A Study of Rheology and Interfacial Activity of Amphiphilic block Copolymers for Enhanced Oil Recovery

by

Najib Mohammad A. Al-Hakimi

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

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In Partial Fulfillment of the
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In

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بسم الله الرحمن الرحيم

﴿ وقل ربي زدني علما ﴾

King Fahd University of Petroleum & Minerals
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DEDICATION

۞ This Thesis is dedicated to
My Parents and all Family ۞

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THESIS ABSTRACT

NAME OF STUDENT : Najib Mohammed Ali Al-Hakimi
TITLE OF STUDY : A Study of Rheology and Interfacial Activity of Amphiphilic Block Co-Polymers for Enhanced Oil Recovery
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In this study two types of amphiphilic block copolymers –diblocks and multiblocks-are synthesized, modified, and characterized with the objective of proposing new amphiphilic block copolymers and studying the rheological behavior and surface and interfacial activities for use in enhanced oil recovery operations. Enhanced (tertiary) oil recovery method can recover- if properly designed- a significant part of residual oil that reaches to two thirds after both primary and secondary recoveries. Two systems of polymers mainly heavily studied in this investigation namely poly(acrylamide-block-styrene) and poly(acrylamied-block-dodecene). Other systems which are copolymers of methylmethacrylates are studied along with homopolymers and random copolymers for comparison purposes. Methylmethacrylate copolymers are then hydrolyzed and characterized, samples HD2, HD6, and HD8.

The rheological behavior and surface/interfacial activities of both systems are thoroughly studied with respect to polymer concentration, salinity, shear rate, temperature, storage time, polymer molecular weight and addition of surfactants. The viscosity of di-polyelectrolytes (HD2, HD6, and HD8) exhibit moderate thickening ability and surface and interfacial activity. However, HD2 exhibits a viscosity of 1000 cps at 0.8 shear rate. Also sample HD8 (sodium poly(methacrylaate-block-vinylemadazol) exhibits the highest surface and interfacial activity demonstrated by low values of surface and interfacial tensions (8.1 and 1.87 mN/m respectively) at 1.5 wt% as polymer concentration or 15,000 ppm. Moreover, this copolymer exhibits salt tolerancy beyond 10 wt% NaCl. For other block copolymers it was found that samples E3 or poly(AM-b-C12) and P12 or poly(AM-b-ST) exhibit higher surface and interfacial activities compared to other multi-block copolymers studied. E3 showed low water-polymer interfacial tension of 0.5 mN/m at 10 wt% NaCl. Multi-block copolymer P12 was found to exhibit the highest thickening ability (10,110 cps.) at high salinity (10 wt%) among other copolymers investigated as well as high surface and interfacial activity (43.1 and 1.01 mN/m respectively) at 10 wt% NaCl and polymer concentration of 1.5 wt%. Therefore P12 considered to be a good candidate for enhanced oil recovery operations.

Generally, all systems of block copolymers exhibit typical shear thinning behavior at low shear rates and constant viscosity at high shear rates. Moreover, increasing polymer concentration give rise to an increase in the polymer solution viscosity and an increase in surface and interfacial activities. Also all polymers exhibit smaller decrease in solution viscosity at high temperatures and storage time.

It is concluded from this study that by controlling the distribution of the hydrophobe sequences along the polymer backbone, and its nature/type/level used, and by varying the experimental design conditions, the polymerization route, the polymer architecture, and the micellar concentration, it was found that longer hydrophobic sequences (blocks) give rise to higher degree of intermolecular hydrophobic interactions/associations and therefore to a greater thickening efficiencies to amphiphilic block copolymer solutions. So it is possible to design polymers that have the ability to simultaneously provide high thickening ability and ultra-low interfacial tensions for the requirements in applications of oil recovery operations and for producing high oil quantities.

MASTER OF SCIENCE DEGREE

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خُلاصة الرسالة

إسم الطالب : نجيب محمد علي الحكيمي
عنوان الرسالة : دراسة الانسياب والنشاط البين سطحي للبوليمرات المشتركة القالبية ثنائية الخواص لإستخدامها في إستخراج البترول بالطريقة المعززة
التخصص : هندسة كيميائية
تاريخ التخرج : ديسمبر ١٩٩٦م.

تم في هذا البحث تصنيع أو تعديل ثم توصيف صنفين من البوليمرات المشتركة القالبيةBlock Copolymers ثنائية الخواص Amphiphilic وذلك بهدف تقديم دراسة لسلوك البوليمرات المشتركة من جهة سلوكها الانسيابي (اللزوجة مثلا) والنشاط السطحي والبين سطحي لغرض استخدامها في عمليات إستخراج البترول بالطريقة المعززة. إن إستخراج البترول بالطريقة المعززة يفضي إلى إنتاج كميات كبيرة من البترول تصل إلى الثلثين التي يتبقى بعد العمليات الأولية والثنائية اذا أستخدمت مواد فعالة في التصميم. لقد درس -على وجه الخصوص- نظامين من البوليمرات في هذا البحث بنوع من التعمق: بوليمرات مشتركة للأكريل أمايد Acrylamide والأستايرين Styrene والنظام الأخر أختص بالبوليمرات المشتركة للأكريل أمايد Acrylamide والدوديسين I-Dodecene . أيضا درست أنظمة أخرى لبوليمرات الميثيل ميثا أكريلايت Methylmethacrylate وبوليمرات أحادية وبوليمرات عشوائية لأغراض المقارنة والمفاضلة. وقدتم عمل تحليل مائي Hydrolysis لبوليمرات الميثيل ميثا أكريلايت تم توصيفها بالطرق المعتادة،حيث ان عينات HD2 ، HD6 و HD8 هي بوليمرات اليكتروليتية.

