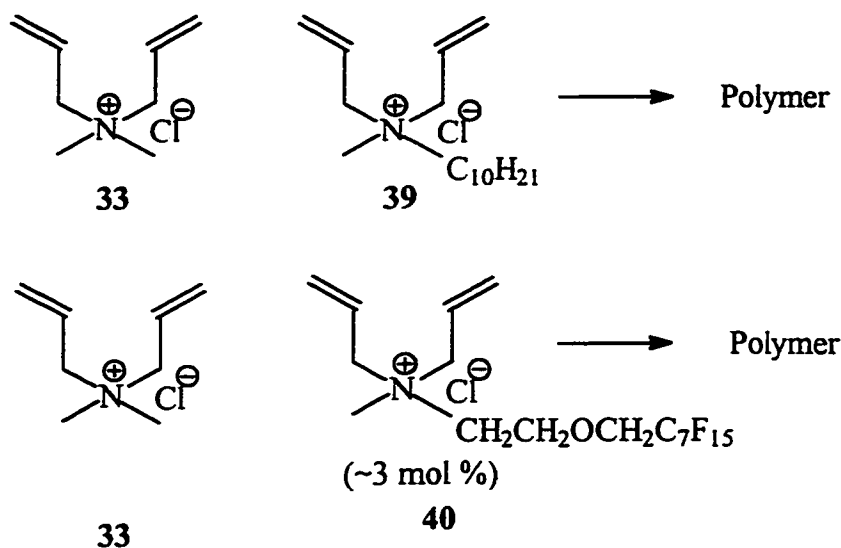


Ion-exchange resins were obtained by the polymerization of the tetraallyl derivatives **37** of 1,n-diaminoalkanes³⁵⁻³⁷. Polyelectrolytes have also been synthesized by terpolymerizing dimethyldiallylammonium chloride with acrylamide and acrylic acid³⁸. These polymers (**38**) are used as dry strengths resins in paper³⁹.

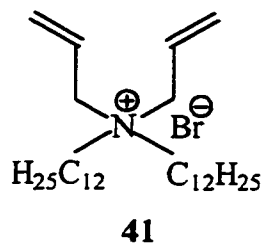


Hydrophobically associating ionic copolymers^{18,40,41} of diallyldimethylammonium chloride **33** with 1-4 mol% of diallyl decylmethylammonium chloride **39** and methyldiallyl-(1,1-dihydropentadecafluorooctaoxyethyl)-ammonium chloride **40** are

synthesized and the copolymer showed significant increases in the viscosity compared to poly(diallyldimethylammonium chloride).



Cyclopolymerization of diallyldodecylammonium bromide **41** for vesicle formation is also reported^{42,43}.



Amphiphilic cyclopolymerization⁴⁴ of diallyldimethylammonium chloride and diallylalkoxybenzylmethylammonium chloride was studied by free radical polymerization in aqueous solution. It was observed that addition of sodium dodecyl sulfate (SDS), below the critical micelle concentration, to the copolymer solution results in a large increase in the viscosity of the polyelectrolyte.

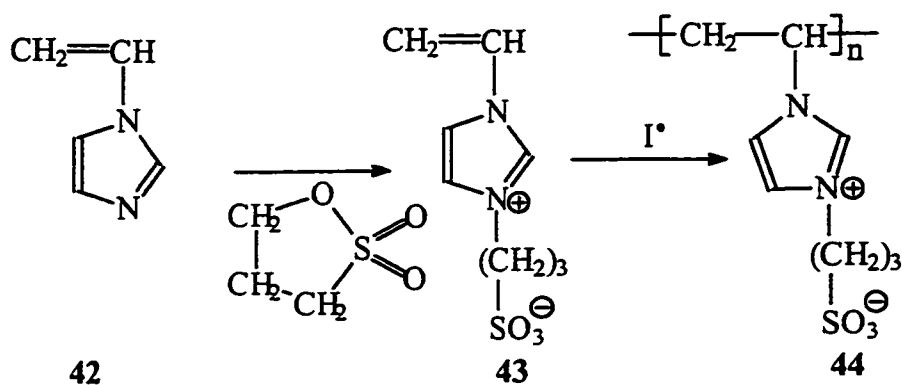
A review and use analysis of poly(dialkyldiallylammonium halides) has been published³. A variety of commercial products have been developed using

cyclopolymerization of these quaternary salts. Poly(dimethyldiallylammonium chloride) is the first polymer in this series to be manufactured by a number of suppliers. It poses optimum functional properties for application to electrographic paper reproduction processes¹. These polymers have also found its application as paper additives. In the water treatment field these polymers are used as flocculants, and coagulant aid in potable water, waste water, coal floatation, foam floatation of metal sulfides, etc. It is also used in the zinc, tin and lead electroplating industries, cosmetic field, as a de-emulsifier of dispersed oils, as a biocide in water, and as a detergent additive.

The copolymers of these quaternary salts with sulfur dioxide¹⁵ have similar industrial uses. Tetraallyl diammonium dichloride salts give ion-exchangers of both superior rate and capacity for use in extraction of uranium¹⁶. Polytriallylamine⁴⁵ is reported to be a thermally regenerated ion exchange process¹⁷ for the cheap removal of salinity from brackish waters. Diallylamine hydrochloride with a suitable crosslinker is reported to give super anion exchanger. Cyclopolymerization of suitable salts have also resulted in the formation of strongly basic ion exchange resins^{35,37}. The hydrophobically associating copolymers may have potential application in enhanced oil recovery and other applications where viscofication of water is of interest.

There has been considerable academic and industrial interest in the preparations of new ionic polymers^{46,5}. These studies included the areas of cationic and anionic polyelectrolytes, since both classes have unique chemical and physical properties. Polyelectrolytes are generally prepared from free radical (homo- and co-) polymerization of an ionic monomer or neutral monomer. In the latter case the subsequent reaction on the preformed neutral polymer leads to ionic polymers. However the first case offers greater

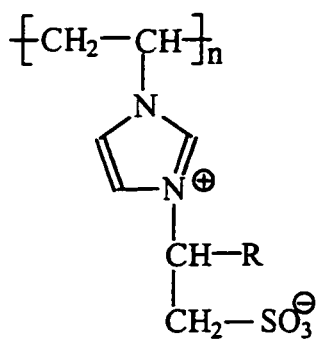
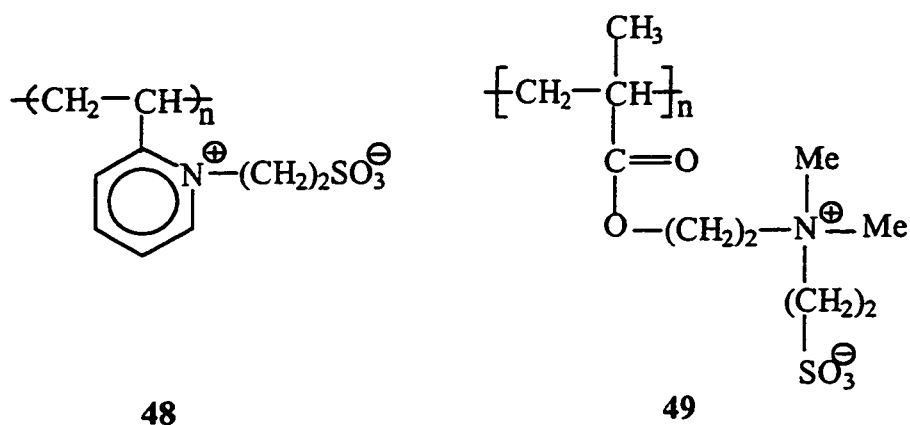
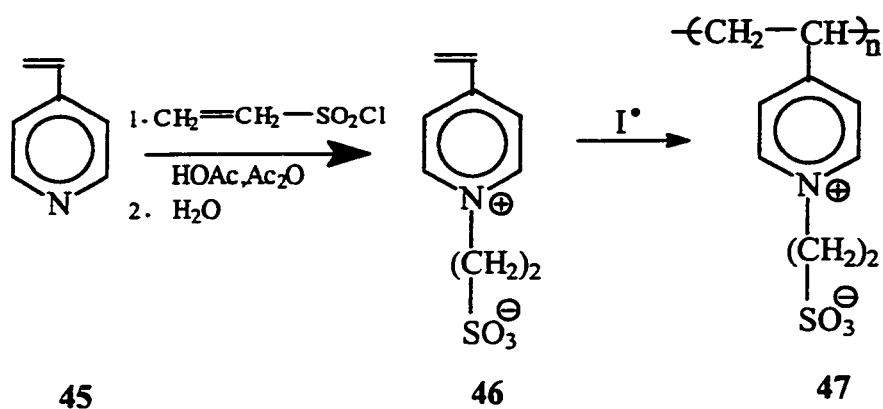
advantage in controlling over the structure and properties of the final polyelectrolyte. The second case is more difficult to control as the amount of charge becomes greater and greater during conversion of a neutral polymer to one of high charge density and as such most reactions rarely go to completion. Ampholytic (zwitterionic) polymers are either formed from polymerization of inner salt (zwitterionic) monomer or from preformed neutral polymer. 2-vinylimidazole has been quaternarized with 1,3-propanesultone to give inner salt **43** which on free radical polymerization yielded the polyampholytic homopolymer **44**⁴⁷.



The polyampholytes have been shown to show unusual properties in aqueous solution^{48,49}. The polymers are insoluble in water and have hydrogel characteristics. However, the polymers could be dissolved in certain aqueous salt solutions. The solution properties are found to depend on the type and concentration of the salt added. In contrast to polyelectrolytes, the reduced viscosities of polyampholytes increases with increased salt concentration. The greater the site binding ability of either the cation or anion, the greater the reduced viscosity.⁴⁹

For the solubilization of polyampholytes by aqueous salt solution, the cations and anions of low molecular weight electrolytes could be considered to enter ionically crosslinked network of the polymer through osmotic forces⁴⁷. These forces cause the polymer to swell when placed in water. The insolubility of polyampholytes in water is attributed to the fact that the osmotic force which tends to draw solvent into the polymer is not sufficient to rupture the ionic crosslinks. Polyampholyte swells until the osmotic forces are balanced by elastic forces of the network. In the presence of added salt (say NaCl) the solvent (H₂O) along with the mobile ions is drawn into the polymer, and the polymer swells as usual. However the mobile ions of the added salt neutralizes a portion of the ionic crosslinks resulting in the continual decrease of the elastic forces which tend to oppose the continued swelling. As a result the polymer swells until the gel finally dissolves.

One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the drastic decrease of the viscosity of their aqueous solutions in presence of added salt (say NaCl etc)⁵⁰. However zwitterionic polymers show "antipolyelectrolyte behaviour"⁵¹ and have low or no solubility in water but greatly enhanced solubility and extensive chain expansion, hence viscosification, upon increasing added salt concentration. A disadvantage in all reported synthesis of polyvinylsulphobetains is the use of sultones, which are carcinogenic compounds⁵². Another disadvantage is that only propane- and butane- sultones are known to yield ampholytic monomer. In order to circumvent the problem the following monomer **46** was synthesized using alkenylsulfonylchlorides⁵³. The monomer on free radical polymerization



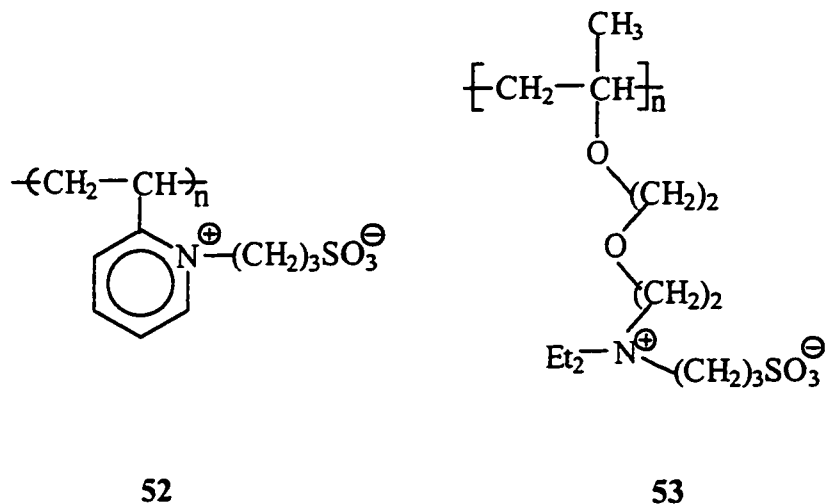
50 R = H

51 R = Me

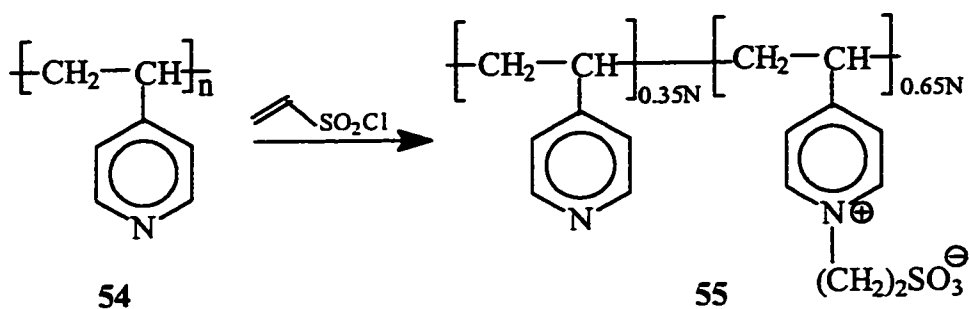
afforded the polyampholyte 47. Likewise, the polyampholytes 48-51 were synthesized. As anticipated the polyampholytes 47-50 are insoluble in water but readily dissolves in aqueous solution of NaCl. Such behaviour has been interpreted^{51,54} by assuming the

presence of a collapsed coil in water due to intrasalt and intrachain interactions. Such interactions are broken up in presence of added low molecular weight electrolytes. While the polyampholyte **50** was found to be insoluble, the polymer **51** readily dissolves in water. The presence of bulky groups near the quaternary centre effectively diminishes the effectiveness of the intrasalt and intrachain interactions. Structural modifications thus effect the delicate balance between intramolecular interactions and hydration. The temperature and molecular weight have also been shown to govern the solubility of polyampholytes⁵¹.

Upto 1987 two other polysulphobetains **52** and **53** are known⁵⁵ to be soluble in water. Their solubility was again attributed to the presence of bulky groups near the quaternary nitrogen centre.



Attempts⁵³ to quaternize the polymer **54** was possible only to the extent of 65%.

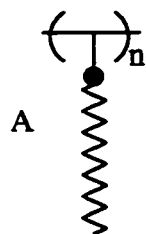


Synthesis and bulk properties of several polyzwitterionic surfactants have been reported^{56,57}. The solubility of these polymers are correlated with their molecular geometry.

Molecular architecture of polyampholytic surfactants (polysoaps) envisages three main type of structures. In structure 56 the charge centres remain close to the polymeric backbone and is called “head-attached” type. The structure 58 represents polymers of the “tail-end” type where the hydrophobic tail is attached to the backbone. Structure 57 represents polyampholyte of the “mid tail-attached” type. Polymer 59 is found to be soluble in formamide and water but insoluble in ethanol. The polymer 60 is soluble in formamide but insoluble in water and ethanol. The polymer 61 however is found to be insoluble in water and formamide but soluble in ethanol. The tail-end attached type polymers as represented by 59 is found to be soluble in water. It was noted that the solubility of these polymers in water is improved by adding salt as expected.

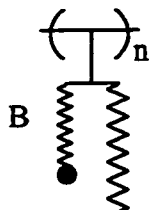
Obviously, the solubility characteristic is mainly controlled by the skin of the polymers exposed to the solvent. Thus ionic/zwitterionic skins require polar solvents and hydrocarbon skins require less polar solvents. In agreement with this the polymer 60 which represents the mid-tail attached type exhibits an intermediate solubility behaviour. These fully zwitterionic polymeric surfactants represent an unconventional but interesting

Hydrophilic head Hydrophobic tail



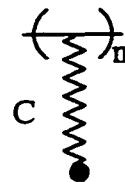
Back bone "head-attached"

56



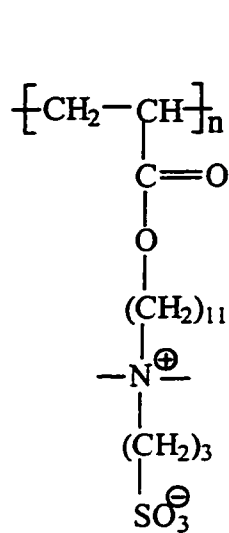
Back bone "mid tail-attached"

57

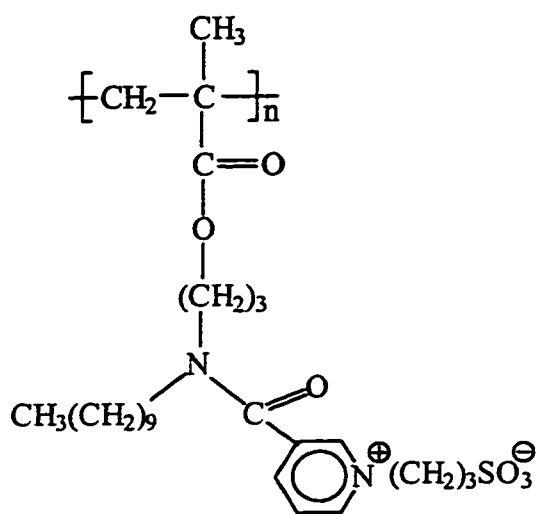


Back bone "tail end-attached"

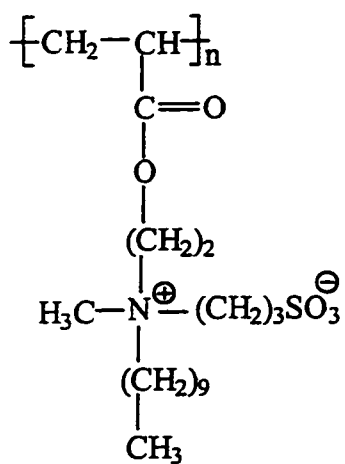
58



59



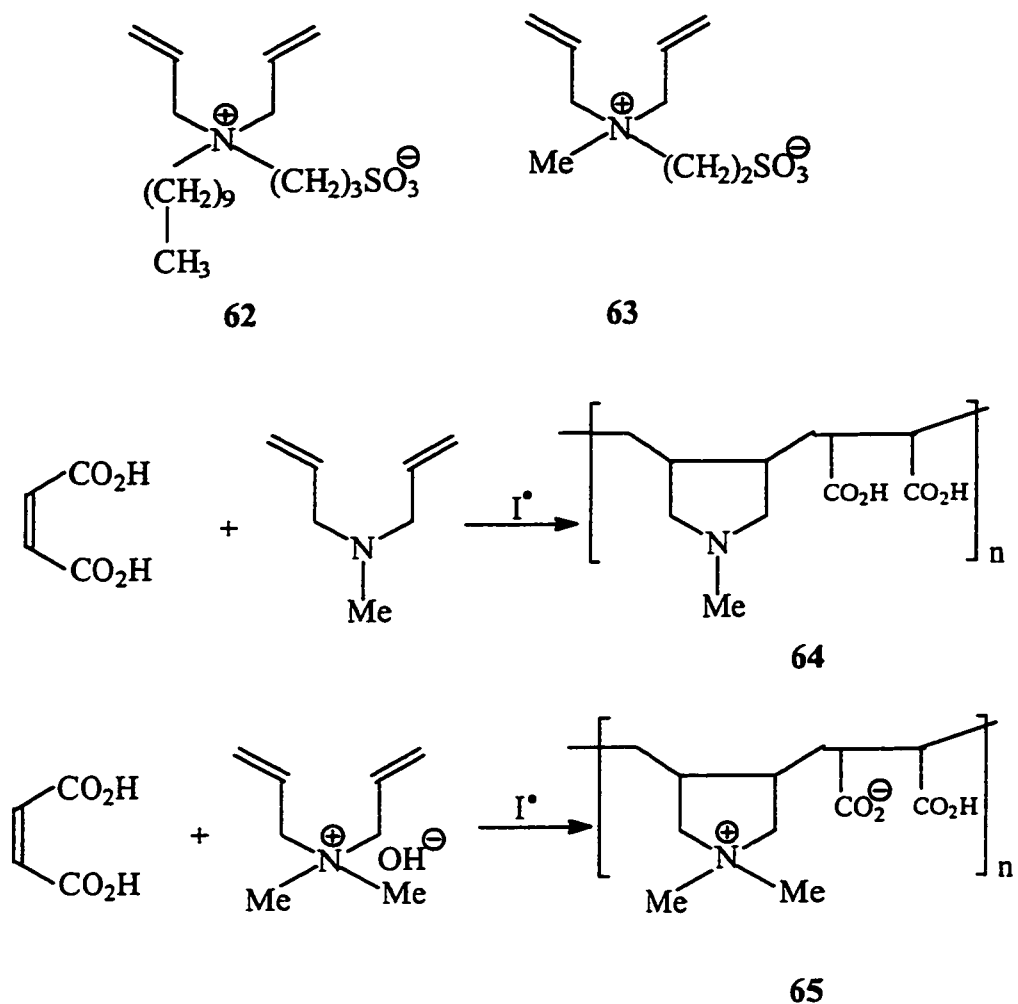
60



61

type of micellar polymers (polysoaps). They combine advantageously the behaviour of ionic and non-ionic polysoaps.