لقد تم دراسة السلوك اللزوجي للبوليمرات مع النشاط السطحي والبين سطحي وذلك مع تغيير تركيز البوليمر ، ودرجة التأين salinity ، ومعدل الشد ، ودرجة الحرارة ، وزمن التخزين ، والوزن الجزيئي للبوليمر ، وأيضا إضافة السرفاكتنت surfactant. ولقد أظهرت البوليمرات التي حللت مائيا لزوجة معتدلة ونشاط سطحي وبين سطحي معتدل. إلا أن العينة HD2 أبدت لزوجة عالية (١٠٠٠ سنتي بويز) عند معدل شد ٠.٨ ولقد أظهرت العينة HD8 (sodium poly(methacrylate-block-vinylemadazol أعلى نشاط سطحي وبين سطحي موضحا بالقيم المنخفضة للشد السطحي والبين سطحي (٨.١ و ١.٨٧ ملم نيوتن/ملم بالتتالي) عند تركيز بوليمري ١.٥ وزن مئوي او ١٥.٠٠٠ جزء من المليون. كذلك ، وجد أن هذه العينة أظهرت تسامحا ملحيا أعلى من ١٠% كلوريد الصوديوم. أما البوليمرات الاخرى وجد أن العينات E3 أو (poly(AM-b-C12 و P12 أو (poly(AM-b-ST لبوليمرات الاكريل أمايد عرضت نشاطات سطحية وبين سطحية عالية مقارنة بالبوليمرات المتعددة الاشتراك المدروسة في هذا البحث. ولقد لوحظ أن العينة E3 أظهرت شد سطحي مع الماء يصل إلى ٠.٥ ملم نيوتن/ملم عند تركيز ملحي ١٠%. ووجد أن البوليمر المتعدد الاشتراك P12 له أعلى لزوجة (١٠.١١٠ سنتي بويز) عند ملوحة عالية ١٠% بين جميع البوليمرات المدروسة. بالأضافة إلى ذلك ، فان هذا البوليمر له شد سطحي وبين سطحي منخفضين (٤٣.١ و ١.٠١ ملم نيوتن/ملم بالتتالي) عند تركيز ملحي ١٠% وتركيز بوليمري ١.٥ وزن مئوي. وهكذا يتبين أن البوليمرP12 هو المرشح الاكثر للأستخدام في عمليات الأنتاج البترولي بالطريقة المعززة.

وبشكل عام ، جميع أنظمة البوليمرات المدروسة تسلك شد ترقيقي نموذجي عند معدلات شد منخفضة ، ووجد أن علاقة اللزوجة مع معادل الشد هي ذات لزوجة ثابتة عند معدلات شد عالية. وأيضا وجد أنه بزيادة تركيز البوليمر ، تكون هناك زيادة في لزوجة المحلول وزيادة في النشاطية السطحية والبين سطحية (قيم منخفضة للشد السطحي). كذلك تبين أن جميع البوليمرات تسلك إنخفاض طفيف في اللزوجة عند درجات حرارة عالية وزمن تخزين طويل.

من هذه الدراسة ، يستنتج أنه بالتحكم بتوزيع المجموعات المتتالية للهايدروفوب hydrophobe على طول سلسلة البوليمر ، وبالتحكم بطبيعة ونوعية ومستوى التوزيع ، وبالتغيير التناوبي في تصميم ظروف التفاعل ، وبتغيير نوعية التفاعل المستخدمة ، وبالتنوع في بنية البوليمر ، وأيضا بالتغيير في التركيز الخلوي

micellar ، كل ذلك أثبت أن وجود مجموعات متتالية هيدروفوبية hydrophobic sequences يعطي درجات عالية من التفاعلات البين جزئية أثناء التفاعل وهذا بدوره يقود إلى درجات لزوجة أعلى لمحاليل البوليمرات المشتركة ثنائية الخواص Amphiphilic block copolymer.

لكل هذه الأسباب ، يتبين من الدراسة أنه بالإمكان تصميم بوليمرات لها مقدرة توفير لزوجة عالية وبنفس الوقت شد بين سطحي عالي الانخفاض لغرض الاستخدام في عمليات الإستخراج البترولي بطريقة التعزيز وذلك بهدف إنتاج بترولي بكميات غير عادية.