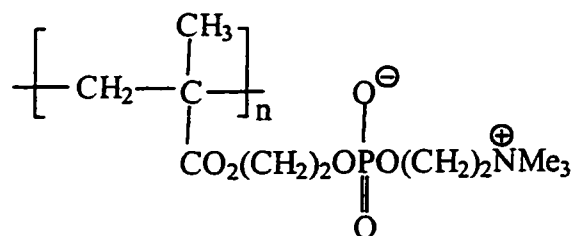
There are only a few mentions in literature of polyampholytes derived from *N,N*-Diallyl quaternary ammonium monomers. Zwitterionic polysoaps are prepared by radical homopolymerization of the monomer 62.



While the homopolymer of the sulfobetaine 63 has been reported in the literature⁵³, the solution properties of the polyampholyte has not been described.

Alternating ampholytic copolymers of maleic acid with allylamine, diallylamine, methyldiallylamine and diallyl quaternary ammonium salt were synthesized by free radical polymerization⁵⁸ (to give for example the copolymers 64, 65 etc.). The copolymers are characterized by viscometry, potentiometry and turbidimetry and their properties are found to depend on pH and ionic strength of the aqueous solutions of the polymers. The influence of the cationic units on solution properties of the polyampholytes is discussed from the aspect of zwitterion formation. It was found that the viscosity of the polymers (e.g. 65) decreases with increasing concentration of added NaCl, a marked contrast to the behaviour observed in case of usual polyampholytes.

pH and ionic strength (I) dependence of the intrinsic viscosity of betain-type polyampholyte (66) have been investigated recently⁵⁹.



66

The linear relationship between $1/\sqrt{I}$ and $[\eta]$ for ordinary polyelectrolyte was also observed for the polyampholyte at low ionic strength, I, near isoionic pH (3.35) and over a wide range of I at other pH. At high I and at pH 4 on the other hand, a reverse tendency is observed i.e. viscosity increases with increasing I, suggesting the release of attracting interactions between different charges with the increase of I. The polyampholyte behaves as a polyelectrolyte when positive charges are excessively populated in the molecule (pH=1.0) and also even when a slight amount of net charges exists in the molecule as long

as the magnitude of I is sufficiently low. Near the isoelectric point, where the net charge in the molecule reduces to null, the intramolecular attraction between oppositely-charged groups on the chain is expected to make the polyampholyte tightly coiled^{60,61} in salt free condition and to be expanded with increasing ionic strength I .

The drag reduction efficiency of several well-characterized water-soluble polyampholytes has been studied⁶². Polyampholytes can reduce the energy loss due to friction in turbulent flow. Polymer molecules interact with vortices that are formed in turbulent flow and dissipate energy necessary for the vortices to grow and thus reduces turbulence.

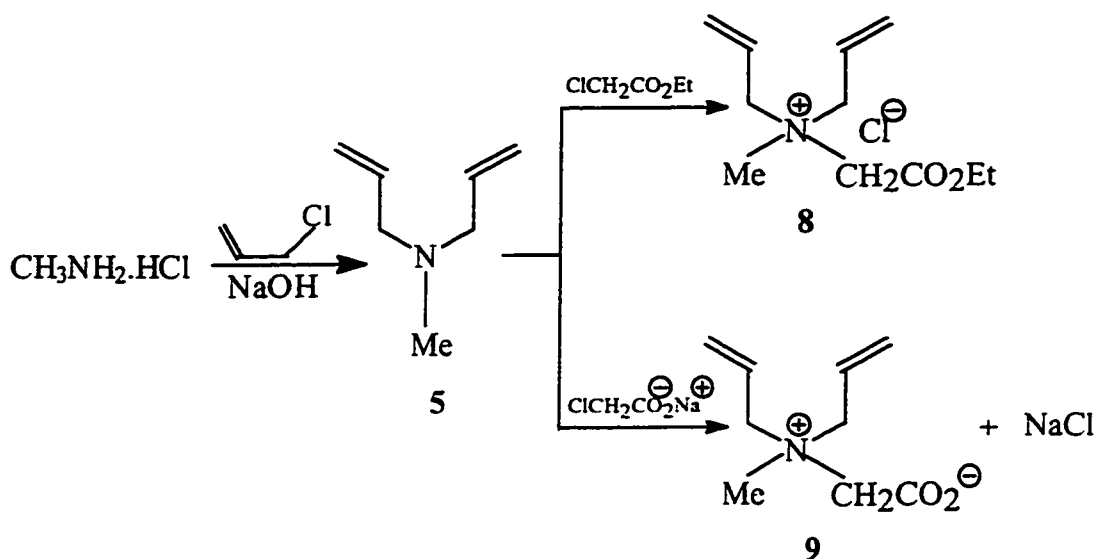
Polyampholytes have found applications⁶³ in biosensors and in amphoteric buffer for electrophoresis. Polyampholytes can also serve as a simple model⁶⁴⁻⁶⁶ for understanding the complex behaviour of random copolymer such as proteins. Preparation of novel biodegradable polyampholyte from partially dicarboxylated chitosan has been reported.⁶⁷ Complexation behaviour of proteins with polyampholytes using turbidimetric titration has been investigated.⁶⁸ Acrylic polyampholytes have been used for protein separations.⁶⁹ Recent⁷⁰ study also include the thermodynamic investigation of the sorption of Fe^{3+} and Cu^{2+} ions by a fibrous polyampholyte.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of Monomer

Methylamine was converted into *N,N*-Diallyl *N*-Methylamine (**5**) by reacting with 2 equivalent of allyl chloride as shown in the Scheme 4.



Scheme 4

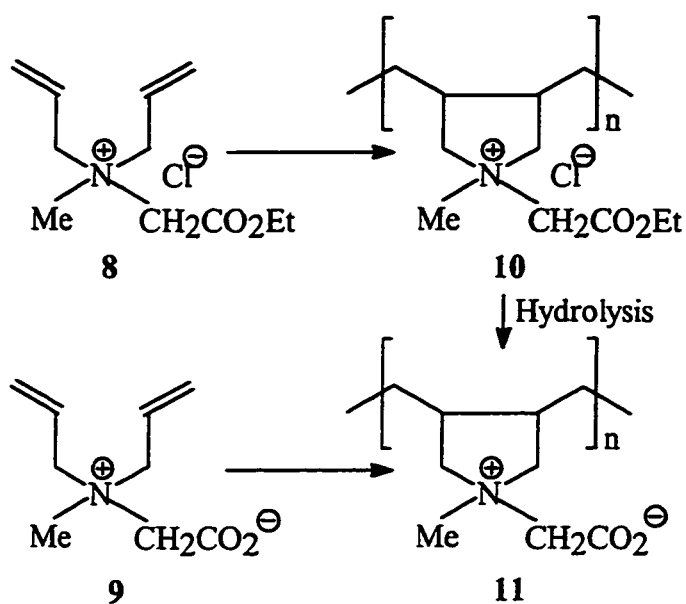
The amine on treatment with ethyl chloroacetate at room temperature afforded the quaternary ammonium salt (**8**) in almost quantitative yield. It is a crystalline solid and found to be very hygroscopic. The monomer was found to be soluble in methanol, acetone and water. The IR spectra revealed the absorption at 1744 cm^{-1} indicating the presence of ester functionality. Strong peak at 3442 cm^{-1} indicates OH absorption due to hygroscopic

nature of monomer. The IR spectrum is shown in Figure 1. The ^1H NMR spectrum of the monomer is shown in Figure 2 which confirms the structure of the monomer.

At this stage, we did not plan to synthesize the corresponding zwitterionic monomer (9). The monomer (9) can well be prepared by reacting the amine (5) with sodium chloroacetate in aqueous or methanol solvents (Scheme 4). However, the reaction would also generate an equivalent amount of sodium chloride, since both of them are expected to be soluble in the same solvent (water), their separation would indeed pose a problem. Sometimes presence of sodium chloride as impurity in the monomer may create problem in the subsequent polymerization reaction.

3.2 Synthesis and Characterization of Homopolymer (10)

While the polymerization of the zwitterion would provide the polyampholyte directly, the electrolyte monomer (8) on the other hand would lead to polyelectrolyte which then has to be hydrolyzed to the polyampholyte (Scheme 5).



Scheme 5

We realized the problem that it may indeed be a difficult task to hydrolyze (10) to (11), since progressive hydrolysis will add increasing amount of negative charge on the polymeric chain. However, presence of positive centre at nitrogen will reduce the negative charge density by formation of intrasalt and it is conceivable that hydrolysis can be forwarded toward near completion.

With this in mind the monomer (8) was subjected to polymerization in water (monomer concentration 70% w/w) using tertiary butyl hydroperoxide as initiator at 75°C using procedure⁷² as described by Butler for the polymerization of diallyl dimethyl ammonium chloride. However we were unable to get even a trace of polymer using the above procedure. The above reaction was repeated under similar conditions using different initiators such as benzoyl peroxide, hydrogen peroxide, metachloroperbenzoic acid, however no polymerization product was obtained in each of the above cases. However, to our delight, the polymerization reaction went smoothly by using ammonium persulfate as

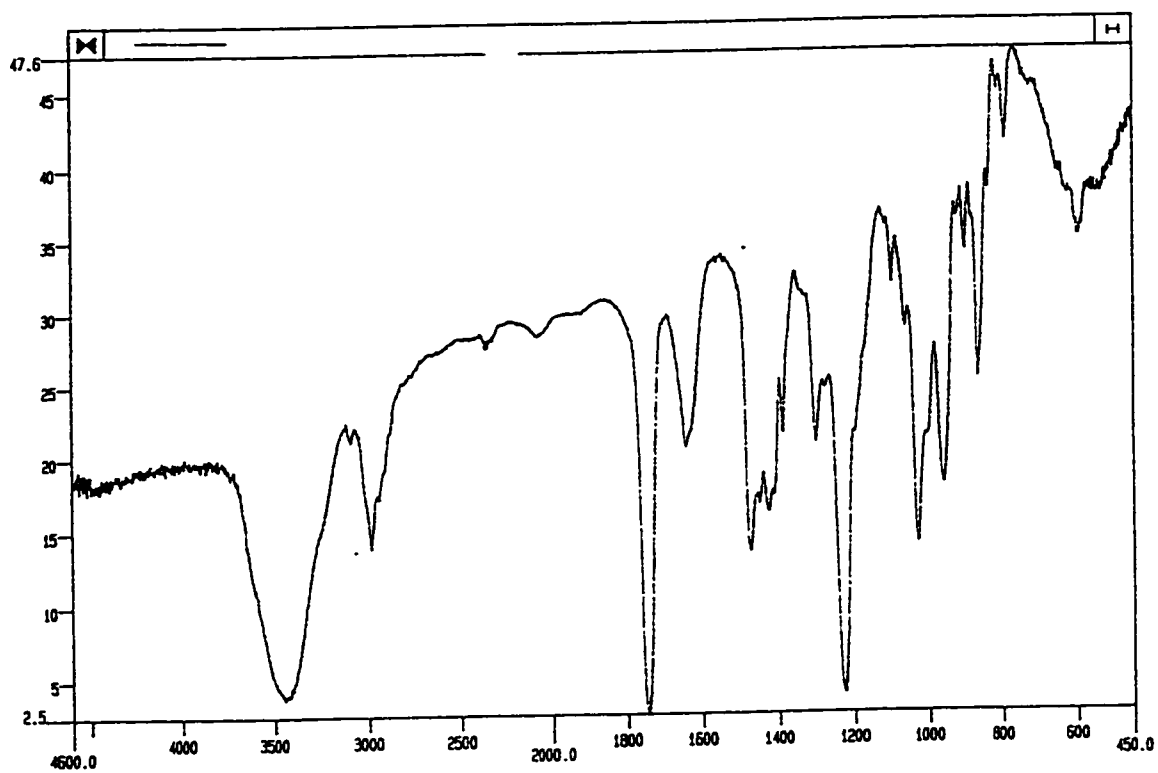


Figure 1 FTIR Spectrum of monomer 8

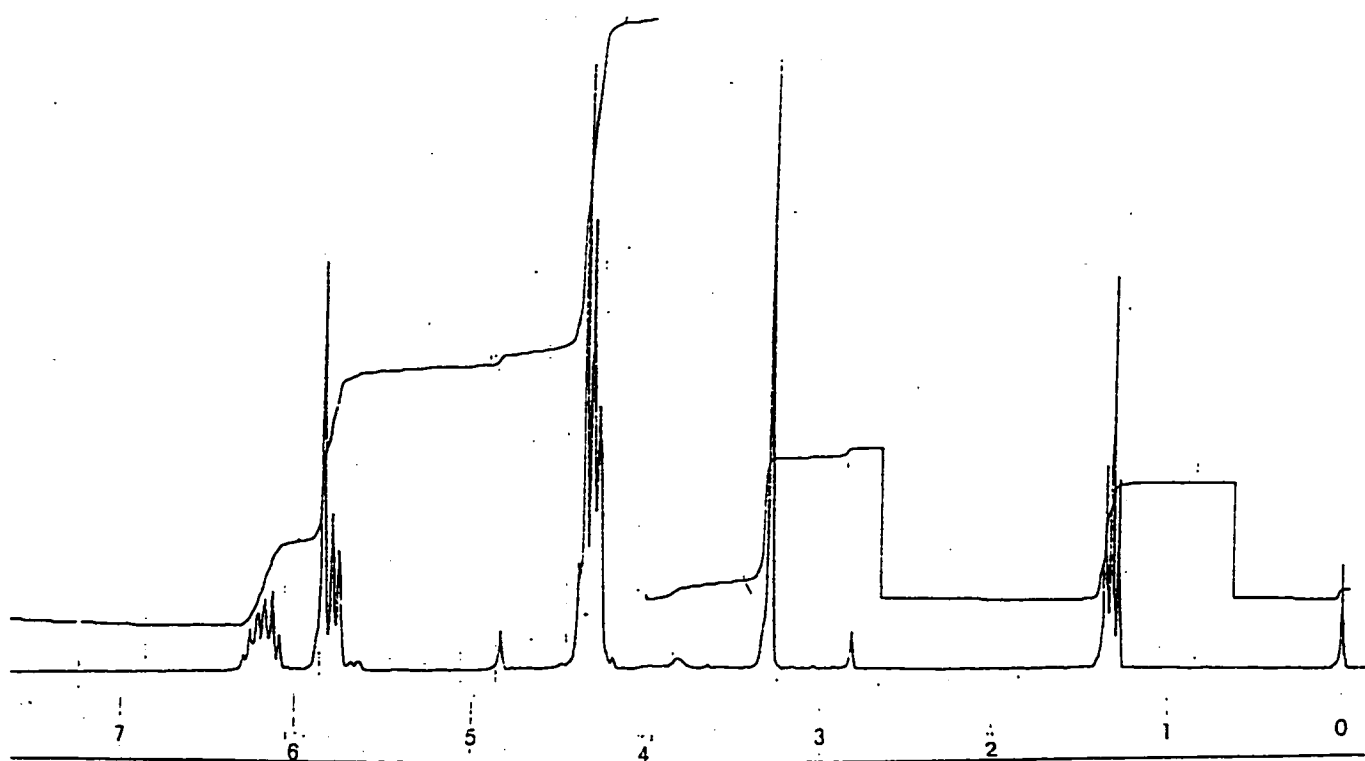
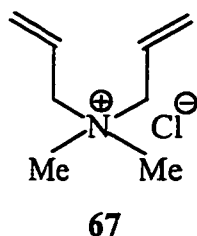


Figure 2 ^1H NMR Spectrum of monomer 8 in D_2O

the initiator. The results of the polymerization under various conditions are given in Table 1. Ammonium persulfate was added to the monomer solution at 80°C and the solution was magnetically stirred at 90°C for 1 hour. As is evident from the table 1, by comparing entry no. 1, 3, 5, 6 and 7, highest yield and intrinsic viscosity is obtained for the polymerization reaction under entry no. 3 with a monomer concentration of 70% (w/w).

Booth et. al.⁴ investigated the factors affecting the cyclopolymerization of dimethyldiallylammonium chloride (67) and reported that polymers with the highest solution viscosity and residual monomer contents were obtained from a 65% monomer solution in water by using ammonium persulfate as initiator at 80-90°C.



The effect of concentration of initiator is represented by entry no. 2, 3 and 4. The result reveal that 15 mg of initiator (APS) per gram of monomer gives the polymer with the highest intrinsic viscosity. Entry no. 8 and 9 display the effect of solvent on polymerization reaction. Using DMSO as solvent, the viscosity or the yield of the polymer were not improved.

The polyelectrolyte (10) was found to be very soluble in water and methanol but insoluble in acetone. The pH of 1% solution of polyelectrolyte (10) was found to be 2.71. The IR and ¹H NMR spectrum of the polymer (10) are displayed in Figure 3 and Figure 4, respectively. Absorption at 1748 cm⁻¹ indicates the presence of ester group. Strong absorption at 3454 cm⁻¹ indicates the hygroscopic nature of homopolymer. The NMR

Table 1: Effect of Solvents, Concentration of Monomer, Initiator (Ammonium persulfate, APS) on Polymerization^a

Entry No.	Monomer Conc. (%W/W)	APS mg/g monomer	Solvent	Temp. °C	Yield (%)	Intrinsic ^b Viscosity dl/g
1	60	15	A	90	35	0.216
2	70	10	A	90	65	0.451
3	70	15	A	90	78	0.555
4	70	20	A	90	63	0.330
5	80	15	A	90	50	0.409
6	90	15	A	90	38	0.416
7	100	15	A	90	~0	---
8	36	15	B	50	38	0.291
9	36	20	B	50	30	0.374

^a Polymerization time: in solvent A (H₂O) 1 hour; in B (DMSO) 20 hour.

^b Viscosity of 1.0-0.0625% polymer solution in 0.1N NaCl at 30°C was measured in Ubbelohde Viscometer (K=0.005989).

spectrum indicates the absence of olefinic protons (unsaturation). The ^{13}C NMR spectrum of the polymer is displayed in Figure 5.

The homopolymers are hygroscopic solids melted in the range of 355-370°C and the colour changed to faint yellow. The differential thermal analysis and thermal gravimetric analysis of a homopolymer sample (Entry No.3, Table 1) are shown in Figure 6.

Viscosity data for the homopolymer (Entry No.3, Table 1) is presented in Figure 7. The plot is typical for polyelectrolyte in general unlike the behaviour of uncharged linear polymers. The reduced viscosity η_{sp}/C Vs. concentration (C) of the quaternary ammonium polymer are strongly concave upwards. This could be attributed to the dissociation of the ionic bond in the solution. As the concentration of the polyelectrolyte decreases the degree of ionization increases and some of the chloride ions leave away the region of the positively charged backbone. This leads to large repulsive force between the positively charged nitrogen remaining in the chain. Usually the counterion hang around in the vicinity of the polyelectrolyte to screen the repulsive electrostatic interactions of the charges on the polymer. However at strong dilution the counterions move around the entire volume to gain entropy leaving the charged polymer chain in an almost neutral environment. The unscreened Coulomb interactions lead to increased hydrodynamic volume hence increased reduced viscosity. At high concentrations, due to reduced degree of ionization, the polymers are not appreciably expanded.

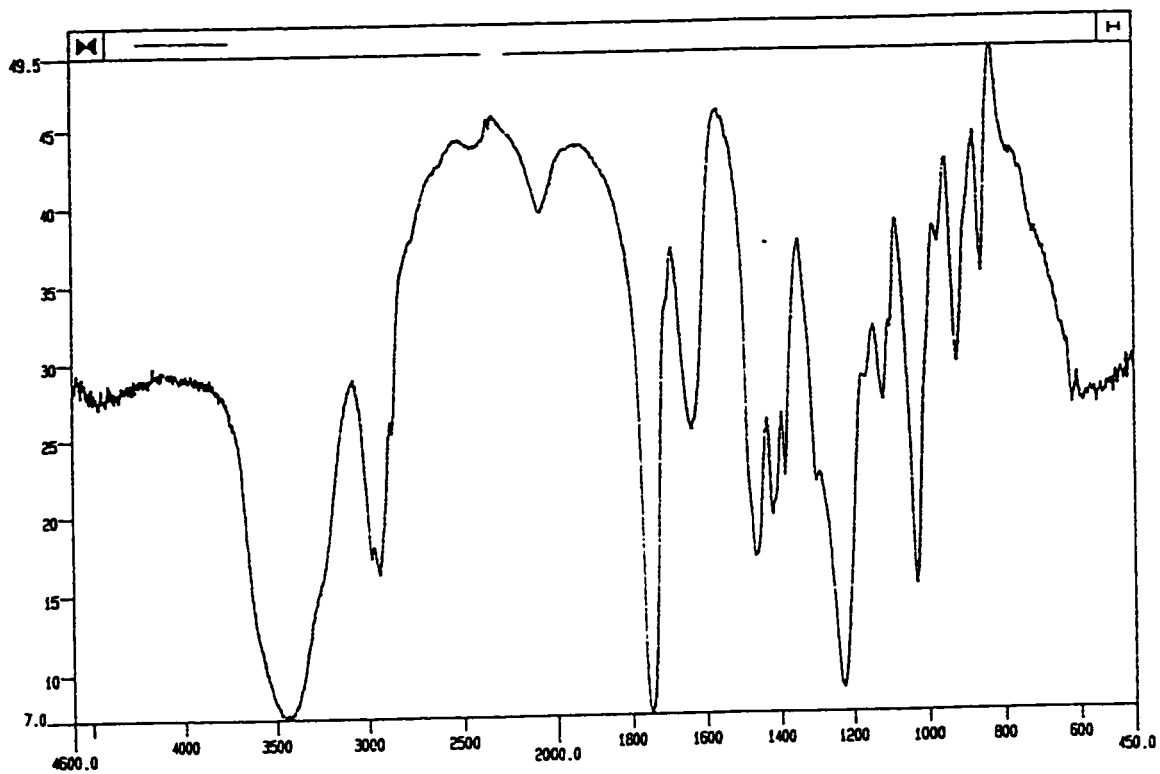


Figure 3 FTIR Spectrum of homopolymer 10

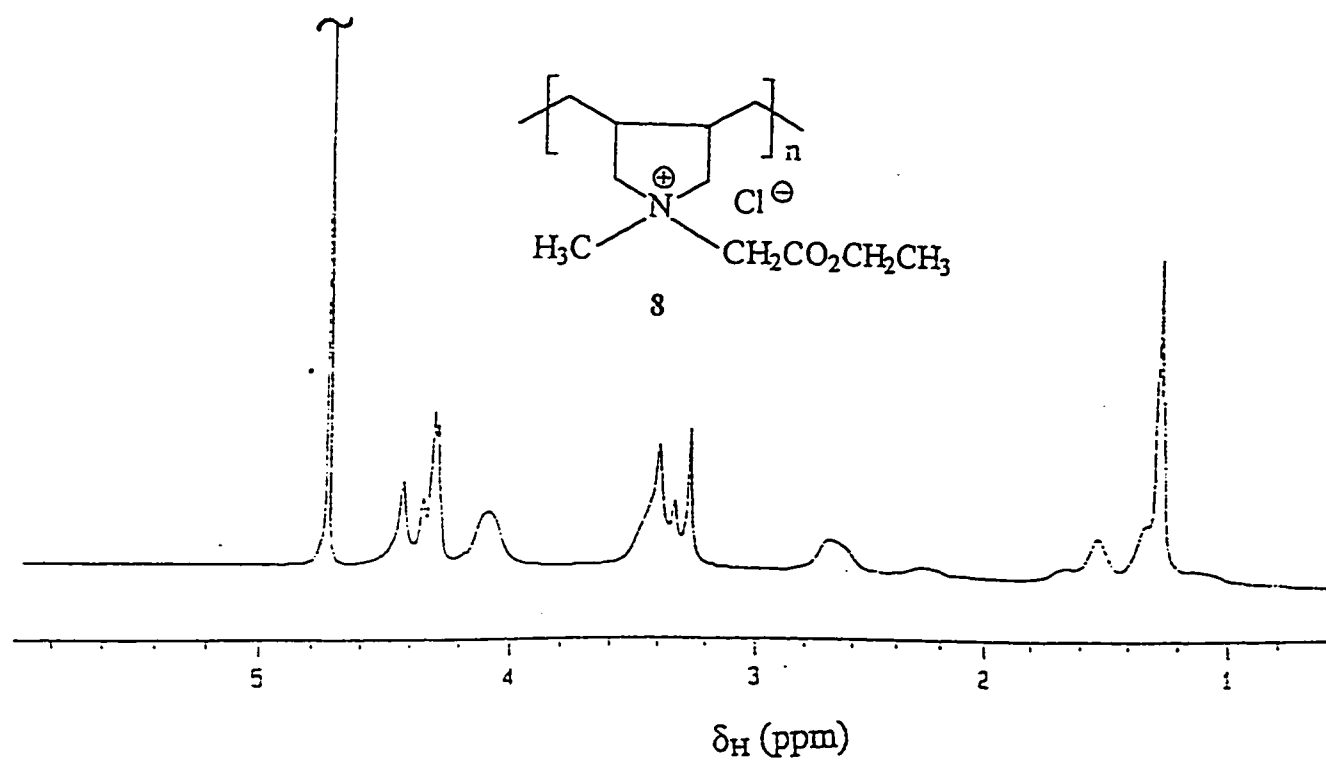


Figure 4 ^1H NMR Spectrum of homopolymer 10 in D_2O

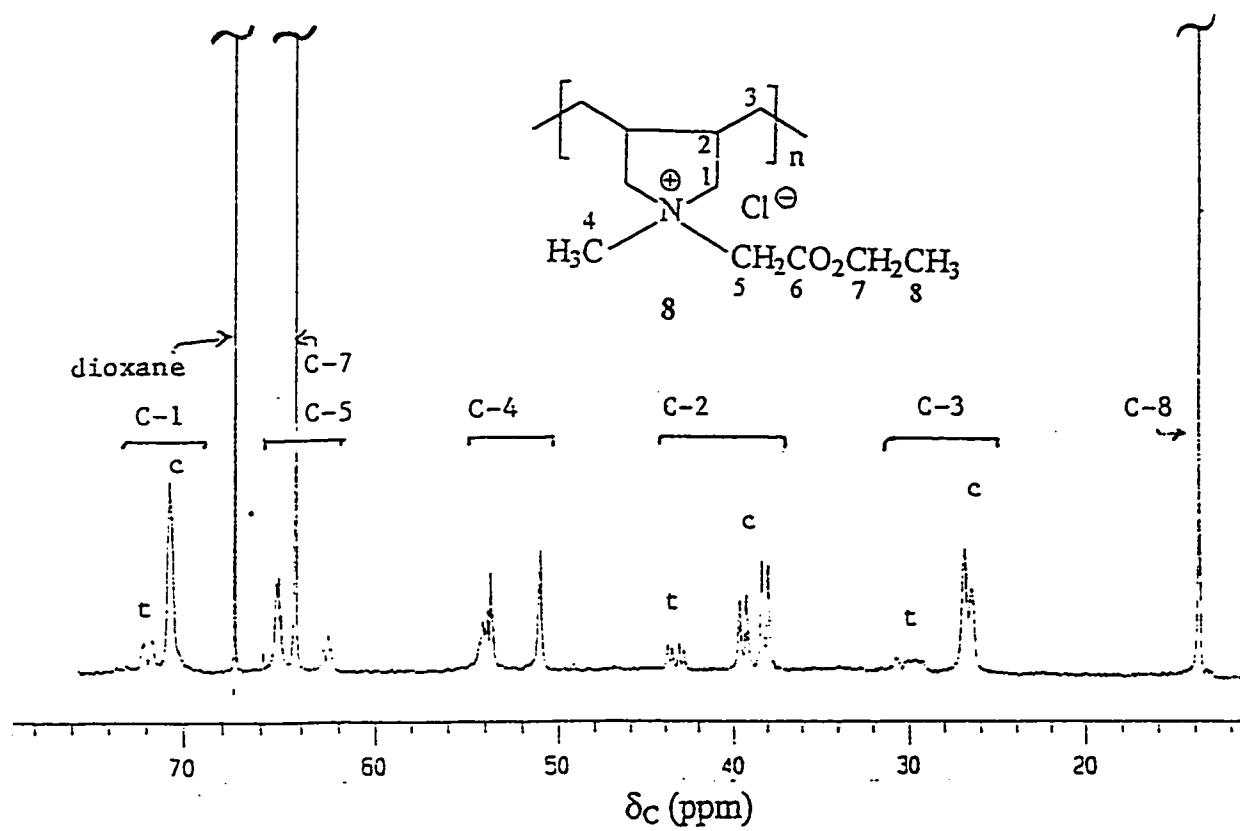


Figure 5 ^{13}C NMR Spectrum of homopolymer 10 in D_2O

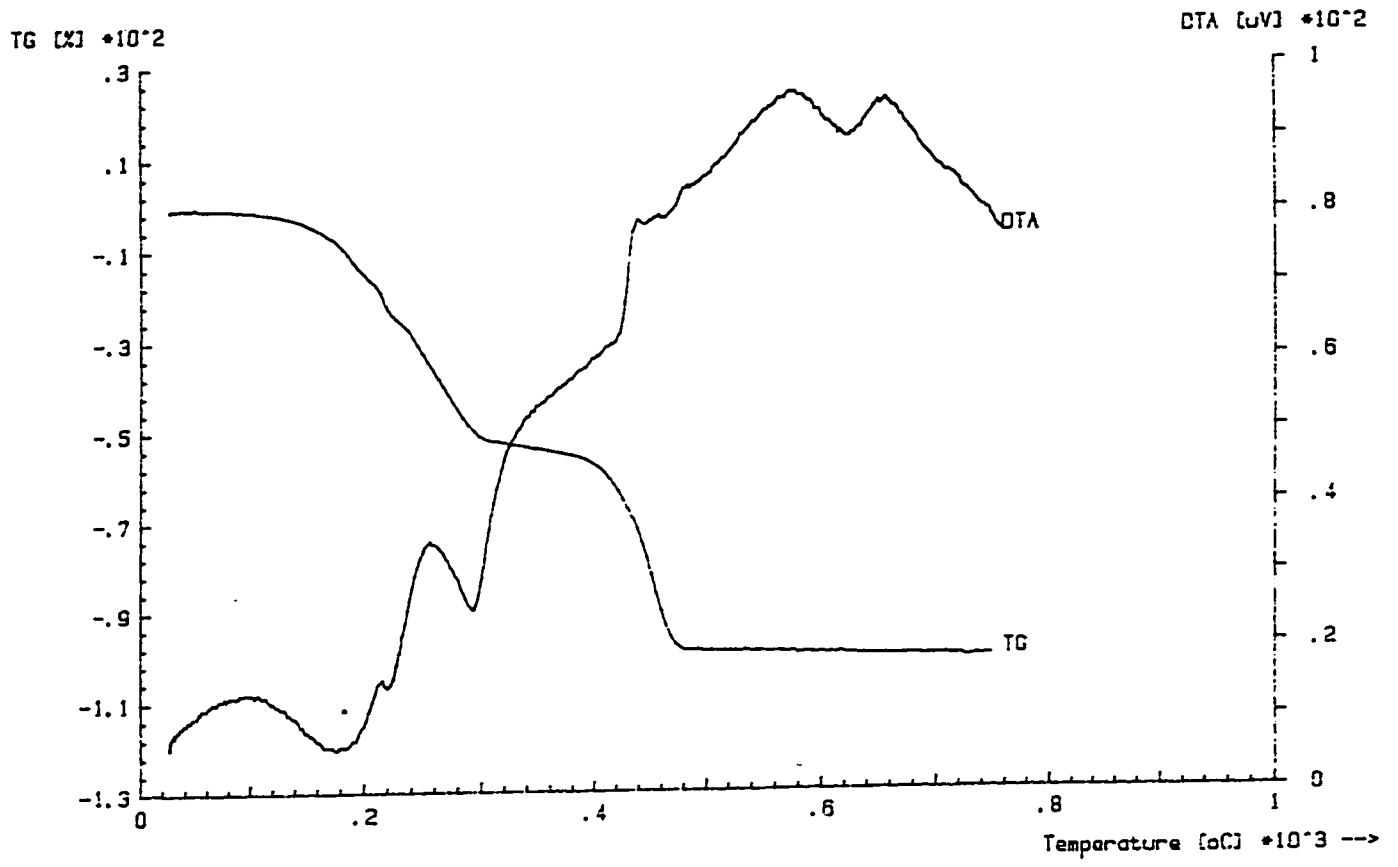


Figure 6 DTA and TGA of homopolymer 10

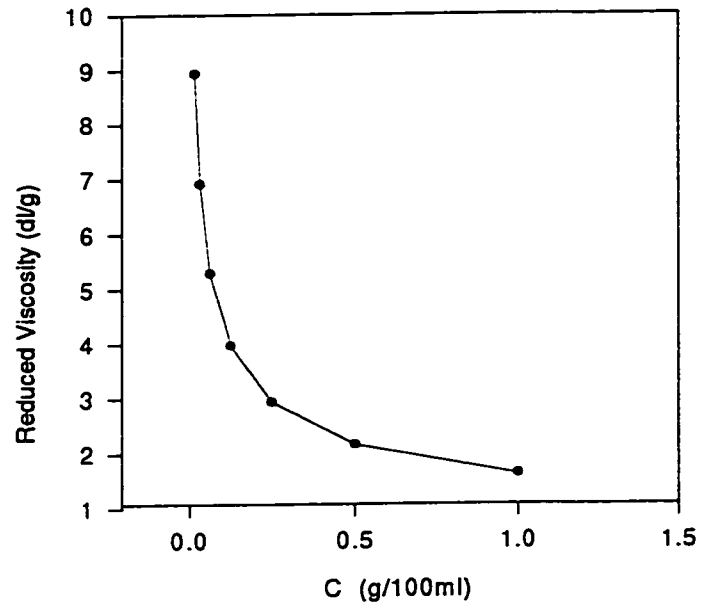


Figure 7: Viscosity behaviour of polymer 10 (entry 3, Table 1) in deionized water

The addition of strong electrolyte like sodium chloride suppresses the ionization of the polymer due to common ion effect and the viscosity behaviour becomes normal as can be seen in Figure 8-15. The term intrinsic viscosity for the quaternary ammonium polymers can not be used in the same sense as for uncharged polymers since it is dependent largely on the concentration of the added salt. By increasing the ionic strength, the screening of the charges on the macromolecular chain can be achieved leading to a decreased macromolecular expansion. This would allow a statistical coil conformation of macromolecules by chain coiling thus reduce the intrinsic viscosity. While Figure 8-15 represent the viscosity behaviour of the homopolymer in 0.1N NaCl solution at 30°C, the viscosity behaviour of a homopolymer from entry no. 3 in 0.2N NaCl is shown in Figure 16. As is evident the viscosity in 0.1 N and 0.2 N NaCl solution of the polymer becomes 0.559 and 0.390 dl/g respectively. Viscosity behaviour is normal since the presence of the added electrolyte suppresses the dissociation of the polymer hence compress the hydrodynamic volume of the polyelectrolyte.