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران ، المملكة العربية السعودية
ديسمبر ١٩٩٦م

CHAPTER ONE

INTRODUCTION

1.1 Oil Recovery Stages

In the petroleum industry, oil passes through various stages of recovery: primary recovery, secondary recovery, and tertiary or *enhanced oil recovery* (EOR). In both primary and secondary recoveries, it has been practiced that only 15-20% of the original oil in place (OOIP) can be recovered by each method. Processes that attempt to recover the remaining 60-70% or two-third (2/3), which is significant, termed EOR. These processes of recovery are classified into three categories namely: (1) *thermal recovery*, (2) *miscible flooding operations*, and (3) *chemical flooding operations*. EOR methods are basically aimed at increasing ultimate oil recovery by using mechanisms for displacing oil by injecting appropriate agents not normally present in reservoirs, such as chemicals, solvents, oxidizers and heat carriers. These techniques are actually employed after waterflood approach is no longer economical. So it is of great importance for either small or big oil producing countries to recover this substantial amount of oil, about two-third, trapped in reservoirs specially because of the existing world oil dwindling reserves. Actually this kind of development should particularly concern those countries that have relatively small oil reserves recoverable by conventional techniques, primary or secondary processes. While these EOR methods address the need to reduce either oil viscosity, oil-brine interfacial tension, or repressurize the formation, many deficiencies still exist which limit the amount of additional oil recovery.

In *thermal flooding*, for example, steam or in-situ combustion is used to reduce oil viscosity by heating the reservoir so that oil can easily be mobiled to the production wells. Carbon dioxide is usually used as a miscible fluid (*miscible flooding*) with the oil and provides reduction in capillary forces that are highly responsible for microscopic displacement efficiency of water and gas. By the reduction of capillary forces, oil-water interfacial tension (IFT) is significantly lowered and hence oil recovery effectiveness is highly improved.

Chemical flooding is the most current efficient used method, but also the one that still requires the greatest effort of research to reduce the cost efficiency ratio. Chemical flooding techniques, that make use of polymers, surfactants, miscible hydrocarbons, alcohols, alkali, and other reagents, are always accompanying water flooding in many ways.

Polymer flooding and Surfactant-Polymer Flooding (SPF) techniques are widely used in EOR operations [121, 122]. These techniques are mainly based on the injection of chemicals that modify field properties, i.e. reducing fingering of the drive fluid (water). Thus reducing the mobility of the aqueous phase or the displacement fluid (polymers plus water) relative to the oil bulk phase and consequently improving the sweep efficiency in favor of oil production. It is well known that polymer flooding can reach reservoir areas unreached by water flooding. The improvement of the reservoir in arial sweep is called the *macroscopic displacement* [23, 123]. An increase in the *microscopic displacement*, however, may be possible by the interfacial tension between the polymer solution and the oil. In Surfactant-Polymer flooding, for example, polymers act only on sweep efficiency at a microscopic scale by increasing the displacing fluid viscosity and hence help provide mobility control, low mobility ratio. While large quantity of surfactants are designed to reduce the capillary number by the reduction of capillary forces, which limits the microscopic displacement efficiency of water, and yield low oil-water interfacial tension. Capillary forces, which govern the situation, are of great technological importance in oil recovery [21, 23, 27, 129].

1.2 Conventional Chemical EOR Techniques

Although *Surfactant-Polymer Flooding* (SPF) method is widely used, it involves, however, significant problems associated with the technique. Problems such as, (1) high polymer sensitivity to mechanical shear stresses encountered during injections, (2) high incompatibility between surfactants and polymers that leads to materials adsorption on rock surfaces, (3) high reduction in the polymer thickening ability inside the formation due to the presence of salts, (4) high loss of polymers and surfactants that adsorb on reservoir rocks, and others. It is worth to note that polyacrylamides (PAM) and partially hydrolyzed polyacrylamides (HPAM) are conventionally heavily used in polymer-surfactant method but still they have major drawbacks.

The thickening ability of PAMs and HPAMs basically relies on a combination of high molecular weight and chain expansion. The latter feature is mainly due to the repulsion of pendent ionic groups, carboxyl groups, along the polymer chain. However, high molecular weight polymers mechanically degrade when subjected to large elongational or shear stresses such as those found in pumps or compressors during injection into reservoir rocks in oil recovery operations. Such degradation that either caused by the breakdown of chains, molecular scission, or by the hydrolysis of PAM result in permanent reduction in polymer molecular weight and in turn loss of viscosification efficiency. Work has been made to control the extent of hydrolysis or the amount of anionically charged carboxyl groups, to minimize adsorption during recovery, by controlled hydrolysis of PAM. Hydrolysis of PAM in high temperature reservoirs is notorious because it leads to viscosity changes and phase separation (precipitation). Studies, however, indicate that hydrolyzed polyacrylamides (HPAM) increasingly mechanically degrade during injection into porous media owing to the presence of divalent cations, such as calcium and magnesium ions, in reservoir. Cations in aqueous solution, in particular divalent cations, shields/screens the ionic charged groups on the polymer causing it to collapse into random coil configuration having a smaller hydrodynamic volume, a charge shielding or *polyelectrolyte effect*. These mechanism causes great loss in viscosification efficiency. Thus, mobility control agents based on another alternative mechanism of viscosification providing improved mechanical stability and salt tolerance relative to PAM and HPAM polymers would be highly desirable.

The chemical and physical interactions that polymer solutions encounter in the reservoir are extremely complex. The ideal polymer must withstand harsh reservoir conditions like high temperatures, i.e. 70-110 °C, for long period of time under various levels of pH, ionic strength, pressure, flow rate, substrate heterogeneity, and shearing. The polymer must resist shear degradation and must not adsorb permanently on rock surfaces. Multi-valent cations present in the aqueous solution can lead to intermolecular interactions on charged polymers (*polyelectrolytes*) causing crosslinking, gel formation, precipitation, and eventually pore clogging [23]. Chromatographic effects on the macromolecules can also be yielded due to the variety of pore sizes of reservoir. Since the larger molecules are excluded from smaller pores, they bypass them in route to larger pores. This eventually results in loss of mobility control owing to polymer slug dispersion. Moreover, oil entrapped in small pores may be completely bypassed, a mechanical entrapment. The polymer must produce large viscosity at low concentrations (i.e. < 1000 PPM) for economical reasons; therefore, large solution dimensions (HDV) of the macromolecule must be maintained. Also polymer solution viscosity must be maintained at elevated temperatures for achieving uniform oil displacement and in turn improving oil recovery as it was investigated for graft and random copolymer architectures [9, 20, 27].

1.3 New Polymers Synthesized for EOR

The yield of the processes mentioned earlier, however, can be further improved by overcoming the main disadvantages of conventional polymers, i.e. PAM & HPAM. This has been investigated, in this study, by using *amphiphilic polymers* that can associate or aggregate in aqueous solutions rather than remain dispersed as single isolated chains. When associative polymers dissolve in aqueous brine solutions, they have the ability to substantially increase the viscosity of the aqueous solution through association. This association is promoted by incorporating hydrophobic moieties to the polymer backbone, moieties in the range of 0.2-2 mol%. Hydrophobic compounds are hydrocarbons that are immiscible with water (nonpolar). Hydrophobic groups in associative polymers aggregate in solution to minimize their exposure to water, in a fashion analogues to that of surfactants above certain concentration called the critical/overlap micelle concentration. Association causes the formation of aggregates, like *micelles* in the case of surfactants, with large hydrodynamic radii (HDR) which is the key factor for the polymer thickening ability. Moreover, such association in solutions is reversible when subjected to shearing force. Also, the enhanced viscosification that is achieved using these associative polymers is mainly due to intermolecular hydrophobic associations/interactions in solutions [10, 23, 47].

The rheological properties of water-based fluids can be controlled with a class of associative copolymers such as hydrophobically associating *block copolymers* or hydrophobic polyelectrolytes. Hydrophobically associating polymers (HAPs) are synthetically derived water-soluble polymers that contain small number of oil-soluble or hydrophobic groups, (Bektruov and Bakauov in 1986 as polymeric surfactants [106, 195]). McCormick, Bock, Schulz, and Wang have also reported in 1987/88 on the utility of HAPs as rheology modifiers [3, 4, 30, 184]. Investigators, however, did not study the possibility of employing HAPs or amphiphilic polymers in the prospective of replacing both polymers and surfactants used in EOR operations. Block copolymers of this type are investigated in this study in an attempt to provide low oil-water IFT (due to their amphiphilic nature that they share with surfactants) and at the same time provide mobility control for EOR operations.

For the last decade, there has been a substantial interest in water-soluble hydrophobically associating polymers. Research have been concentrated in this area include copolymers of acrylamide and hydrocarbon derivatives of acrylates, methacrylates or alkylacrylamides and hydrocarbon derivatives of cellulose-based polymers [8, 9, 68]. This interest has been increased over the years owing to the extensive technical applications for such polymers in areas such as EOR, cosmetics, detergents, paper making industry, paints, metal working/hydraultic/drilling fluids, mineral/ceramic/material processing systems and in biology/medicine systems. Di-block and multi-block copolymers, based on different monomers that one block possesses hydrophobic nature and the other hydrophilic, are synthesized and characterized as candidates for EOR operations in this study. The polymerization route and solution behaviors/properties of these copolymers are investigated as well.

Chemical engineers collaborate with petroleum or reservoir engineers in investigating solution chemical properties and behaviors and designing materials suitable for EOR operations. The role of chemical engineers in providing fluid flow mechanisms, heat and mass transfer operations, interfacial phenomenon, multi-component adsorption, thermodynamics of solutions, and developing new techniques for enhancing oil production is of great contribution to petroleum industry. The ideal polymer should exhibit no adsorption, good injectability, compatibility with brine and other additives, long term stability against high temperatures, high shear stress and micro-organisms, a low mobility ratio of about one and a reduced interfacial tension (IFT) to improve microscopic displacement.

The advantage of associative block co-polymers over high molecular weight (MW) samples (nonionic homo-polymers; i.g. polyacrylamides), is that under increasing shear the physical links between chains are disrupted but reform back with decreasing shear, a reversible mechanical behavior in which the material viscosity is conserved. On the other hand, high (MW) samples are irreversibly mechanically degrade when subjected to high shear stresses that are usually experienced during injection into subterranean oil-bearing formation. Furthermore, HAPs can produce a constant or even an increasing viscosity as temperature or electrolyte increases. Such properties give rise to particular rheological behaviors as a function to shear rate, i.e. shear thinning and/or thixotropic behaviors, a non-newtonian flow behavior. In addition, hydrophobically associating block copolymers of nonionic type are found to be highly salt tolerant materials even at high temperatures, a property of great importance to chemically EOR operations.