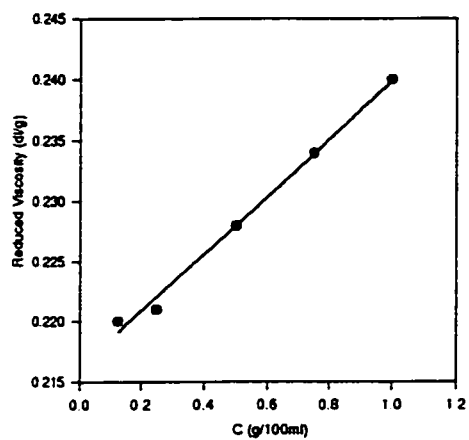


Figure 8: Viscosity behaviour of polymer 10 (entry 1, Table 1) in 0.1 N NaCl

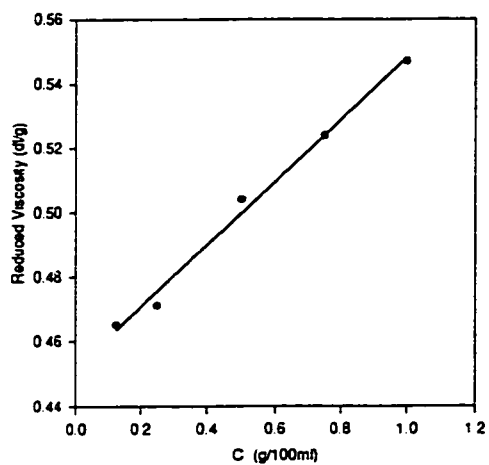


Figure 9: Viscosity behaviour of polymer 10 (entry 2, Table 1) in 0.1 N NaCl

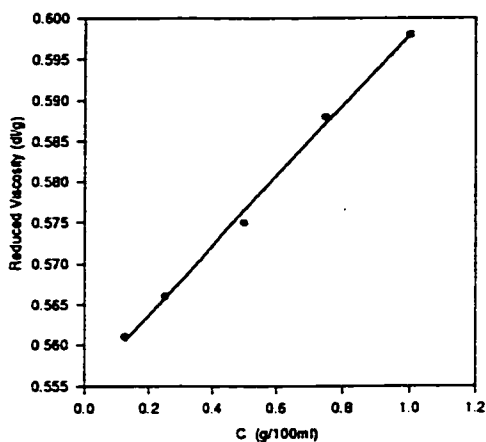


Figure 10: Viscosity behaviour of polymer 10 (entry 3, Table 1) in 0.1 N NaCl

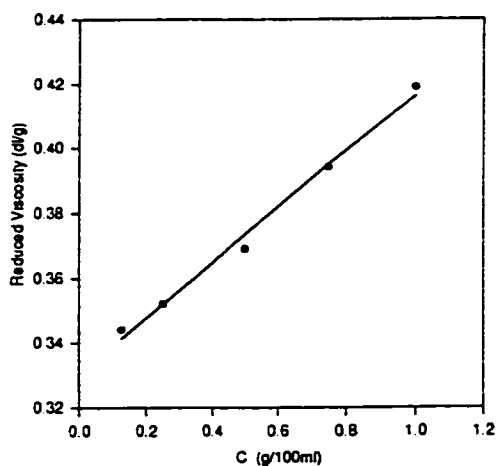


Figure 11: Viscosity behaviour of polymer 10 (entry 4, Table 1) in 0.1 N NaCl

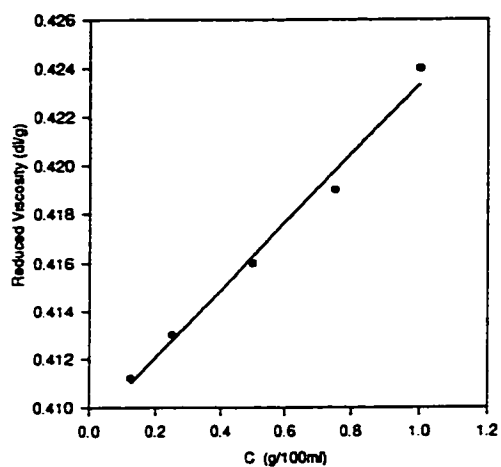


Figure 12: Viscosity behaviour of polymer 10 (entry 5, Table 1) in 0.1 N NaCl

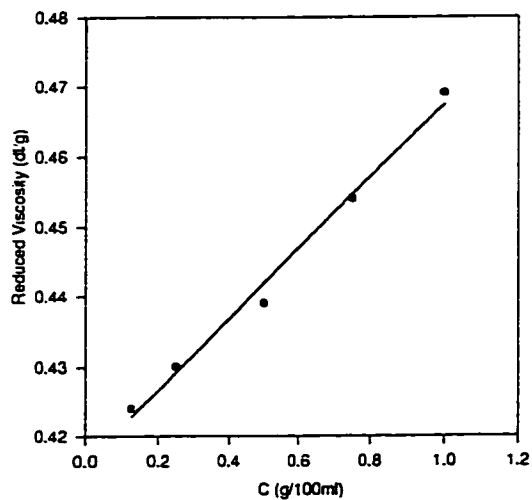


Figure 13: Viscosity behaviour of polymer 10 (entry 6, Table 1) in 0.1 N NaCl

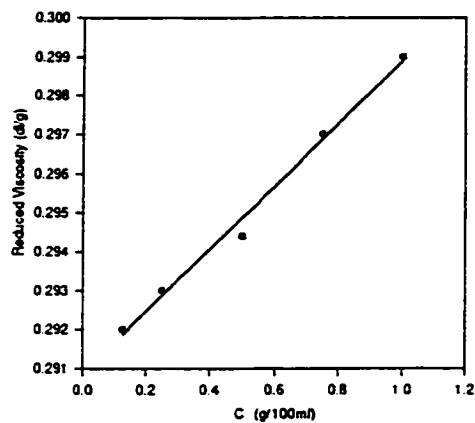


Figure 14: Viscosity behaviour of polymer 10 (entry 8, Table 1) in 0.1 N NaCl

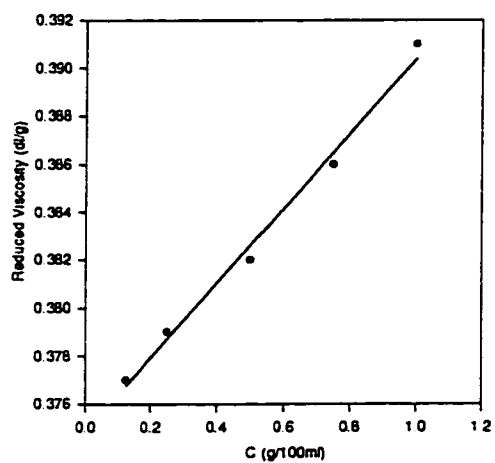


Figure 15: Viscosity behaviour of polymer 10 (entry 9, Table 1) in 0.1 N NaCl

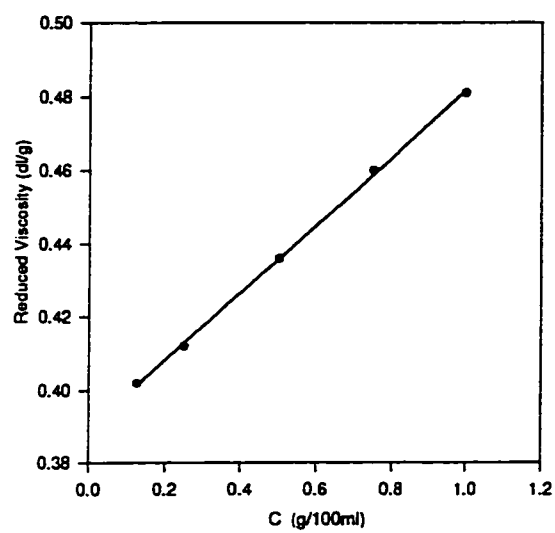
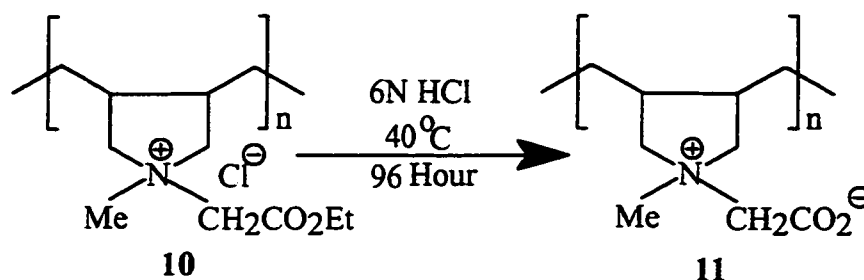


Figure 16: Viscosity behaviour of polymer 10 (entry 3, Table 1) in 0.2 N NaCl

3.3 Conversion of the Polyelectrolyte (10) to Polyampholyte (11)



The homopolymer (Sample, entry no.3, Table 1) was hydrolyzed under acidic condition (6N HCl, 40°C) to give the hydrolyzed polyzwitterion (11) in excellent yield. The hydrochloric acid in the reaction mixture is removed by dialyzing against deionized water followed by basification (NaHCO₃) and dialysis against distilled water (see under experimental section). The polymer was recovered by freeze drying. The IR, ¹H and ¹³C NMR spectra are shown in Fig. 17, 18 and 19, respectively. The absorption around 1628 cm⁻¹ indicates the presence of CO₂⁻ functionality. It is evident, after comparing the ¹H spectra of the homopolymer (Fig. 4) and hydrolyzed homopolymer (Fig. 18), that the CH₃-C-O protons which appeared at δ 1.25 ppm for the homopolymer is not present in the spectrum of the polybetaine thus indicating the removal of the CH₃CH₂O group after hydrolysis. Similar observation is made from the ¹³C NMR spectrum. The carbon of the ethyl groups (Fig. 5) disappeared in the spectra of the polyampholyte (Fig. 19).

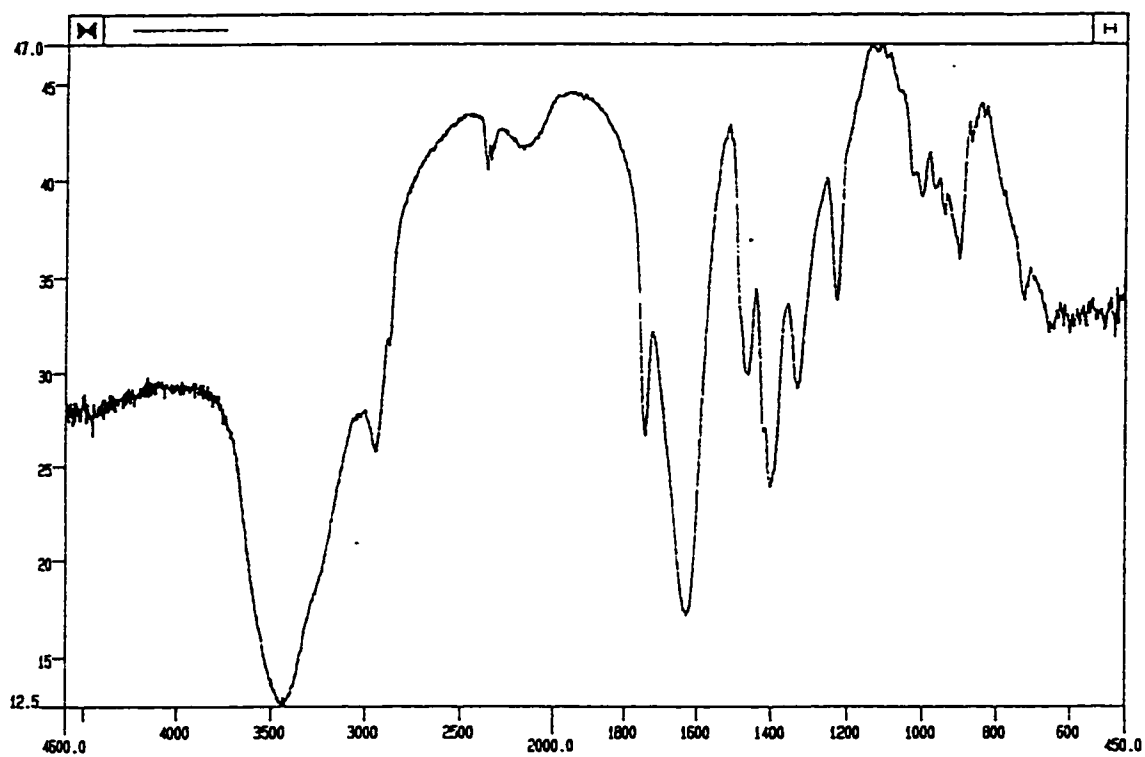


Figure 17 FTIR Spectrum of hydrolyzed homopolymer 11

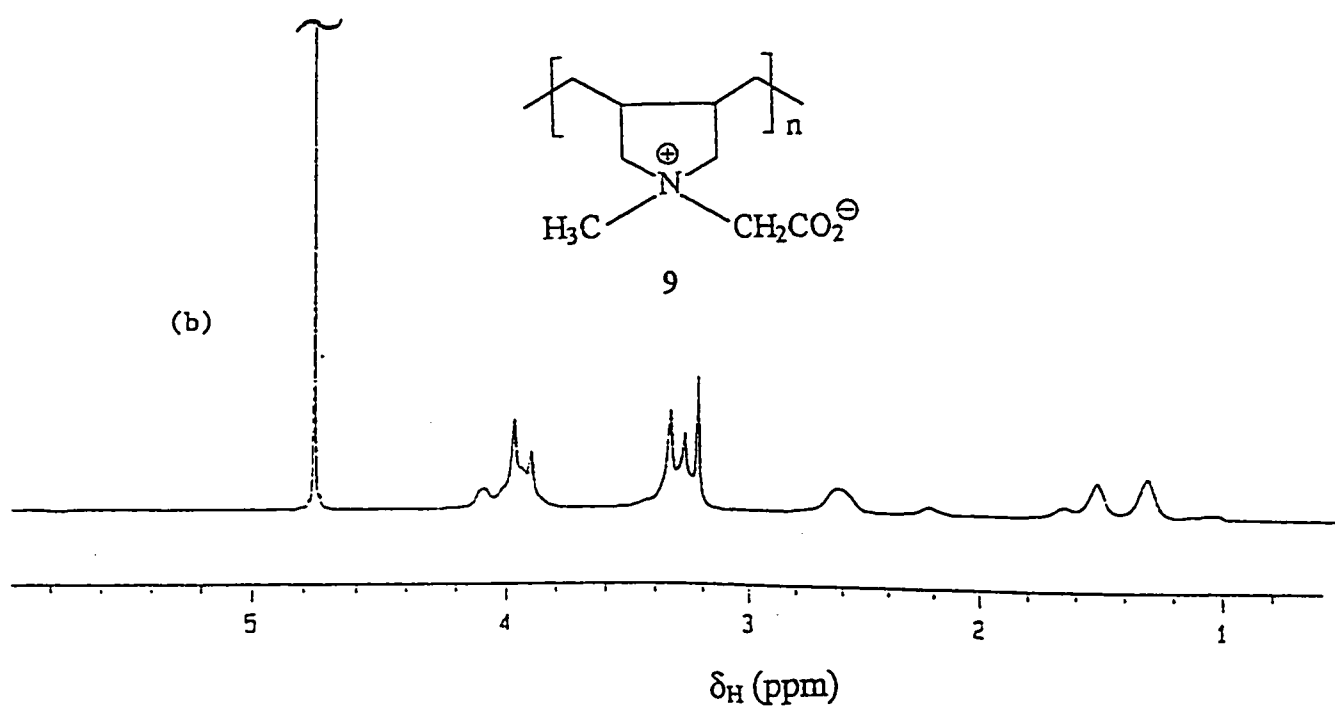


Figure 18 ^1H NMR Spectrum of hydrolyzed homopolymer **11** in D_2O

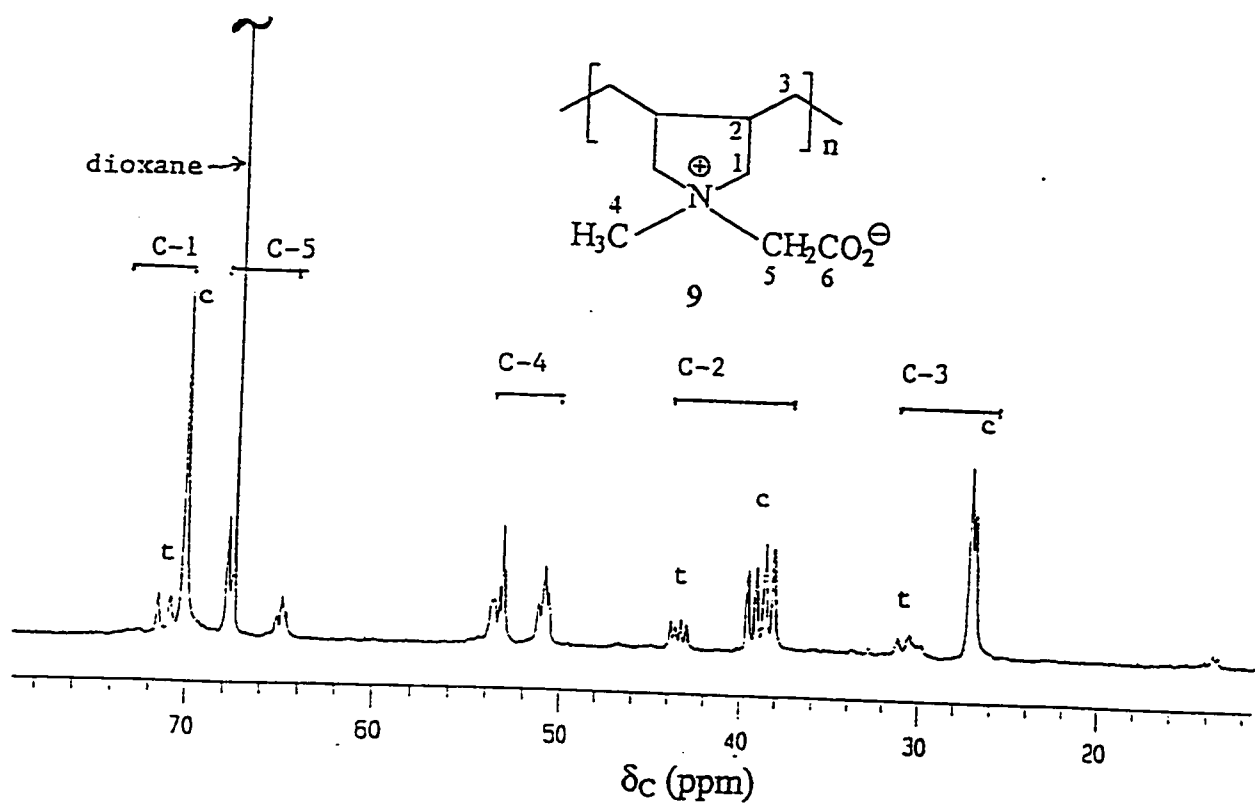


Figure 19 ^{13}C NMR Spectrum of hydrolyzed homopolymer 11 in D_2O

The polymer did not melt even at 400°C. The sample changed its colour at 300°C to yellowish brown. The differential thermal analysis and thermal gravimetric analysis of the hydrolyzed homopolymer are shown in Figure 20. The pH of 1% solution of polymer (11) was found to be 8.17.

The solubility behaviour of the polyelectrolyte and polyampholyte is shown in Table 2. The polyampholyte (11) was found to be soluble in most of the protic solvents. Overwhelming majority of reported polyampholytes are known to be insoluble in water. Viscosity behaviour of the polyampholyte (11) in presence and absence of added salt NaCl are presented in Figure 21-26 and Table 3. It is interesting to note that while in absence of added salt NaCl the viscosity curve for the polyelectrolyte is concave upwards (see Figure 7), the corresponding curve for the polyampholyte are straight line curve just like the behaviour observed for normal polymers (see Figure 21). The another important feature is that while the presence of NaCl decreases the intrinsic viscosity for the polyelectrolyte the opposite is true i.e; increasing concentration of NaCl increases the intrinsic viscosity of the polyampholyte. In Figure 27 the effect of NaCl concentration on intrinsic viscosity is illustrated. It is possible to consider Figure 27 to be composed of two straight lines. The first line with the higher slope may be attributed to the site binding of the chloride ion by the quaternary ammonium centre. This line reflects relatively rapid change in the intrinsic viscosity as the chloride ion concentration is increased. The second line, characterized by slower rate of change of intrinsic viscosity, may be due to atmospheric binding of the anion by the polyampholyte. At lower concentration of added salt site binding of anion predominates and as the salt concentration is increased, more and more of the potential

Table 2: Solubility^{a,b} of homopolymer (10) and Corresponding Polyampholyte (11)

	ϵ	(10)	Intrinsic Viscosity of 10 (dl/g)	(11)	Intrinsic Viscosity of 11 (dl/g)
Water	78.4	+		+	0.345
Methanol	32.7	+		+	
Formic acid	58.5	+		+	
Formamide	111.0	+		+	0.494
Ethylene glycol	37.3	+		+	
Triethylene glycol	23.7	+		\pm	
Acetic acid	6.15	+		-	

^a 2%(w/w) of polymer solution was made after heating the mixture at 70 °C for 1 hour and then bringing the temperature back to 23 °C.

^b ‘+’ indicates soluble; ‘-’ indicates insoluble; ‘ \pm ’ indicates partially soluble.

Table 3: Intrinsic Viscosity of Polyampholyte 11 in aqueous solution containing different concentration of added salt NaCl

Polymer	[NaCl] (N)	Intrinsic Viscosity ^a dl/g
11 ^b	0	0.345
11	0.1	0.373
11	0.5	0.413
11	1.0	0.447
11	1.5	0.465
11	2.0	0.478
10 ^c	0	— ^d
10	0.1	0.556
10	0.2	0.390

^a Viscosity of 1.0-0.0625% polymer solution at 30 °C was measured in Ubbelohde Viscometer (K=0.005989).

^b Obtained by hydrolysis of the homopolymer from entry no. 3 of Table 1.

^c homopolymer of entry no. 3 from Table 1.

^d concave upward, see Fig. 7.