A property of most hydrophobic/associative polymers, which has not been advantageously taken for EOR processes, is their ability to reduce the interfacial tension. The reason for this is the amphiphilic nature of these polymers that share with surfactants, which are amphiphilic compounds as well. The degree of surface/interfacial activity is a strong function of polymer structure [15]. Amphiphilic compounds; i.g. soaps, surfactants, and detergents, are those that consist of both hydrophilic moiety (polar) and hydrophobic one (non-polar) in the same molecule. This definition holds whenever water is the solvent. Copolymerization of hydrophilic monomer with hydrophobic monomer can result in an **amphiphilic water-soluble block copolymer** by appropriate polymerization route, usually free radical copolymerization. Block copolymer structure has a marked effect on solution properties and therefore flow behaviors. An advantage of such copolymers is the compatibility with surfactants due to the presence of association. In surfactant-polymer technique, however, the concept of polymer compatibility with surfactant does not exist owing to the competition for association by surfactant molecules with polymer molecules which is usually result in a reduction in polymer solution viscosity [15].

Amphiphilic molecules self-assemble in aqueous solution above a well-defined critical concentration to form large aggregates known as micelles that can either have a cylindrical or a spherical geometry depending on molecular architecture, solution composition, and the temperature [22]. Such configuration has a profound effect on aqueous solutions. Amphiphilic compounds tend to concentrate as a mono-layer at a water interface, with the tendency increasing both the hydrophilic and hydrophobic character of the amphiphile become more pronounced. At the interface these compounds are rearranged so that the hydrophilic portion remains in contact with the aqueous solution while the hydrophobic portion is removed from the water. Such molecular orientation is responsible for sharp reduction in surface or IFT observed experimentally when small quantities of amphiphile are added to an aqueous solution. For this reason these compounds are called surface -active agents, active at the surface or interface [22].

Although the air-liquid surface tension of small molecules has been studied, very little work is available on liquid-liquid interfacial tension of copolymers in general, and block copolymers in particular. In addition, no work has been done on optimizing the block copolymer structure to simultaneously establish high viscosity and low surface/interfacial tensions for applications in areas such as EOR. One work has been done, parallel to this work, on optimizing the polymer structure of random and alternating copolymers to simultaneously provide high viscosity and surface/IFT activity for EOR processes [16, 17, 98].

1.4 Role of Capillary and Viscous Forces

Mobility control and *capillary number* concepts are of great technological importance in all oil recovery processes mentioned earlier where each works with different mechanism and for different kind of oil or reservoir. Mobility has to do with movements or microscopic displacement efficiency of the reservoir fluids relative to each other. Capillary number or sweep efficiency is related to the interactions of the chemicals in the reservoir. For example adding a polymer to an aqueous solution would improve not only sweep efficiency, that is achieved by high viscosification to aqueous solutions relative to the oil, but also enhances microscopic displacement efficiency and eventually improves oil recovery [23, 95].

A variety of processes are designed to eliminate or at least reduce the so-called "surface forces" within the crude-oil-displacing fluid-reservoir rock system in the past decade. When displacement is carried out by flooding with an immiscible fluid such as water or gas, the surface forces or capillary forces are responsible for trapping a large portion of the oil within the interstices (rock pores) and therefore limit the recovery efficiency of displacement processes [22]. Capillary forces will clearly be eliminated if the drive fluid is preceded by a slug of bank of fluid which is miscible both the reservoir oil and with the displacing phase. Water-soluble surfactants, such as petroleum sulfonates, can be employed to eliminate the tendency of the oil phase to remain trapped in the pores of the rock, i.e. low-tension water flooding. Thus in order to achieve ultra-low values of the oil-water interfacial tension and therefore good oil sweep efficiency and/or improved microscopic displacement and eventually improved oil recovery, different mechanisms have to be designed.

The driving/displacing fluid such as water should control the mobility of reservoir fluids. So mobility control (or control of viscous forces) is an important aspect in reservoir flooding otherwise the pusher fluids, i.e. water, would breakthrough ahead of the oil (fingering). In principle, fluid thickeners can be added to the driving fluids to make them more viscous than the oil phase so that such fluids can push the oil ahead through the pores into the production wells.

1.5 Study Objectives

The possibility of increased efficiency and thus better economics in the coming future will depend upon new laboratory discoveries. Improving enhanced oil recovery (EOR) chemical methods through investigations and applications permits the reach of ideal polymers that can replace mobility control agents and surfactants used in conventional techniques.

Present commercial copolymers, with one or two exceptions, have not been tailored for EOR use. The efficient oil recovery is of great importance to oil producing countries to increase their limited reserves. Moreover, when water-flooding technique is no longer economical after primary and secondary recoveries. At this point oil remaining in the earth accounts for **two-third** of the original oil in place. Such significant quantity of oil can be recovered by improving both arial and vertical sweep efficiency and/or by reducing the interfacial tension between flood media and oil. So, indeed EOR is an on going technology open to great improvements.

The ultimate goals of this research are, first to design a hydrophobically modified block copolymer that is useful in increasing oil recovery during water flooding operations and, second to study the solution behavior of such copolymers so as **to simultaneously provide mobility control and ultra-low oil-water interfacial tension (IFT)** for EOR applications.

The **objectives** planned to be achieved in this study are:

(1) To synthesize water-soluble amphiphilic block copolymers by conventional and/or novel methods through incorporation of hydrophobic moieties in their structure. Molecular weights, structure (di-block or multi-blocks), polymer type, block length/type, and number of hydrophobic moieties will vary in designing the candidates.

(2) To synthetically design two types of amphiphilic block copolymers: linear di-block, and multi-blocks, in varied conditions. Free radical solution copolymerization technique is going to Employed with the utilization of micellar copolymerization.

(3) To study the rheological behavior of the block copolymer solutions to determine the effects of polymer concentration, temperature, salinity on solution viscosity at different rates.

(4) To measure surface and interfacial tension (IFT) at the air/oil-polymer aqueous solution interface for different polymer solutions at various concentrations, temperature, and salinity (NaCl content). Bearing in mind that ultra-low IFT is preferably needed in EOR operations.

(5) To measure the viscosity of polymer aqueous solutions for different polymers at various concentrations, temperature, and salinity (NaCl, $CaCl_2$ content). Bearing in mind that high viscous and salt tolerant materials are preferably needed in EOR operations.

(6) To study the thermal and mechanical stability of the polymer solutions by noticing any change in viscosity over a long period time (aging behavior).

(7) To compare the solution rheology of the synthesized block co-polymers with either the random copolymer solution,
or the polyacrylamide homopolymer solution, whenever
the same polymerization route is used.

(8) To compare the solution surface and interfacial activity
of the synthesized block co-polymers with either
the random copolymer, or the polyacrylamide homopolymer
synthesized, whenever the same polymerization route is used.

CHAPTER TWO

LITERATURE REVIEW

2.1 Chemical EOR Processes

Enhanced oil recovery (**EOR**) is technically related to the recovery of the remaining two-third of the original oil in place from sub-terranean oil bearing formations after both primary and secondary recovery operations are no longer economical. Once reservoir pressure energy is depleted by the primary recovery, oil production can be maintained at economical level by injecting either water or gas; secondary recovery, to keep reservoir pressure at the desired level. EOR is collectively referred to several operations: thermal recovery, water flooding, miscible flooding, caustic flooding, surfactant-polymer flooding , and chemical or polymer flooding. Only polymer flooding is going to be considered in this research.

The residual oil in reservoirs is believed to be in the form of immobile globules distributed through the pores of reservoir rocks. Two major forces: capillary and viscous forces, are proven to be fundamentally responsible for the immobility of these globules. In chemical flooding techniques, chemicals are basically injected so that these forces can be modified in favor of oil production. In fact capillary forces limit the microscopic displacement efficiency of the displacing fluid, i.e. water solution, throughout the reservoir. So adding chemicals to reduce the capillary force by altering interfacial properties of the oil/brine/rock system is significantly important concept. Moreover, the displacement of residual oil in porous media is related to the competition between viscous and capillary forces that should be altered and is usually expressed by a capillary number N_c,

$$N_c = \frac{\eta_w . k . q}{(IFT)_{o/w}} \tag{2.1}$$

where η_w is the aqueous solution viscosity (polymer plus water). Residual oil can not be displaced or mobilized until a critical value of N_c is reached during flooding, which depends on interfacial parameters, i.e. rock wettability and oil/brine interfacial tensions (IFT). For typical waterflood conditions, N_c crit. = 10^{-6} and has to be increased three or four order of magnitude in order to have a near zero-order oil saturation [23]. It is generally practiced that as N_c increases, the oil displacement efficiency also increases [99]. The enhancement of N_c can be only achieved by either increasing the viscosity of the drive water, η_w, or decreasing the interfacial tension between oil and drive water, $(IFT)_{o/w}$ or both as can be seen from Equation (2.1). IFT is also related to the pressure drop, **ΔP**, across the interface of water and oil. The lower the ΔP, the lower the IFT and hence the higher the oil displacement efficiency,

$$\Delta P = \frac{2 * (IFT)_{o/w}}{r} \tag{2.2}$$

Therefore, in any case the IFT must be significantly reduced for any enhancement in oil microscopic displacement and in turn oil recovery to occur. Also the sweep efficiency of the drive fluid, i.e. water plus polymer, can be improved if its viscosity is high enough to prevent fingering, a major problem in water flooding operations that usually results in premature breakthrough to the production wells. So to thicken the drive fluid or increase solution viscosity, high molecular weight (MW) water-soluble polymers are added to the injected water. The solution becomes less mobile relative to oil resulting in increased sweep efficiency. Additionally, surface active agents or simply surfactants may be added to the solution, as it is practiced in polymer-surfactant flooding technique, to achieve even more sweep efficiency and in turn more oil recovery. Therefore in order to control the mobility of the flood, the driving fluid has to be less mobile than the mobility of the oil or fingering would occur. This is visualized by a term called mobility ratio, M, normally expressed as,

$$M = \frac{m_w}{m_o} = \frac{k_w/\eta_w}{k_o/\eta_o} \tag{2.3}$$

where m and k represent mobility and permeability of reservoir rock respectively to each phase, water or oil [27]. The desirable value of the mobility ratio is close to unity or less, whereas high M , say M ≈ 10-30, indicates “fingering”. Also the proportions of the unswept area to swept area greatly depends on mobility ratio. Thus, M can be practically decreased by either lowering oil viscosity, η_o, (application of heat) or increasing the viscosity of the driving fluid, η_w , (application of introducing high MW polymers).