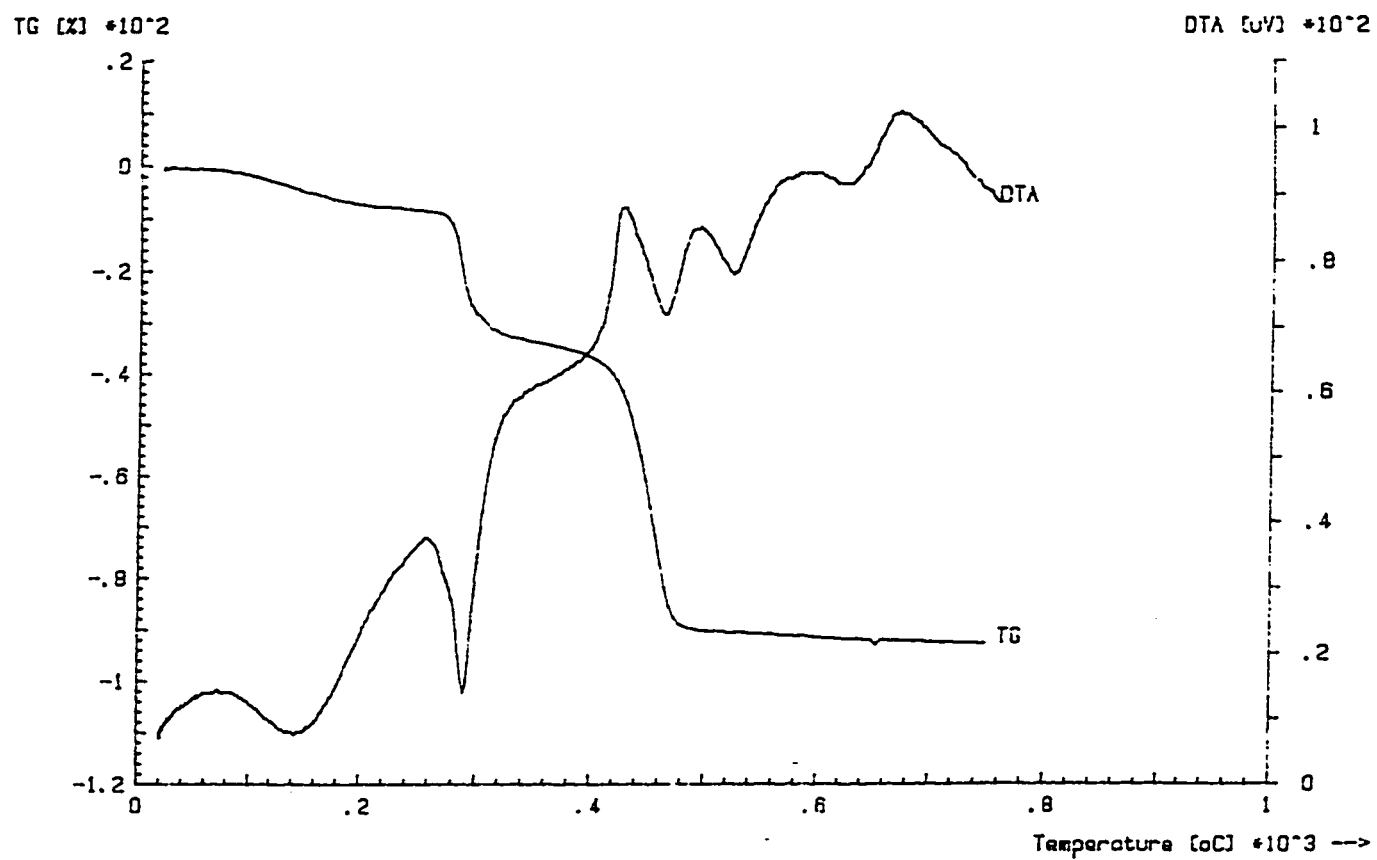


Figure 20 DTA and TGA of hydrolyzed homopolymer 11

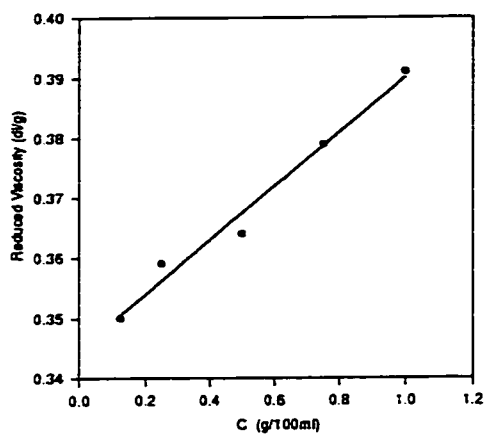


Figure 21: Viscosity behaviour of polymer 11 in deionized water

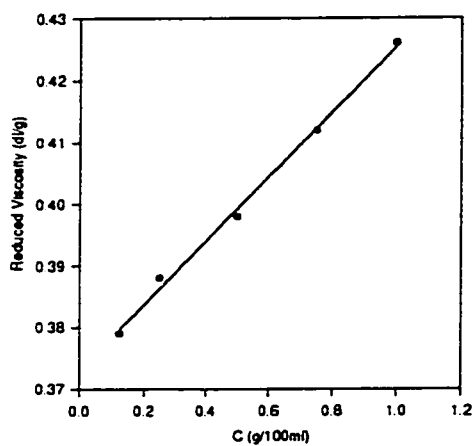


Figure 22: Viscosity behaviour of polymer 11 in 0.1 N NaCl

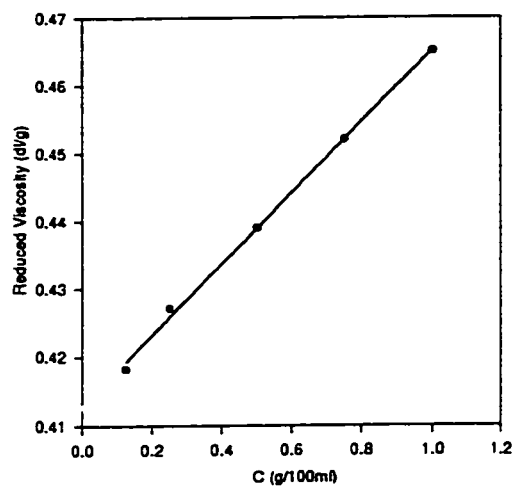


Figure 23: Viscosity behaviour of polymer 11 in 0.5 N NaCl

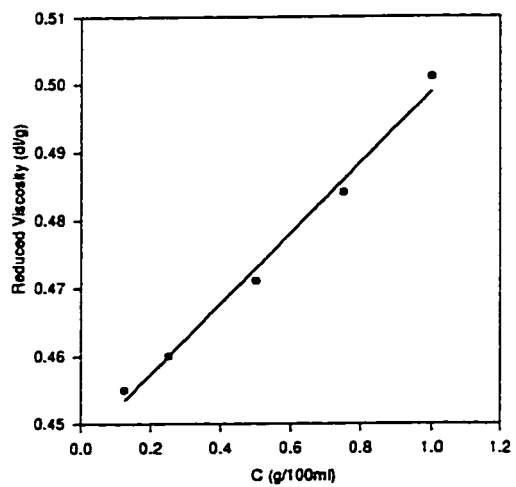


Figure 24: Viscosity behaviour of polymer 11 in 1.0 N NaCl

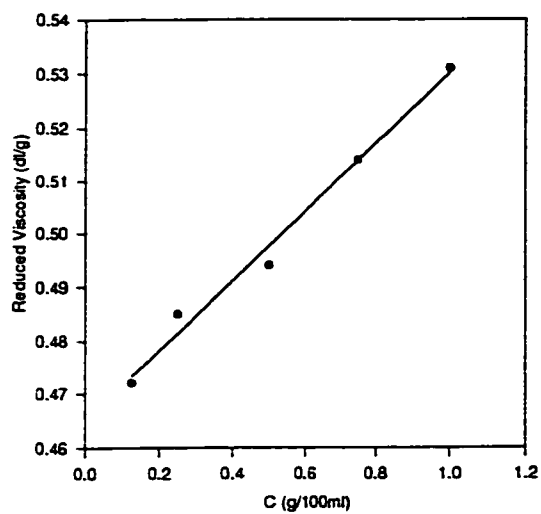


Figure 25: Viscosity behaviour of polymer 11 in 1.5 N NaCl

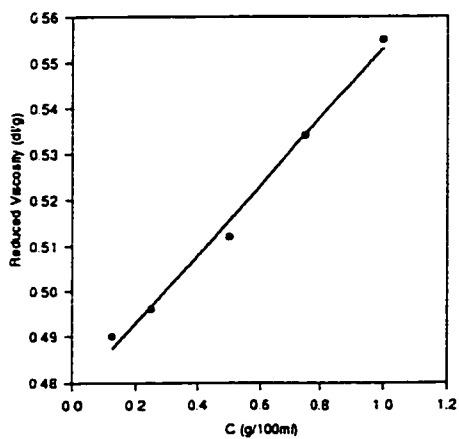


Figure 26: Viscosity behaviour of polymer 11 in 2.0 N NaCl

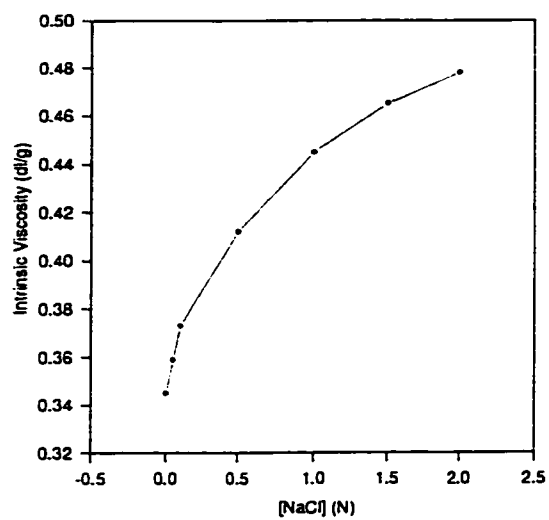


Figure 27: Effect of NaCl concentration on intrinsic viscosity for polymer 11

binding sites are occupied and finally there would be no site available for further site binding. Initial rapid increase in viscosity becomes less rapid as the tendency to site binding decreases. In the second stage, the atmospheric binding tends to predominate and the increase in viscosity begins to lessen.

The presence of inorganic salt disrupts the intramolecular interaction of the quaternary ammonium and carboxylate groups, thus causes the tightly coiled polyampholyte to behave as a flexible coil as shown in Figure 28. The addition of salt makes the polyampholyte to achieve a more rod-like conformation in order to relieve the

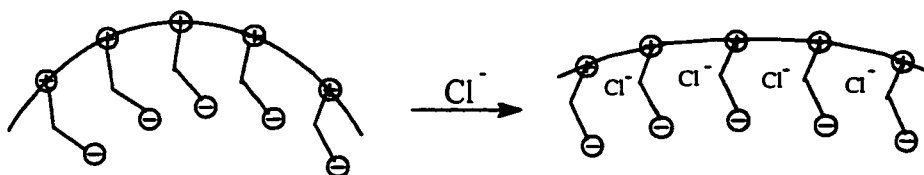


Fig. 28

repulsion between pendant carboxylate anions. However, presence of the Na^+ cation can also shield the pendant anions. It seems apparent that while the cationic charge on the polymer chain could be effectively neutralized by strongly binding chloride anions, the anionic pendant group is not shielded to that extent by the cation, Na^+ . The hydration shell for a positively charged ion (e.g; Na^+) in water is generally fairly large hence the distance of closest approach is not sufficient to neutralize effectively the charge on the pendant carboxylate anions so the overall effect of the addition of NaCl is to make the polymer more rod-like hence to increase the intrinsic viscosity of the polyampholyte solution. Increase of intrinsic viscosity with increase of added salt indicates increasing chain

expansion as a result of coulombic interaction between charge of the polymer and the added ions. This type of behaviour has been characterized as “anti-polyelectrolyte”.

The reduced viscosities of the polyampholyte in aqueous KCl, KBr and KI solution of the same added salt concentration were studied and are illustrated in Figure 29 and Table 4. Similar experiment were conducted employing a common anion, chloride. The results obtained are shown in Figure 30 and Table 4.

It is observed that for the common cation potassium (K^+), the intrinsic viscosity increases as the anion is changed from Cl^- to Br^- to I^- . Iodide, having the smallest charge to radius ratio, is more polarizable hence it can approach closely to the cationic centre in the chain thus effectively neutralizing the charge. One important feature of this investigation is that divalent cations Ca^{2+} , in $CaCl_2$ is known to precipitate anionic polyelectrolytes from aqueous solution even at low concentration, did not precipitate the polyampholyte (11).

3.4 Copolymerization of the monomer (8) with SO_2

The copolymer of quaternary ammonium salt in sulfur dioxide (SO_2) are reported to produce particularly good flocculants. The polysulfones are used as adhesives, thickeners and paints. We explored the possibility of preparing polysulfone by copolymerizing the monomer (8) with SO_2 in solvent dimethyl sulfoxide (DMSO) using ammonium persulfate (APS) as initiator.

Table 4: Effect of Anion and Cation on the viscosity behaviour of Polyampholyte (11)

Solvent (0.5 M)	Intrinsic Viscosity (dl/g)
KCl	0.368
KBr	0.400
KI	0.423
NaCl	0.412
NH ₄ Cl	0.397
LiCl	0.346
CaCl ₂	0.391

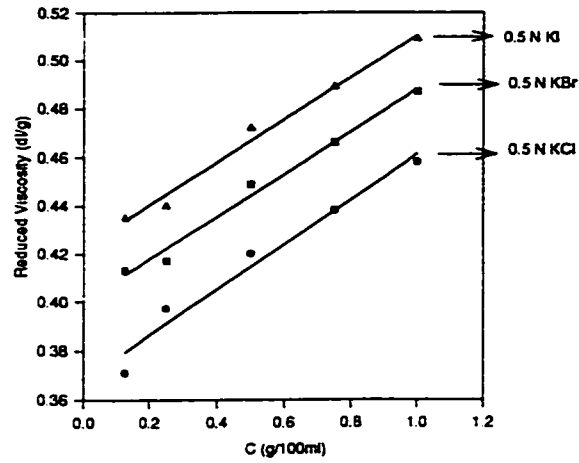


Figure 29: Viscosity behaviour of polymer 11 in salts of common cation, K^+

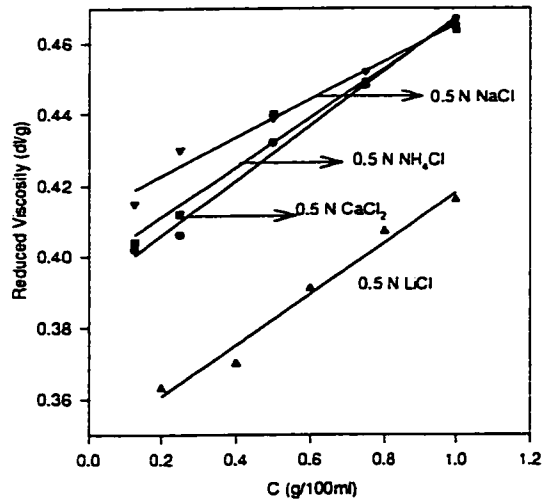
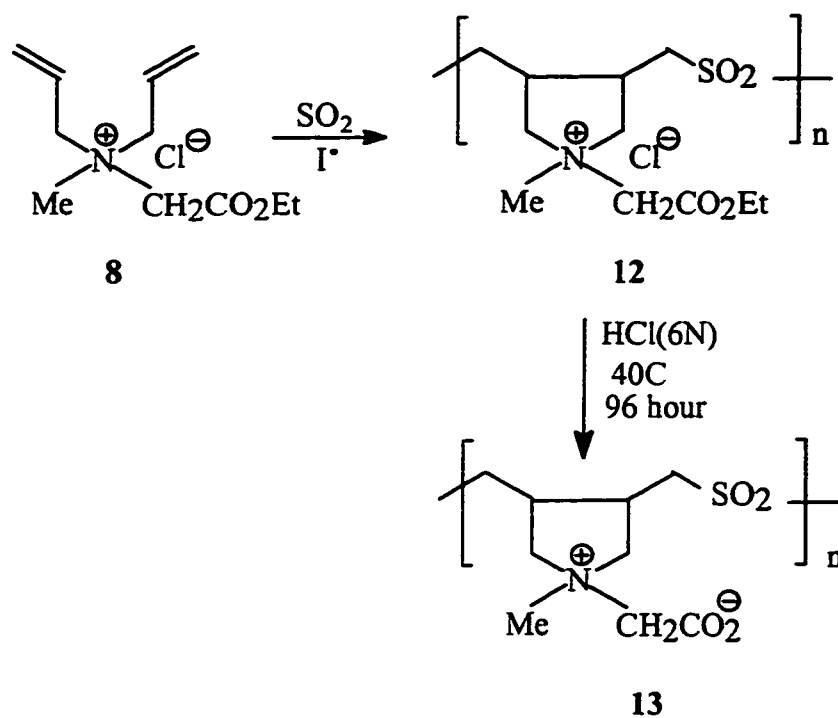


Figure 30: Viscosity behaviour of polymer 11 in salts of common anion, Cl^-



Scheme 6

The results of polymerization reaction are shown in Table 5. As is evident from Table 5 for a 1:1 mol ratio of monomer and SO_2 , the isolated yield of the polymerization reaction is maximum (82%) at 50°C and minimum (43%) at 35°C (Entry No. 1-4, Table 5). However opposite is true for the intrinsic viscosity in 0.1N NaCl solution. Maximum intrinsic viscosity of 1.90 dl/g is obtained at 35°C and the viscosity decreases with the increase in temperature of the copolymerization and at 50°C it became 0.836 dl/g. The intrinsic viscosity of 1.90 dl/g is astonishingly high for polyelectrolyte indicating the high molar mass for the polymer. The viscosity behavior of polymer sample (Entry 2, Table 5) in 0.1 N NaCl and in the absence of NaCl are shown in Figure 31 and 32 respectively. Polymerization reaction carried out at 50°C (Entry No. 4 & 5) using different

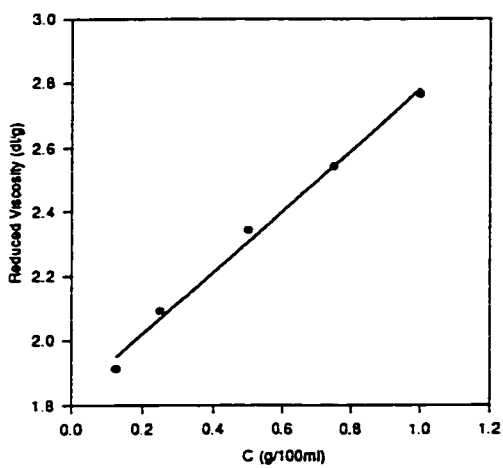


Figure 31: Viscosity behaviour of copolymer 12 (entry 2, Table 5) in 0.1 N NaCl

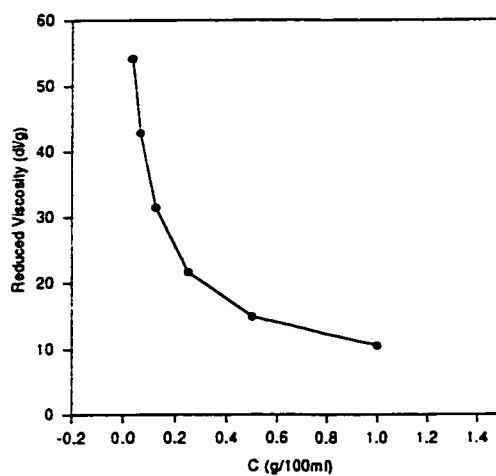


Figure 32: Viscosity behaviour of copolymer 12 (entry 2, Table 5) in deionized water

concentration of the initiator (APS) indicates that increasing the initiator concentration decreases the viscosity. For a polymerization reaction using 2:1 mol ratio of monomer and SO₂ gave the highest intrinsic viscosity value of 1.03 dl/g for the three polymerization reactions run at 50°C.

The yield of 109% (Entry 6) based on 1:1 monomer complex M/SO₂ presumably indicates that the alternating copolymer may contain some homopolymer because the monomer (**8**) was used in excess.

The copolymer is found to be soluble in methanol and water but insoluble in acetone. The pH of 1% solution of copolymer (**12**) was found to be 2.62. The elemental analysis of the hygroscopic polymer indicates the presence of monomer (**8**) and SO₂ in an approximately 1:1 ratio hence suggesting the formation of alternating copolymer.

Melting point of the polymer was found to be 240-250°C and it decomposed turning to brown colour. The thermal gravimetric analysis and differential thermal analysis is shown in Figure 33.