2.2 Surfactant-Polymer Flooding Studies (SPF)

Surfactant-polymer flooding (SPF) operation is one of the most employed methods in tertiary recovery. In the last decade a lot of research has been devoted to the effectiveness and practicality of this method. The commercial synthetic water-soluble polymers; i.e., polyacrylamides (PAM) and partially hydrolyzed polyacrylamides (HPAM), are extensively used in this method and in fact their action of viscosification depends on a combination of chain expansion and high MW criteria to provide high thickening ability to the drive fluid, i.e. water solution. Surface active agents are also extensively used in this method to provide low IFT between oil and the brine solution. However, so many problems are accompanied with this method. Problems like the incompatibility of surfactants and polymers, the degradation of polymers, and the adsorption on reservoir rocks of the materials have potential effects on the recovery [100, 123].

Polymers injected along with surfactants are mainly used for mobility control purposes to effectively improve the water-flooding operation by viscosifing the aqueous solutions that are used as pusher fluids. Surfactants, on the other hand, are mainly used to reduce the capillary forces (surface forces) that are responsible for trapping a large portion of the oil phase within the interstices or pores of the rocks. Thus IFT between oil and water can be greatly reduced. In surfactant-polymer flooding a successive injection of an aqueous or surfactant slug followed by a dilute polymer solution into the reservoir makes the displaced oil droplets to coalesce and form an oil bank. The formation of an oil bank is highly improved by minimizing the entrapment of oil in the porous media by the action of surfactants. By this mechanism the leading edge of the oil bank just formed coalesces with additional oil ganglia and then by means of pusher fluids these banks are pushed to the production wells [23, 27, 38]. This technique, However, require a considerable amount of materials, polymers and surfactants, to eventually achieve any breakthrough.

There has been a considerable body of research in this technique, among those, Totonji et. al [100] who studied the application of this method for Saudi oil reservoir conditions, i.e. salinity, rock permeability and wettability. Baviere et. al. also studied the mobility control by polymers along with the reduction of capillary forces by surfactants in porous media [101]. Also in 1981, Shah D. reviewed a great deal of work in surfactant/polymer method for EOR and particularly the polymer retention in porous media [23, 102]. Chilingarian and Donaldson have also reviewed this kind of method spatially its process and operation methodology [103].

2.2.1 Deficiencies Attached to SPF Method

Surfactant-polymer (SPF) flooding technique is currently used in EOR processes. Aqueous solutions of appropriate surfactant slugs and one type of water soluble polymers; i.e. polyacrylamides (PAM), hydrolyzed PAM, polysaccharides, and xanthans; are injected in the field to yield low oil-water IFT and mobility control respectively. With successive injection of these materials displaced oil droplets coalesce and form an oil bank with which another leading edge coalesces forming additional oil ganglia and so on [5, 23, 100, 102, 120].

Experiences and applications, however, have shown that this method has many deficiencies resulted from operations during recovery. A lot of research has to be done to overcome these problems: (1) the high sensitivity to mechanical shear stress when using high molecular weight polymers like polyacrylamides, such sensitivity causes the polymer to degrade permanently; (2) The incompatibility and sensitivity of surfactant floods to reservoir fluids (dispersions) and rock adsorption put a serious limitation on the use of this technique [100, 113, 114]; and (3) the presence of divalent ions in the solutions is very notorious, particularly calcium ions, which may exchange with sodium ions of petroleum sulfonates increasing their molecular weight and decreasing oil recovery effectiveness. Moreover, these ions shield the ionic charged groups on the polymer backbone causing it to form a random coil configuration and hence reduce polymer thickening ability [4]. Another problem is (4) the incompatibility between surfactants and polymers in buffer solutions at the boundary where they mix. This incompatibility leads to phase separation and alteration of phase composition from the original design. (5) Adsorption of surfactants and/or polymers on reservoir rocks also causes a lot of loss to these relatively expensive materials that in turn put a limitation to this process. (6) The thermal stability of polymers has to be taken in consideration where polyacrylamide is not thermally stable at high temperatures (~ 90 °C). It precipitates within 60 days from solution in hard brines. This degradation is attributed to short term free radical attack and long term hydrolysis of groups attached to the structure of macromolecules. (7) Another way of possible polymer degradation is mechanical and biological degradation [4]. In addition to the above, there are many more limitations attached to this method. They involve poor sweep efficiency of the drive or a displacing fluid having a higher mobility than the oil in place. These deficiencies collectively result in an instability observed by viscous fingering of the drive water through the oil and hence reduction in oil recovery effectiveness [20].