The IR spectra shown in Figure 34 of the copolymer indicates the presence of SO₂ into the polymeric backbone. The two strong bands at 1306 and 1126 cm⁻¹ were assigned to the asymmetric and symmetric vibrations of SO₂ unit. The strong absorption at 1748 cm⁻¹ indicates the presence of ester functionality. The hygroscopic nature of the polymer is revealed by the presence of strong band around 3450 cm⁻¹. The NMR spectrum of the copolymer is shown in Figure 35 and is in quite agreement with the assigned structure of

Table 5: Effect of Concentration of Monomers, Initiator and temperature on M/SO₂ Copolymerization

Entry No.	Monomer. (mmol)	SO ₂ (mmol)	DMSO	APS (mg)	Time (hour)	Temp. (°C)	Yield ^a (%)	Intrinsic ^b Viscosity dl/g
1	50	50	10.5	85	15	35	43	1.90
2	50	50	10.5	85	15	40	77	1.83
3	50	50	10.5	85	10	45	77	1.48
4	50	50	10.5	85	3	50	82	0.836
5	50	50	10.5	170	3	50	87	0.604
6	50	25	10.5	85	3	50	109	1.03

^a Based on 1:1 monomer comp of M/SO₂

^b Viscosity of 1-0.03125% polymer solution in 0.1N NaCl at 30°C was measured in Ubbelohde Viscometer (K=0.005989).

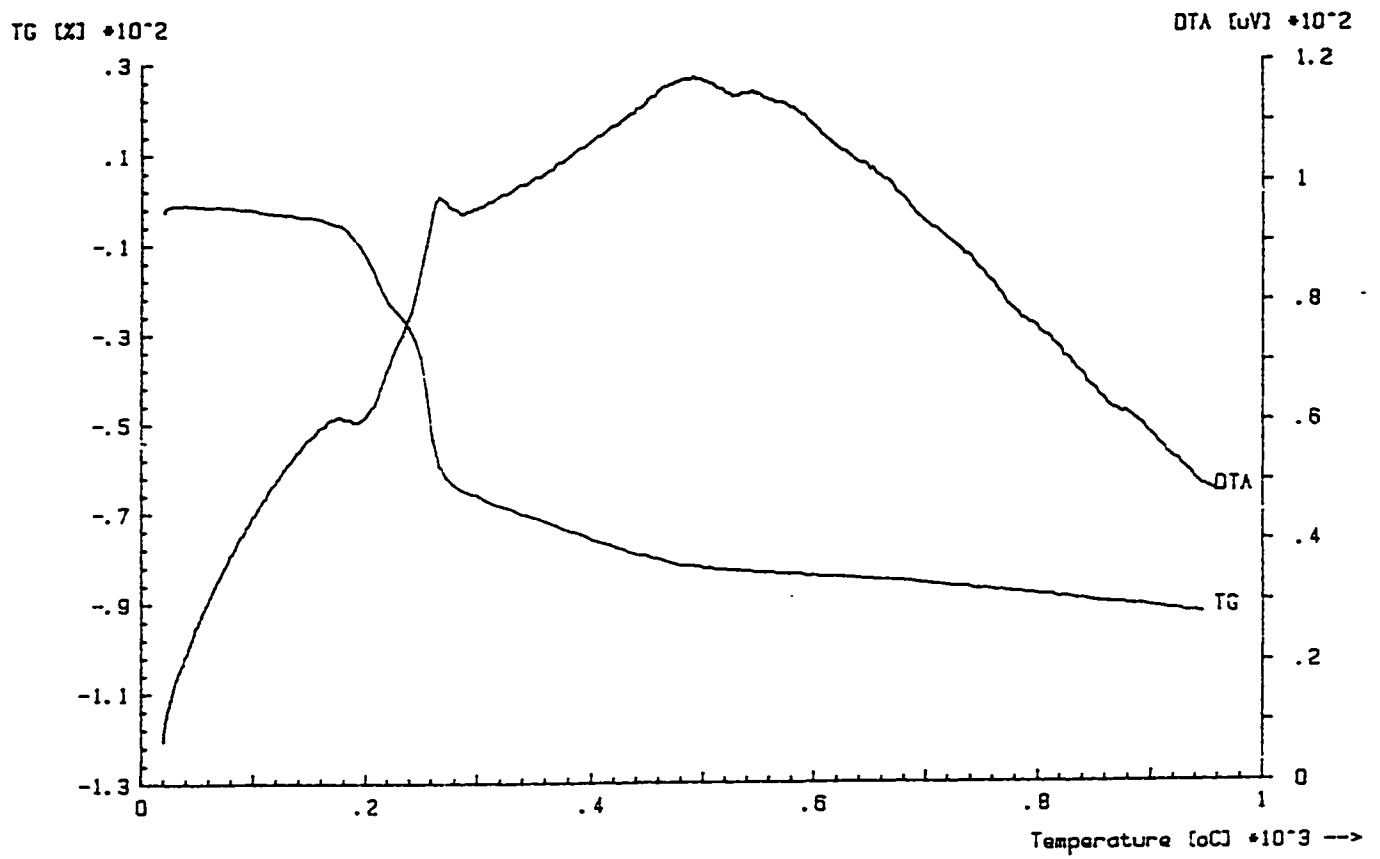


Figure 33 DTA and TGA of copolymer 12

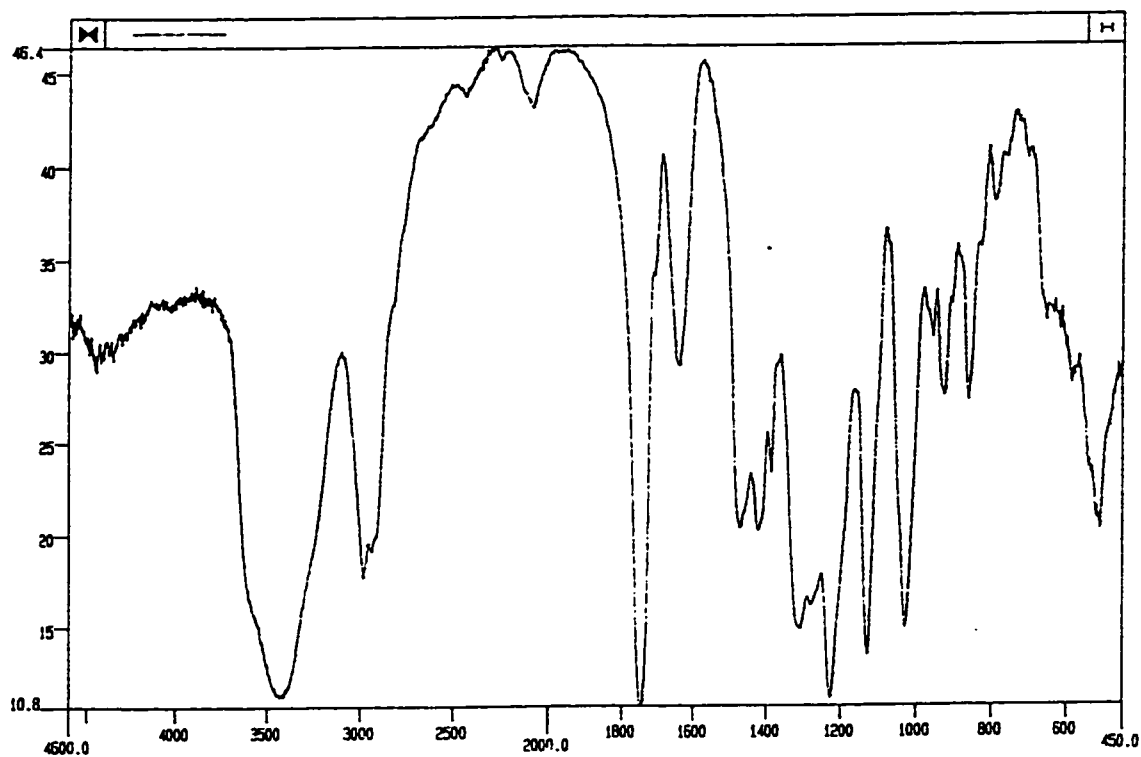


Figure 34 FTIR Spectrum of copolymer 12

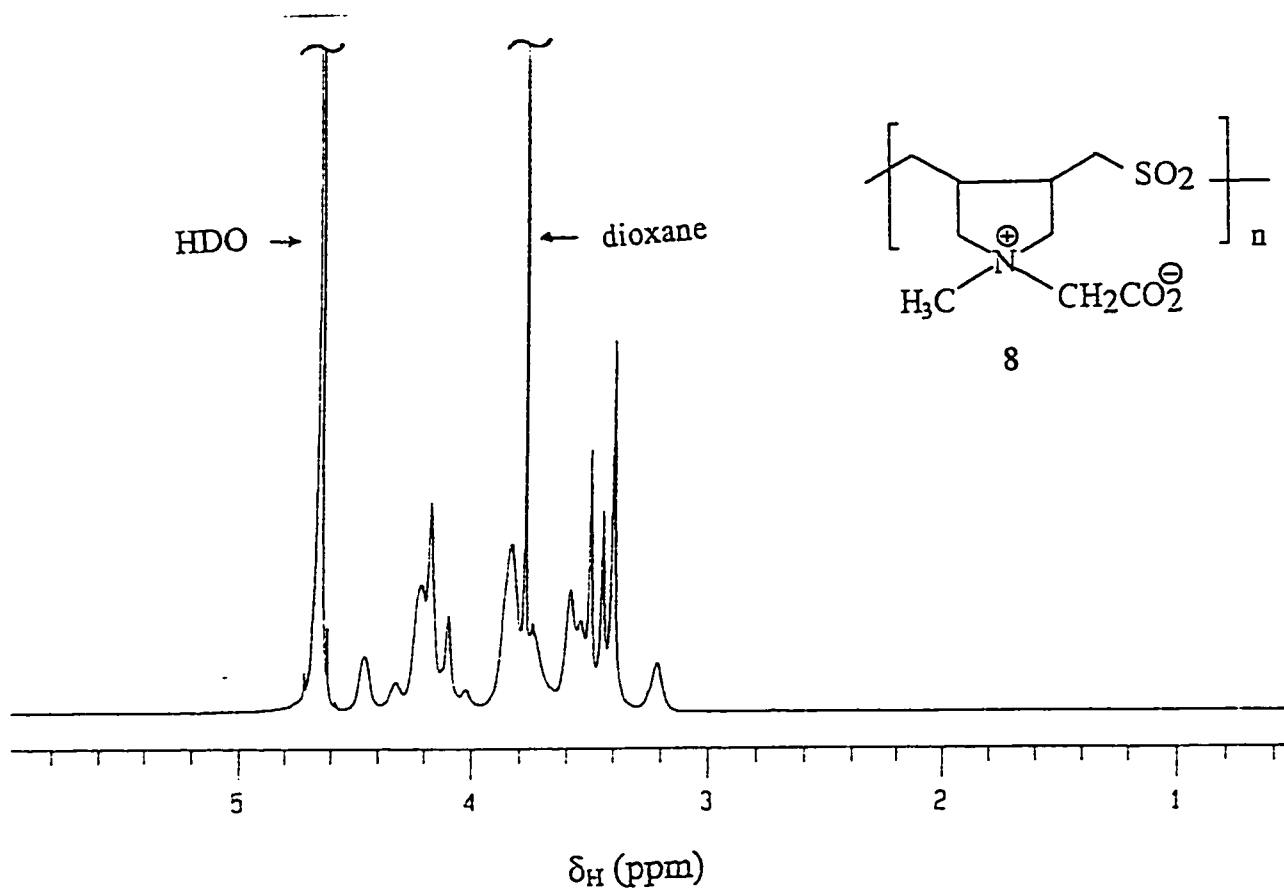


Figure 35 ^1H NMR Spectrum of copolymer 12 in D_2O

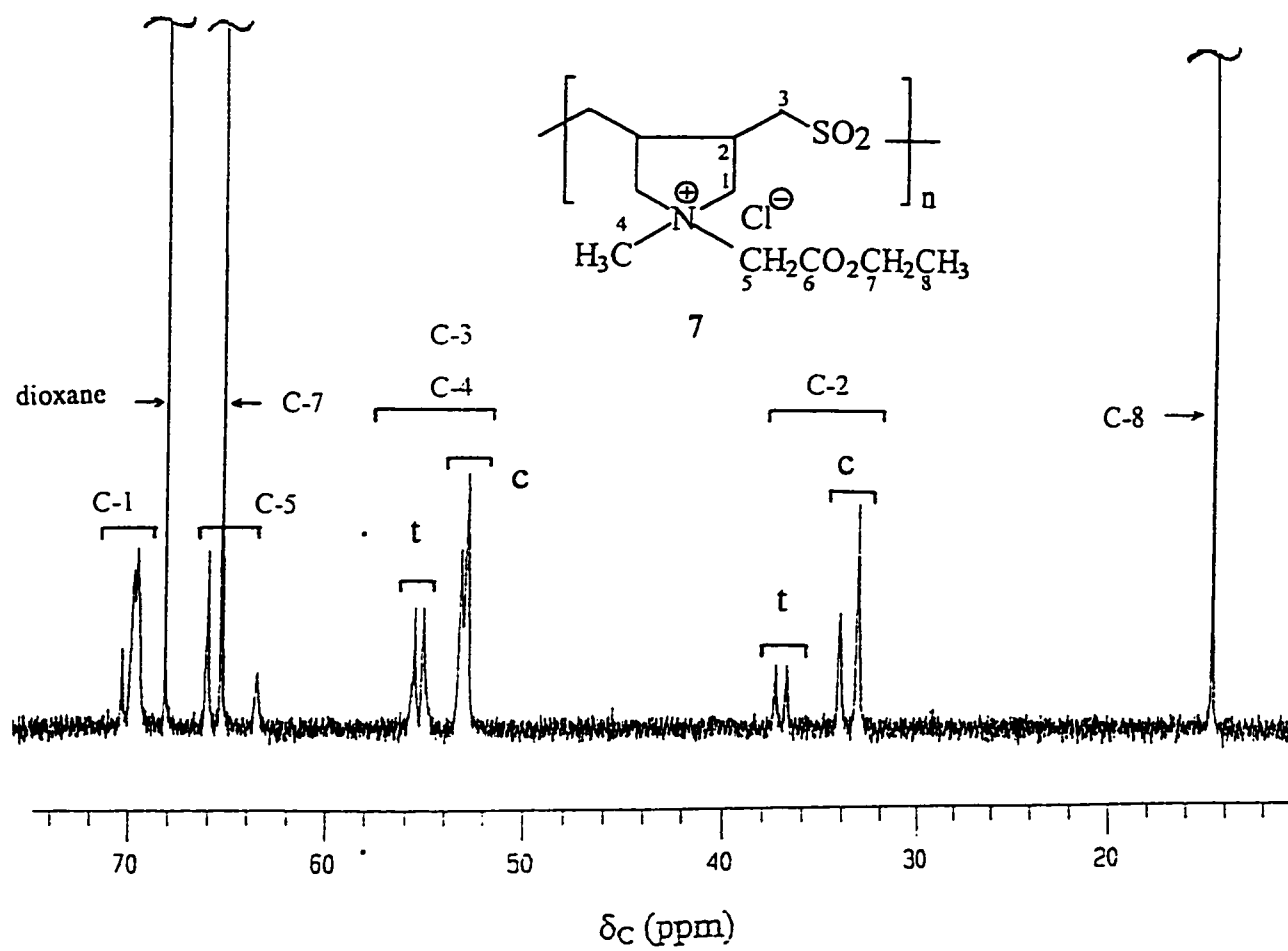
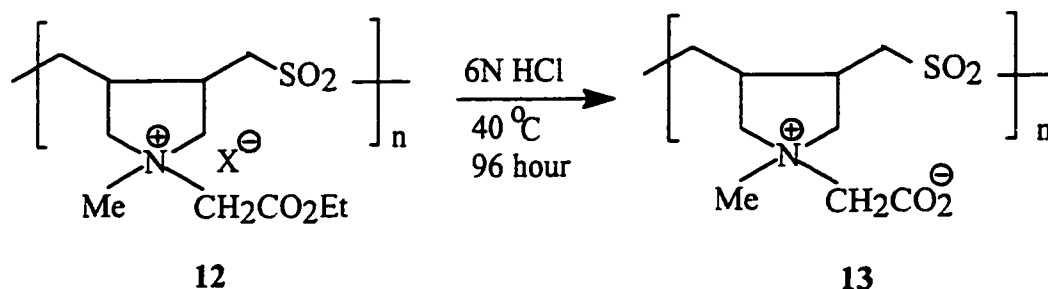


Figure 36 ^{13}C NMR Spectrum of copolymer 12 in D_2O

the polymer. Compared to the NMR spectrum of the homopolymer (Figure 4) the signals of the ^1H protons are shifted downfield due to the presence of electronegative SO_2 moiety in the polymeric backbone. The ^{13}C NMR spectra is shown in Figure 36.

3.5 Hydrolysis of Copolymer (12) to Polyampholyte (13)

The copolymer (12) from Entry 2 (Table 5) was hydrolyzed under acidic condition to give the polyampholyte (13) in excellent yield (86%). The detailed procedure for isolation of the polyzwitterion (13) was given under experimental section. The white polymer has a melting range of 270-280°C and turned to dark brown. The TGA and DTA is shown in Figure 37. The elemental analysis were in reasonably good agreement taking into consideration the hygroscopic nature of the polymer. The pH of 1% solution of polyampholyte (13) in 0.1 N NaCl was found to be 7.22.



The IR spectrum (Figure 38) indicates the absence of absorption due to ester functionality. The absorption at 1628 cm^{-1} was attributed to the carboxylate functionality. The strong bands at 1300 and 1126 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit. The ^1H and ^{13}C NMR spectra are shown in Figure 39 and 40, respectively. To our delight both the NMR spectra revealed the complete hydrolysis of the ester

functionality to the carboxylate group. The $\text{CH}_3\text{-CO}$ proton and ^{13}C signals of CH_3CH_2 group were absent in the spectra.

^1H and ^{13}C NMR spectra were measured in D_2O at 580 MHz and 125.65 MHz, respectively, on JEOL LA 500 spectrometer. p-dioxane ($\delta=67.4$ ppm) and DSS were used as internal standard for ^{13}C spectra and ^1H spectra, respectively. The ^1H and ^{13}C NMR spectra of these polymers 10, 11, 12 and 13 are shown in Figure 4, 5, 18, 19, 35, 36, 39 and 40 respectively, excepting the carbonyl resonances which are observed around 166 ppm. For the copolymers 12 and 13 the proton signals are shifted down field in comparison to their homopolymers due to the presence of electronegative SO_2 group. The hydrolysis of the ester group is complete as indicated by the absence of sharp triplet due to methyl group at $\delta=1.25$ ppm in ^1H spectra. The assignment of the ^{13}C peaks are based on our earlier work^{19b}. In the copolymer unfortunately N-methyl and the C-2 signals are accidentally overlapped.

C-2 signals of the homopolymers show eight well-resolved lines; four weak lines for the trans and other four for the cis. Large unequal splitting of the cis can be assigned to the difference in the configuration i.e. N^+ and small splitting of equal intensity can be attributed to the different configuration of the adjacent rings, as these can add in two ways (R or S) with equal probabilities. The C-2 of polymers do not show these splittings, presumably an intervening S atom can mask the configurational differences between adjacent rings. Integration of relevant peaks in the ^{13}C NMR spectra yields the percentage of trans to be 17-23% in these polymers.

Solubility of the copolymer (12) and its corresponding polyampholyte (13) is shown in Table 6. The solubility of the polymers in solvents at room temperature was

established for the 2% w/w solution after preheating at 70°C for 1 hour. The critical minimum salt concentration (CSC) required to promote water solubility at 23°C was measured by titration of 1% w/w solution of sufficiently high concentration with deionized water. The accuracy of the CSC values was obtained by visual determination of the first cloud point was approximately $\pm 1-2$ %. The respective influence of the cation and anion nature on the CSC values are shown in Table 7. For a common anion, Cl⁻, the CSC values remain in a narrow range of 0.069-0.073 M. However, for the chloride salts Li⁺ and Ca²⁺, the CSC values (0.992 and 0.306 M, respectively) are found to be considerably large. The sequence of increasing solubility power (decreasing order of CSC values) was found to be:



The hydration shell of cations in water is generally fairly large due to their large charge/radius ratio and presumably cannot approach close enough to effectively neutralize the charge on the carboxylate group. For a common cation, K⁺, the CSC values are very sensitive to the nature of anion. The sequence of increasing solubilizing power is found to be:



Thus the concentration of KCl required to promote water solubility is found to 27 times more than that of KI. The iodide being most polarizable (soft) increases the solubility of the polyampholyte. For a common bromide anion, the K⁺ and (n-C₃H₇)₄N⁺ salts are found to have similar solubilizing power.

Table 6: Solubility^{a,b} of copolymer (12) and Corresponding Polyampholyte(13)

	ϵ	(12)	Intrinsic Viscosity of 12 (dl/g)	(13)	Intrinsic Viscosity of 13 (dl/g)
Water	78.4	+		-	
Methanol	32.7	+		-	
Formic acid	58.5	+		+	
Formamide	111.0	+		+	0.859
Ethylene glycol	37.3	+		-	
Triethylene glycol	23.7	+		-	
Acetic acid	6.15	-		-	

^a 2%(w/w) of polymer solution was made after heating the mixture at 70 °C for 1 hour and then bringing the temperature back to 23 °C.

^b '+' indicates soluble; '-' indicates insoluble; '±' indicates partially soluble.

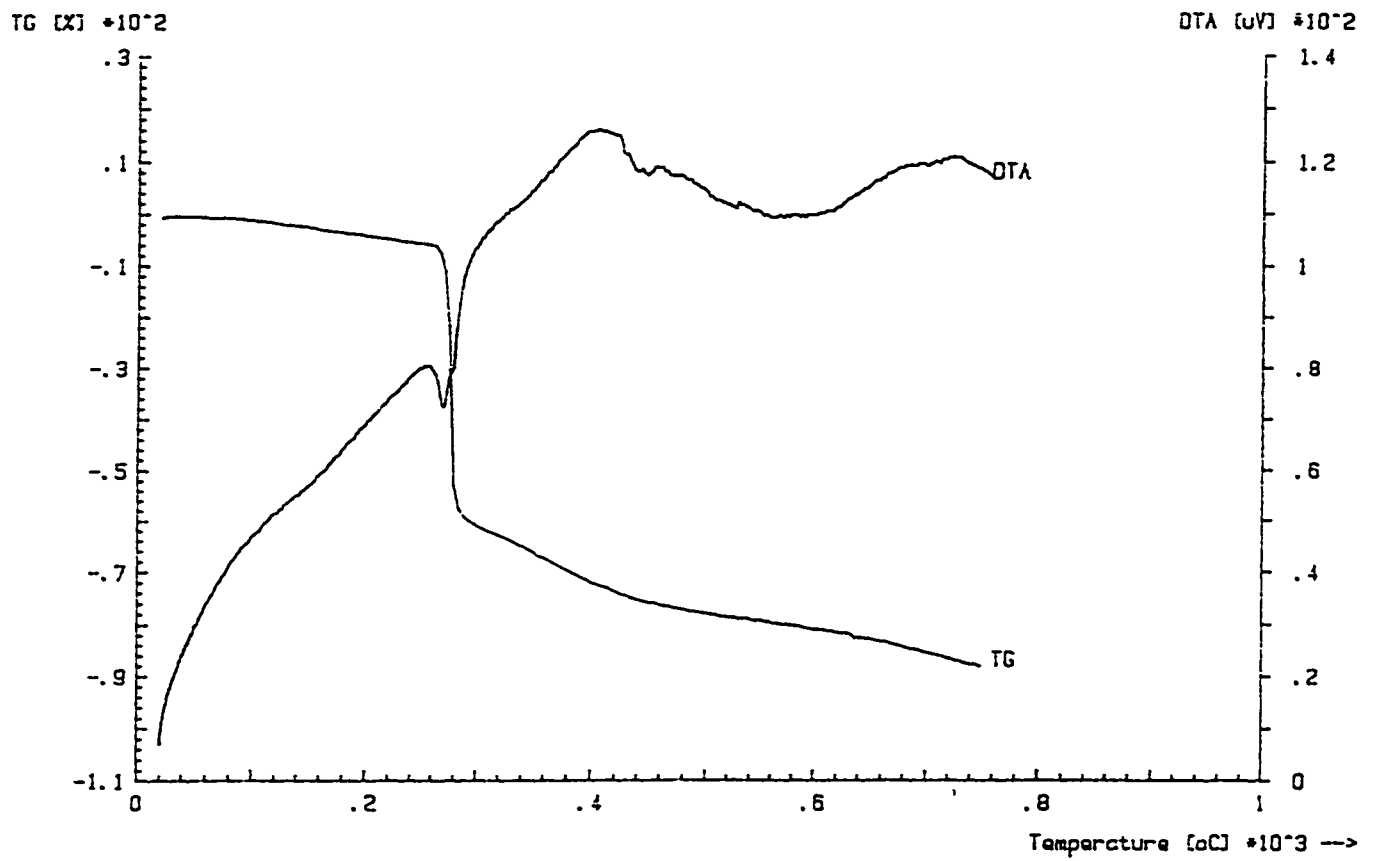


Figure 37 DTA and TGA of hydrolyzed copolymer 13

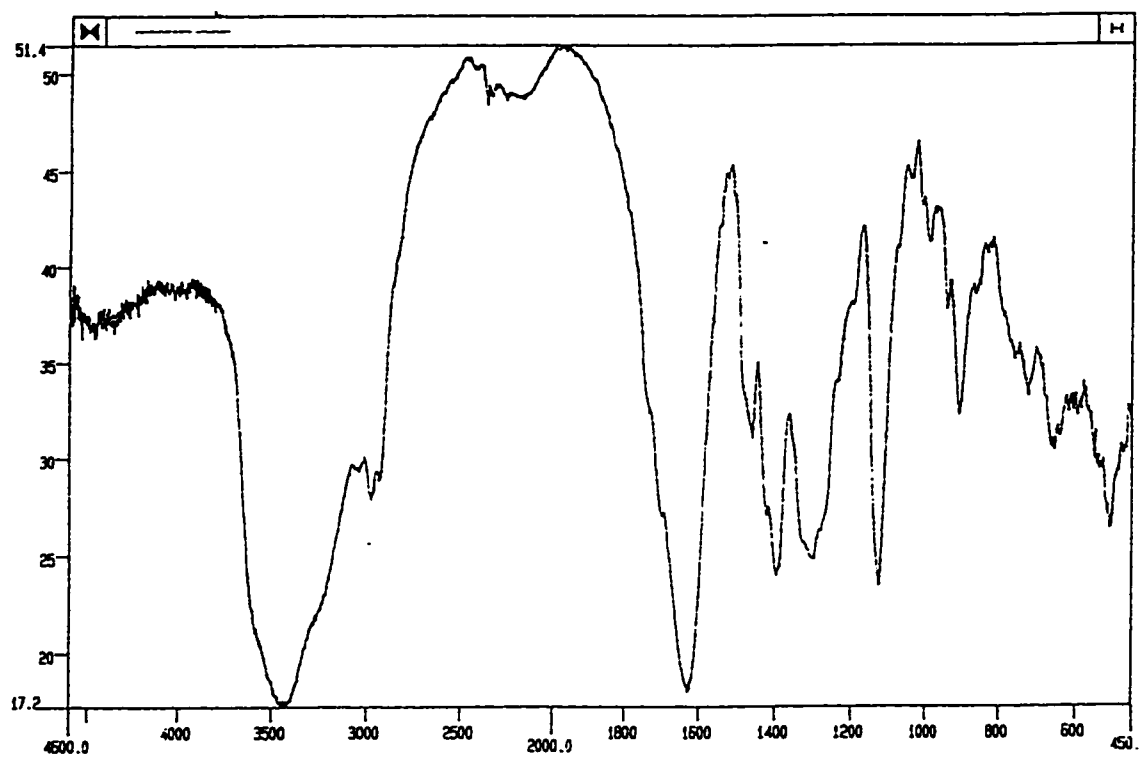


Figure 38 FTIR Spectrum of hydrolyzed copolymer 13

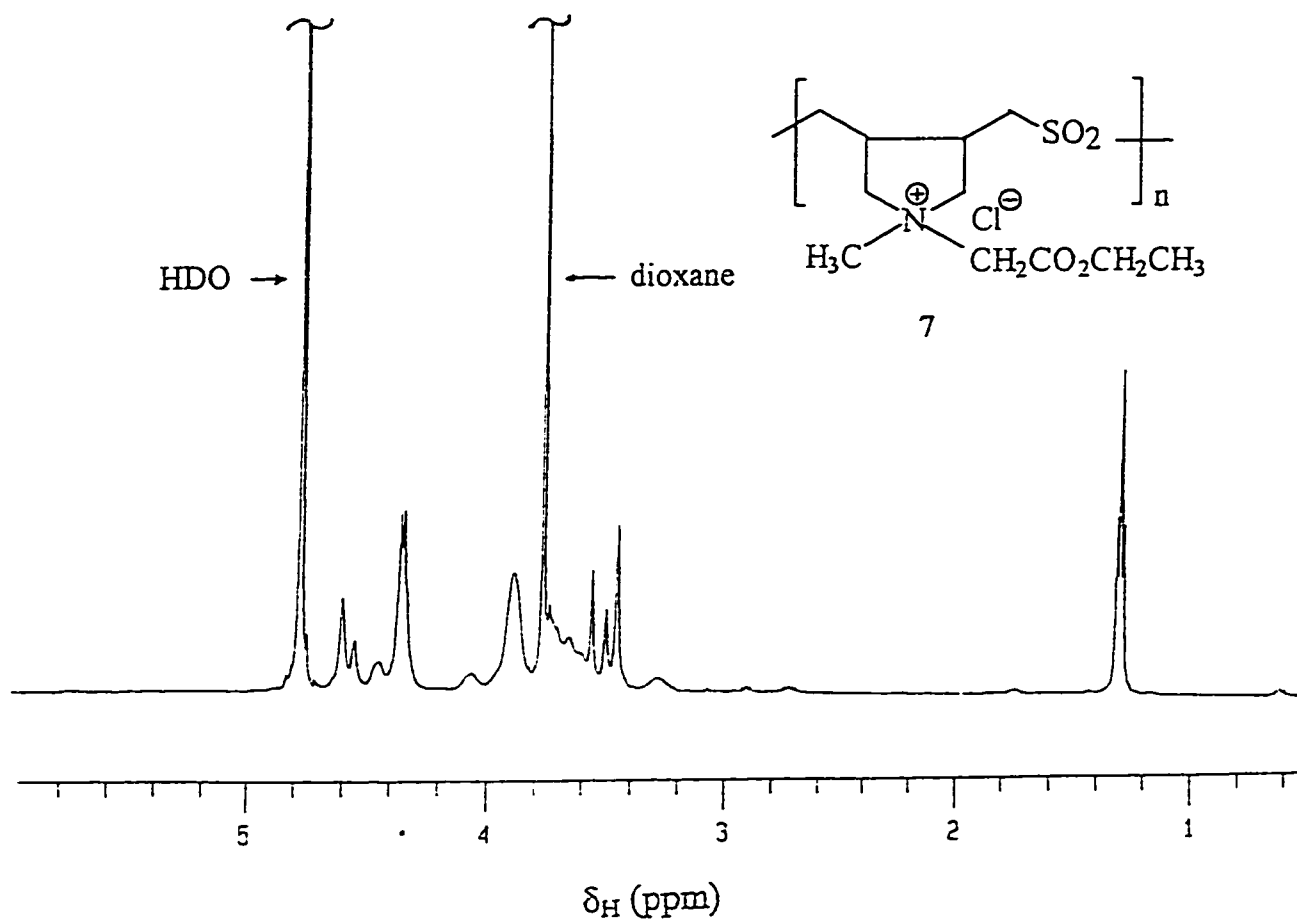


Figure 39 ^1H NMR Spectrum of hydrolyzed copolymer **13** in D_2O

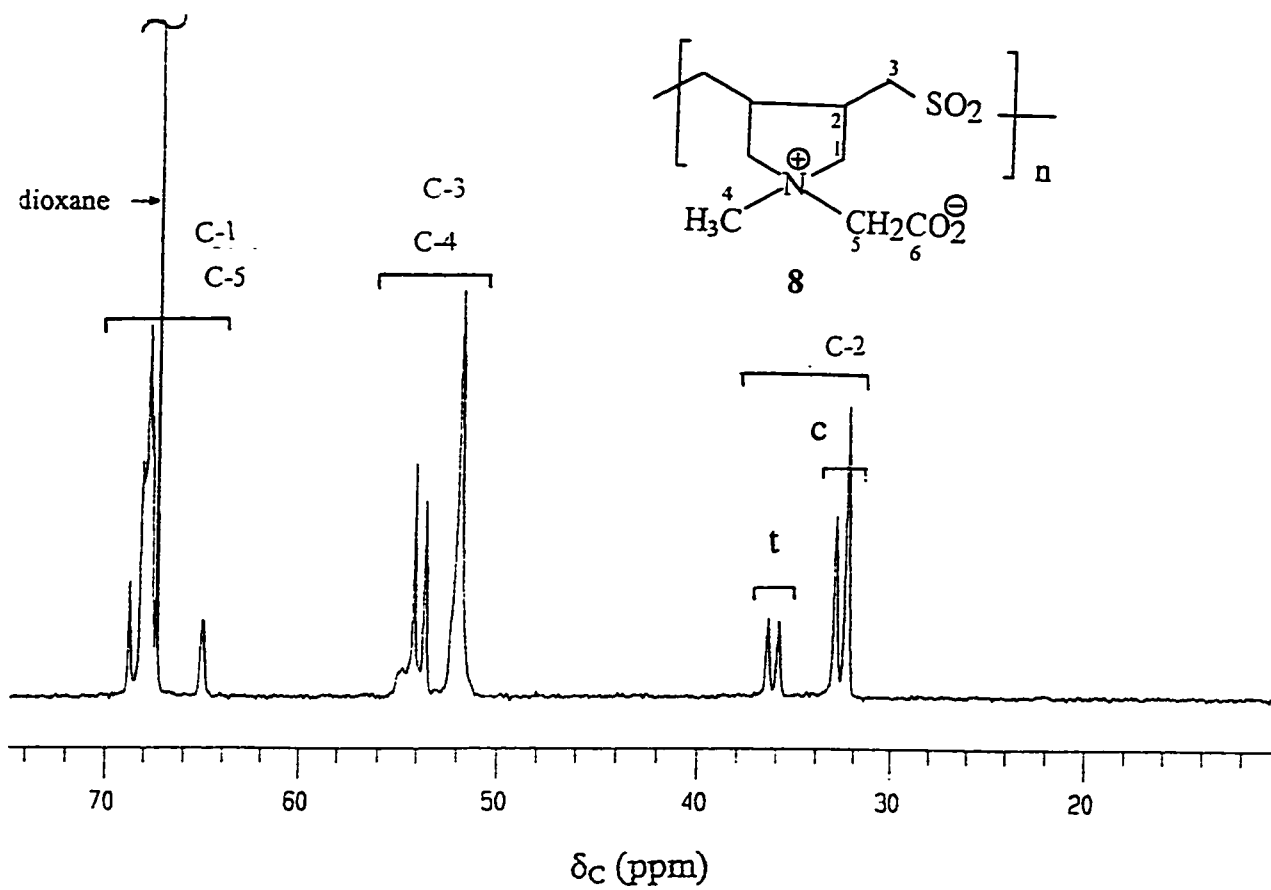


Figure 40 ^{13}C NMR Spectrum of hydrolyzed copolymer 13 in D_2O

As anticipated for zwitterionic polymers the polyampholyte (13) was insoluble in water but dissolved readily in aqueous solutions of salts including divalent cation, Ca^{2+} which is known to precipitate out polyelectrolytes. Such behaviour has been interpreted^{51,54} by assuming presence of collapsed coil in water as a result of inter- and intra-chain interactions leading to a 3-dimensional ionic network (or ionic crosslink). For the solubilization of polyampholyte in aqueous salt solution, the low molecular weight anions and cations of the added electrolyte enter the ionically crosslinked network of the polymer through osmotic forces. These forces causes the polymer to swell when placed in water. The insolubility of the polyampholyte (13) in water could be attributed to the fact that the osmotic force which draws water into the polymer is not of sufficient strength to rupture the ionic crosslinks. The polymer swells until the osmotic forces are balanced by the elastic forces of the network. In the presence of added salt, the solvent as well as the mobile ions are drawn into the polymer and swelling happens. However mobile ions of the added salt neutralize a portion of the ionic crosslinks and as such the elastic forces which opposes continued swelling are gradually decreased and swelling continues until the gel finally dissolves.

Effect of cation and anion on the viscosity behaviour of the polyampholyte (13) is given in Table 8. Intrinsic viscosity is a measure of the hydrodynamic volume of the polymer. The intrinsic viscosity in the presence of different electrolyte should indicate the influence of these added salts on the hydrodynamic volume of the polymer chain. The reduced viscosities of the polyampholyte in aqueous KCl, KBr and KI solutions of the same added salt concentration (0.5 M) were studied as illustrated in Figure 41 (Table 8).

**Table 7: Critical Salt Concentration
for aqueous solutions of
polyampholyte (13) at 23°C**

Salt	CSC (M)
LiCl	0.992
NaCl	0.069
KCl	0.070
KBr	0.014
KI	0.0026
NH ₄ Cl	0.073
CaCl ₂	0.306
(C ₃ H ₇) ₄ NBr	0.012

Iodide anion being most polarizable and effective in neutralizing the cationic charge on the backbone increases the hydrodynamic volume hence viscosity of the polyampholyte. An analogous viscosity experiment was carried out using a common anion Cl^- and the results obtained are shown in Figure 42 and Table 8.

The viscosity behaviour of NaCl and KCl are found to be similar whereas that for LiCl and CaCl_2 was different. It is interesting to note that the cation and anion effects observed in the viscosity measurement were similar to those observed in the cloud point determination experiments. The viscosity data in presence of $(^n\text{C}_3\text{H}_7)_4\text{NBr}$ and in solvent formamide in absence of added salt are presented in Figure 43 and 44, respectively.

The effect of salt concentration on viscosity was determined for the polyampholyte (13) using various concentration of NaCl was determined. Viscosity data and Huggin's constant, k' , determined using Huggin's equation, were presented in Table 9 and Figure 45.

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 \quad (\text{Huggin's equation})$$

It is possible to consider Figure 43 as composed of two straight lines. The first line with a higher slope is attributed to the site binding of the Cl^- by the positive centre on the polymer chain. The second line with a lower slope is characterized by a slower rate of change of intrinsic viscosity and may be due to atmospheric binding of the anion by the polyampholyte. Further it may be seen from the Table 9 that as the NaCl concentration increases the slope increases, the Huggin's constant, k' decreases and the intrinsic viscosity increases. This decrease in Huggin's constant may be associated with an increased solvent-polymer interaction.

Table 8: Effect of anion and cation on the viscosity behaviour of the polyampholyte (13) at 30°C in water containing 0.5 M

H ₂ O (0.5 M)	Intrinsic Viscosity (dl/g)
KCl	0.652
KBr	0.811
KI	0.833
LiCl (1.5 N)	0.178
NaCl (1.5 N)	0.917
NaCl	0.652
KCl	0.652
NH ₄ Cl	0.623
CaCl ₂	0.474
(C ₃ H ₇) ₄ NBr	0.874
Formamide	0.859

Table 9: Effect of NaCl concentration on the intrinsic viscosity and Huggin's constant k' of polyampholyte (13)

NaCl Conc. (M)	Intrinsic viscosity (dl/g)	k'
0.1	0.325	0.709
0.2	0.425	0.602
0.3	0.534	0.458
0.5	0.652	0.382
1.0	0.814	0.369
1.5	0.917	0.340
2.0	1.02	0.324

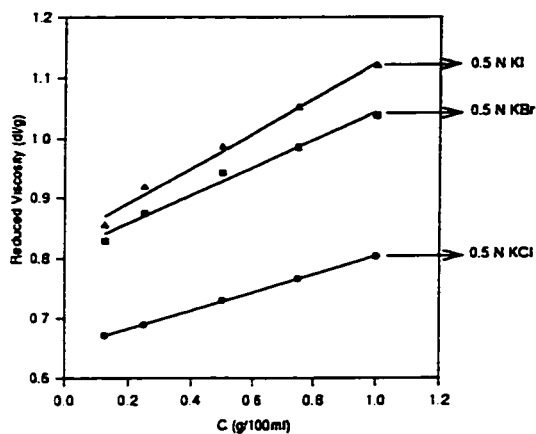


Figure 41: Viscosity behaviour of polyampholyte 13 in salts of common cation, K^+

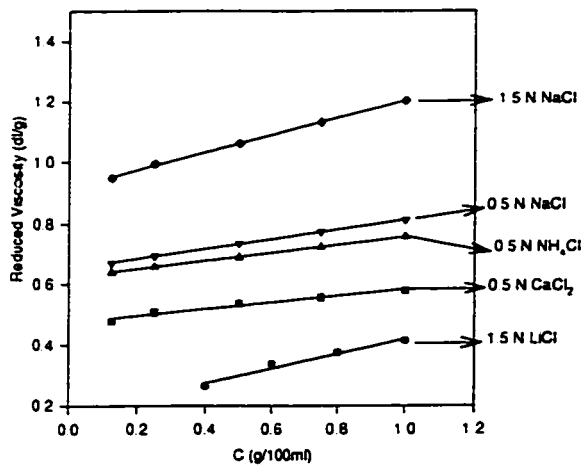


Figure 42: Viscosity behaviour of polyampholyte 13 in salts of common anion, Cl^-

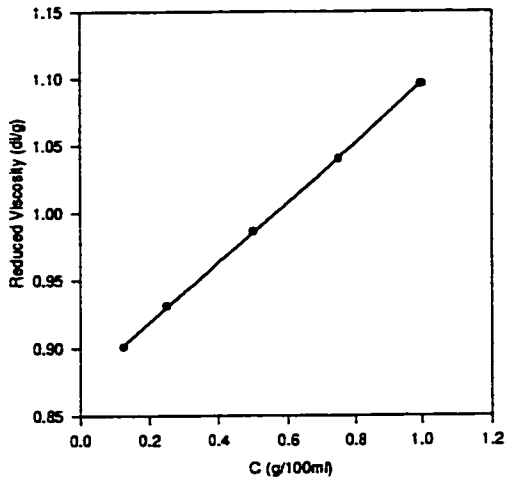


Figure 43: Viscosity behaviour of polyampholyte 13 in $n(C_3H_7)_4NBr$

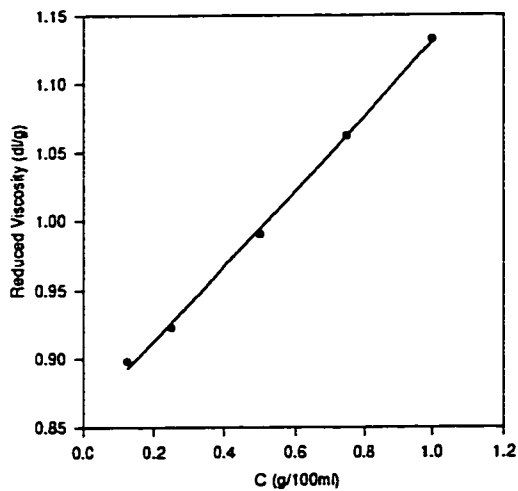


Figure 44: Viscosity behaviour of polyampholyte 13 in formamide

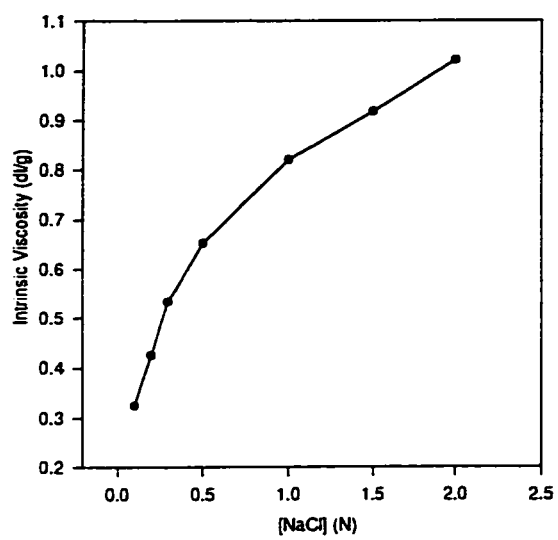


Figure 45: Effect of NaCl concentration on intrinsic viscosity for polyampholyte
13

CHAPTER 4

CONCLUSION

Polyampholytes present great potential for application due to their interesting aqueous solution properties⁷⁴. The solubility in water is controlled by electrostatic interactions and enhanced viscosity upon increasing ionic strength makes the polymer well adapted to high salinity media. One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the drastic decrease of the viscosity of their solutions upon increasing ionic strength. The antipolyelectrolyte effect observed for the polyampholytes can be enhanced by proper hydrophobic modification of the polyampholyte. The polyampholyte (11) and (13) in this study were synthesized in excellent yields. The high intrinsic viscosity and salt tolerance associated with the copolymer 13 paves the way to prepare hydrophobically modified polyampholyte (terpolymer) of the type 13 containing few mole percent of long chain hydrocarbon attached to the nitrogen in place of the N-Methyl group. The synthesis and solution properties of these polymers would indeed enrich the relatively limited literature on polyampholytes.

CHAPTER 5

EXPERIMENTAL

All m.p.s. are uncorrected. Elemental analysis were carried out in Carlo-Erba elemental analyzer Model 1102. Ir spectra were recorded on Perkin Elmer PC 16 FT-IR and are reported in wave numbers (cm^{-1}). ^1H NMR spectra were measured in solvents as mentioned using TMS as internal standard on a Jeol 500 spectrometer. Viscosity measurements were made by Ubelohde. Deionized water was used in polymerization reaction under nitrogen atmosphere. Ammonium persulfate and t-butylhydroperoxide (80% in ditertiarybutylperoxide) were used as received. Chromatographic separations were carried out by flash silica. All glassware were cleaned using deionized water. All chemicals were used as received.

5.1 *N,N*-Diallyl-*N*-Methylamine

A modified literature procedure⁷¹ for the reaction of methylamine with allyl chloride was followed for the synthesis of diallylmethylamine. A solution of methylamine hydrochloride salt (67.5 g, 1.00 mol) in water (40 cm³) in a three-necked round-bottom flask placed in an ice bath was agitated vigorously with a mechanical stirrer. Allyl chloride (168.4 g, 2.2 mol) and a solution of sodium hydroxide (140 g, 3.5 mol) in water (140 ml) were added separately over a 2 hour period. The slurried mixture was then agitated at 0°C for 1 hour, at 36°C for 3 hour and at 60°C for an additional 3 hour. The mixture was cooled and filtered. The residue was washed ether (100 cm³). The organic layer was separated and the aqueous layer was extracted with ether (3×150 cm³). The combined organic extract was dried over NaOH (50g) and fractionally distilled at atmospheric pressure through a 15 inch Vigreux distilling column. The product (70 g, 62.8%) was collected at 110-112°C as a colourless liquid.

δ_{H} (200MHz, CDCl₃) 2.20 (3H, s), 3.00(4 H, d, J 7.0 Hz), 5.20(4 H, m), 5.92(2 H, m).

5.2 *N,N*-Diallyl-*N*-Carboethoxymethyl-*N*-methyl Ammonium Chloride (8)

A solution of *N,N*-diallyl-*N*-methyamine (55.5 g, 0.50 mol) and ethyl chloroacetate (100 g, 0.82 mol) was stirred at 20°C. After 24 hour the reaction mixture contained two layers which on further stirring over 24 hour became one layer. The ¹H NMR spectrum revealed the absence of any unreacted amine. The reaction mixture (viscous liquid) was agitated with ether (3×100 cm³) and each time the upper ether layer was decanted off. This

was done in order to remove excess ethyl chloroacetate. Finally the thick liquid was slurried in methanol (30 cm³) and poured over magnetically stirred ether (150 cm³). The upper layer was decanted off. The thick viscous colourless liquid was dried under vacuum at 50°C until constant weight (111g, 95%). When kept in the refrigerator the viscous liquid was crystallized as colourless crystals, m.p. 55-59°C (Closed Capillary).

(Found: C,56.3 ; H,8.7 ; N,5.9 ; C₁₁H₂₀NO₂Cl requires C,56.52 ; H,8.63 ; N,5.99%).

ν_{\max} (KBr) 3442, 2984, 2940, 1748, 1638, 1472, 1422, 1386, 1306, 1226, 1126, 1028, 954, 924 and 860 cm⁻¹.

δ_{H} (CD₃OD, 200mhz) 1.30 (3H, t, J 7.0 Hz), 3.27 (3H, s), 4.32 (8H, m), 5.77 (4H, m), 6.14 (2H, m).

δ_{C} (D₂O) 14.5, 49.8, 59.7, 64.8, 66.4, 125.1, 131.2, 166.5 (dioxane 67.8 standard).

Because of hygroscopic nature, the quaternary ammonium salt was stored inside desiccator.

5.3 Polymerization of (8) using tert-butylhydroperoxide

A solution containing 70% monomer by mass was prepared by adding the monomer (4.049 g) and deionized water (1.735g) in a 10 cm³ round bottomed flask. To the reaction mixture was added 8 drops (40 mg) of tert-butylhydroperoxide and the contents in the closed flask was stirred at 50°C for 24 hour and 70°C for 24 hour. Viscosity of the mixture did not change and there seemed to be no polymerization. The ¹H NMR spectrum revealed the absence of any polymer. Upon pouring the reaction mixture into acetone no white precipitate was obtained indicating the absence of any polymer.

The above reaction was repeated under similar conditions using different initiators [benzoyl peroxide (55 mg), hydrogen peroxide (30%, 80 mg), metachloroperbenzoic acid (50 mg)]. However no polymerization product was obtained.

5.4 General Procedure for the Polymerization of (8) using Ammonium Persulfate

In a 10 cm³ round bottom flask containing a magnetic stirrer, was taken the monomer (5.0 g). Appropriate concentration of the monomer was achieved by adding deionized water. The flask was purged with N₂. The closed flask was heated to 75°C and briefly opened under N₂ to add the initiator ammonium persulfate. The mixture was stirred and heated at 90°C for 1 hour. After 5-10 minutes of the addition of the initiator, the solution became viscous. At the end, the transparent viscous liquid was poured onto acetone (25 cm³). Acetone was decanted off. The polymer (sticky semisolid) was dissolved in methanol (5 cm³) and coprecipitated in acetone (25 cm³). The process was repeated three times. The white polymer was dried under vacuum at 60°C until constant weight. Because of the hygroscopic nature, the polymer was stored inside desiccator. m.p. (closed capillary) 355-370°C (colour turned to faint yellow toward the end).

Found: C, 56.1; H, 8.8; N, 5.85. C₁₁H₂₀NO₂Cl requires C, 56.52; H, 8.63; N, 5.99%

ν_{\max} . (KBr) 3454, 2980, 2940, 1748, 1636, 1468, 1420, 1386, 1226, 1118, 1028, 924 and 860cm⁻¹.

5.5 General Procedure for the Copolymerization of the monomer (8) with SO₂

The solvent DMSO was dried over CaH₂ (24 hour) and distilled under vacuum keeping the bath temperature around 70-80°C. A stock solution of SO₂ in DMSO was prepared by absorbing known amount of SO₂ in a known quantity of DMSO. In one such case, 0.274 g of the stock solution was found to contain 1.00 mmol of SO₂. To a dry flask (25 cm³) containing the monomer (10.0 g, 42.8 mmol) required amount of SO₂ was added from the DMSO-SO₂ stock solution. Sometimes free DMSO was added for dilution. The mixture in the closed vessel was briefly heated at 50°C with stirring to achieve a homogeneous solution. The required amount of APS (as listed in the Table 5) was added and the closed flask was magnetically stirred at 50°C for 12 hour. The reaction mixture viscosified within 10-20 minutes after addition of the initiator and the magnetic stirrer stopped moving after 1 hour. The reaction mixture remained transparent throughout the polymerization process. The mixture was dissolved in methanol (20 cm³) and precipitated in acetone (150 cm³). This process was repeated three times. The resulting hygroscopic white polymer was dried at 50°C under vacuum until constant weight.

m.p. (Closed Capillary) 240-250°C (decomposed, turned brown).

(Found: C, 44.0 ; H, 6.8 ; N, 4.55. C₁₁H₂₀NO₄ClS requires C, 44.36 ; H, 6.77 ; N, 4.71%)

ν_{\max} . (KBr) 3430, 2984, 2940, 1748, 1638, 1472, 1422, 1386, 1306, 1226, 1126, 1028, 954, 924 and 860 cm⁻¹.

5.6 Acidic Hydrolysis of the Homopolymer (10)

A solution of the homopolymer (10 g) in water (80 cm³) and conc. hydrochloric acid (80 cm³) was stirred in a closed flask at 40°C for 96 hour (or until the hydrolysis of the ester group was completed as indicated by disappearance of ethyl proton signals in the NMR spectrum). The aqueous solution was then dialyzed against deionized water (to remove HCl). The solution was then basified with excess NaHCO₃ and again dialyzed against deionized water to remove excess NaHCO₃ (checked by AgNO₃ test). The polymer solution was then freeze dried and finally the flaky white polymer was dried at 60°C under vacuum until constant weight is obtained. Yield: 6.1g (84%) m.p. (Closed Capillary): did not melt even at 400°C. At 300°C onwards the colour changed to yellowish brown.

(Found: C, 63.4 ; H, 9.15 ; N, 8.1. C₉H₁₅NO₂ requires C, 63.87 ; H, 8.93 ; N, 8.28%)

ν_{\max} . (KBr) 3442, 2924, 1628, 1460, 1402, 1332, 1226, 1002, 900cm⁻¹.

5.7 Acidic Hydrolysis of the Copolymer (12)

A solution of the copolymer (10.0 g) in water (100 cm³) and concentrated HCl (100 cm³) was stirred at 40°C for 96 hour (or until the hydrolysis was complete as indicated by ¹H NMR spectrum). During the hydrolysis, the homogeneous solution became heterogeneous at the end of the second day. The hydrolyzed polymer was slowly separating. At the end, the solution was cooled to room temperature and the aqueous layer was decanted off leaving the polymer in the flask. The polymer was washed with distilled water (2×30 cm³). Then 50 cm³ of water was added to the polymer and the polymer was neutralized by addition of NaHCO₃. After the polymer was completely dissolved, the

aqueous solution was dialyzed against deionized water to remove excess NaHCO_3 (tested by AgNO_3 test). During dialysis the polymer kept depositing on the walls of the dialysis bag. At the end the polymer was collected and soaked in acetone and kept overnight. The white polymer was dried at 50°C under vacuum until constant weight was obtained. The polymer was stored inside desiccator. Yield: 6.7g (85.5%).

m.p. (Closed Capillary) $270\text{-}280^\circ\text{C}$ (turned dark brown)

(Found: C, 46.0 ; H, 6.6 ; N, 5.85. $\text{C}_9\text{H}_{15}\text{NO}_4\text{S}$ requires C, 46.33 ; H, 6.48 ; N, 6.00%).

ν_{max} . (KBr) 3422, 2972, 2926, 1628, 1458, 1394, 1300, 1126, 906 cm^{-1} .

5.8 Solubility measurements and cloud point titrations in aqueous salt solutions

Solubility of the polyampholytes in organic solvents at room temperature was established for the 1% wt/wt solution, after preheating at 70°C for 1 hour.

The Critical (minimum) Salt Concentration (CSC) required to promote water solubility at 23°C was measured by titration of 1% wt/wt polymer solution at sufficiently high salt concentration with deionized water. The accuracy of the CSC values obtained by visual determination of the first cloud point was approximately $\pm 1\text{-}2\%$.

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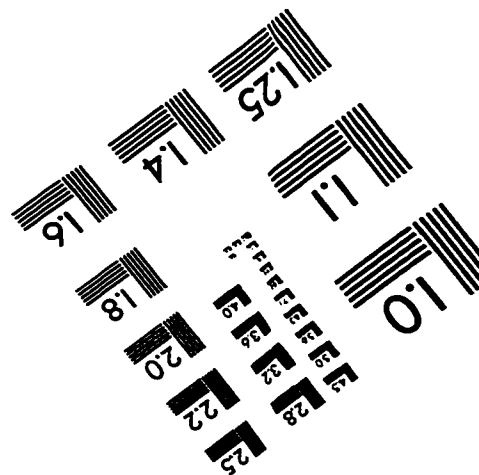
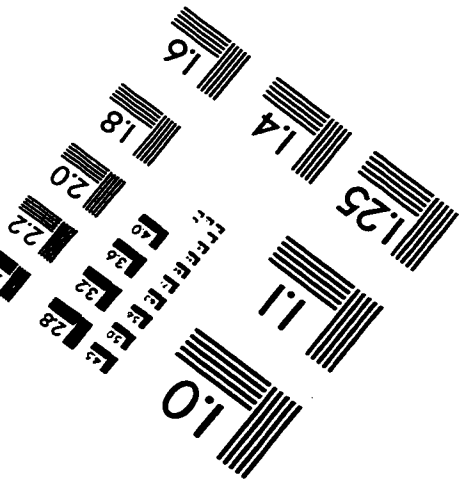
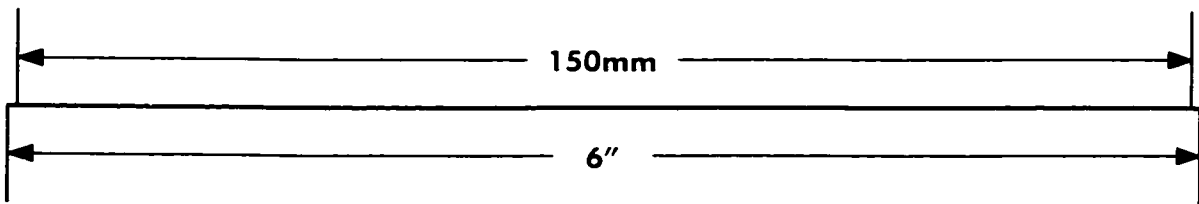
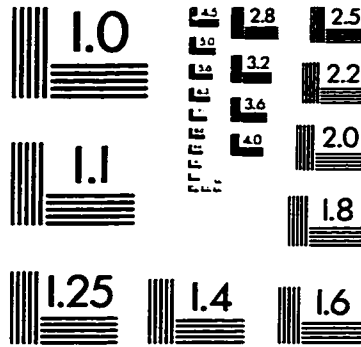
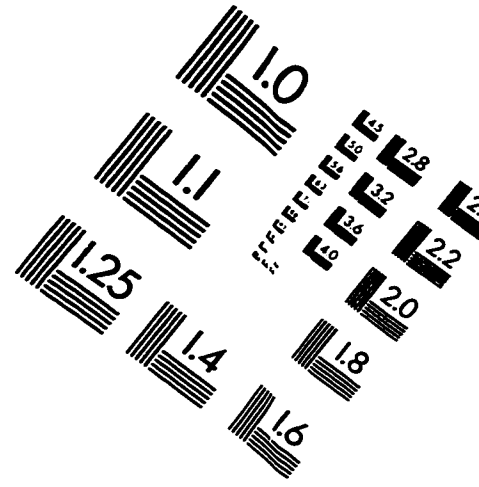
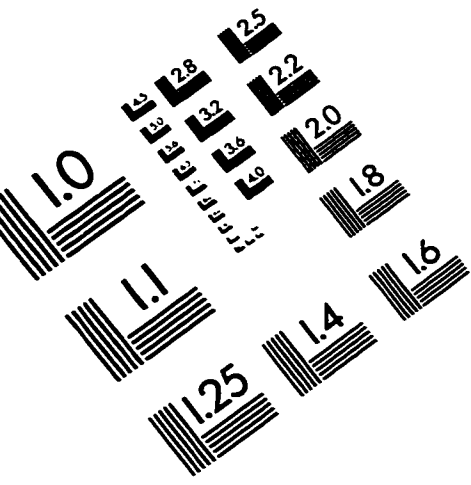
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IMAGE EVALUATION TEST TARGET (QA-3)



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