2.3 Hydrophobically Associating Amphiphilic Copolymer Studies

Hydrophobically Associating polymers (HAPs) are those polymers that consist of a water-soluble polymer containing a *small number* of hydrophobic groups. So they are Amphiphilic in nature with low hydrophobic content to insure water solubility and basically differ from known low molecular weight amphiphilic compounds (surfactants) [22, 23, 96]. Many researchers working in polymers for EOR applications, usually non-associating polymers, reported the characterization of polymers in terms of solution viscosity, but rare investigations on surface activity or interfacial activity of polymers accompanied the study for EOR utility. So the study of the solution rheological properties accompanied with surface/interfacial activity study of amphiphilic hydrophobically associating block copolymers for EOR applications is a novel idea in this field. The relating of the surface/interfacial activity and the thickening ability to the *structure* of block copolymers, di- or multi-block, from their amphiphilic nature is investigated in this research. Such relationships can then be utilized and expanded to design appropriate polymer systems capable of reducing the oil-water IFT to very low values (as much as 10^{-3}

dynes/cm) and at the same time having a high thickening ability in the presence of brine solutions and resemble reservoir environment. If an inexpensive polymer can be synthesized providing the two main features to brine solutions, the design of new chemical enhanced oil recovery technique could be possible and the problems accompanying conventional surfactant-polymer method could be alleviated. The typical structure of block copolymers is shown in Figure (2-2).

Bock and coworkers [4], investigated the use of HAPs of AM derivatives with n-vinyle-pyrolidone functionality to improve the thickening ability of aqueous solutions for EOR application. So it was concluded that such polymers when dissolved in brine aqueous solutions have the ability to substantially increase their viscosity to higher values. By using this kind of polymeric viscosifiers (HAPs) the control of displacement fluid mobility in oilfields result in more uniform sweep efficiency and improved oil recovery.

Schulz and coworkers have reported on the synthesis and solution properties of the copolymer of acrylamide and surfactant macro-monomers which showed interesting solution properties such as enhanced viscosity [91]. The investigation in the rheological and photophysical behaviors water-soluble polymers forming hydrophobic associations in aqueous solutions is also performed by Ezzel et. al in 1991 [14]. Zhang et. al [93], also have studied the solution properties of a fluorocarbon-containing hydrophobically associating polyacrylamide copolymer that found to have thickening ability in solutions.

Welssen et. al [104], did some investigations on the properties of water-soluble comb-like amphiphilic polymers and found that they exhibit surface activity with CMC of 1.5 g/l , with surface tension of 38-45 mN/m. McCormick and coworkers also reported in many areas on the applicability of some random and graft copolymers for mobility control and found that these polymers are slightly salt tolerant [20, 28, 33, 68, 75].

In 1996 [26], Volpert, Selb, and Candau have investigated the influence of hydrophobic structure on rheology of amphiphilic associating block polyacrylamids prepared by micellar copolymerization. They concluded that at similar hydrophobe levels double-chain hydrophobes considerably enhance the thickening efficiency with respect to single-chain hydrophobes. Schwab and Hellwell [29], also reported that diblock polyelectrolytes of styrene-vinyl-n-alkylpyridinium halides are highly effective, shear stable thickeners even at low concentrations. However, such materials do suffer from brines which result in coil collapse and a drastic reduction in viscosity.

Hydrophobically associating and amphiphilic block copolymers synthesized and studied in this novel investigation for oil recovery aimed to replace the materials used in current surfactant-polymer method in EOR operations. Material properties are investigated to provide both ultra-low oil-water interfacial tension and at the same time good mobility control in flooding operations. The use of associative polymers to improve the viscosification efficiency of brine solutions is one of the current concepts in literature of this field.

The selection and design of polymers to successfully develop hydrophobically associating amphiphilic salt tolerant block copolymers for EOR use capable of providing both ultra-high interfacial activity and high mobility control will be extracted from the studies and variables that lead to promising desirable results for successful chemical oil recovery operations.

2.4 Rheological Studies of Copolymer Solutions

Solution rheology in polymers is a subject of research that has not been touched thoroughly. Studies of polymer solution rheologies can help guide the choice, type, and architecture of polymers to produce macromolecules of sizable aggregates to give the required viscosification for EOR operations since polymers are believed to considerably increase the viscosity of water during waterflood operations. Stokes law and the self-avoiding-walk model are relating both size and molecular weight to polymer solution viscosity.

Viscosity is a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force. The dissipation is in a form of friction, and in an adiabatic system. results in an increase in the temperature of the system. Viscometers measure this friction and therefore functions as a tool of rheology. In flooding operations (*flow behavior in porous media*) the required viscosity can be related to relative permeability of the reservoir rock and its porosity by the Darcy relation which usually describe the flow of Newtonian fluid in porous media:

$$q = \frac{k \,.\, A \,.\phi .\Delta P}{\mu . L} \tag{2.4}$$

where:

q = volumetric flow rate
k = absolute permeability
A = cross sectional area
ϕ = porosity
μ = viscosity
ΔP = pressure drop
L = length
$\lambda = k / \mu$ = fluid mobility

For polymer solutions and other non-Newtonian fluids, this equation must be modified because viscosity is not constant. Nevertheless, for a given set a flow conditions, an apparent viscosity can be calculated using the Power Law Model ($\tau = K\,\gamma^n$) and applied to the Darcy equation which if applied it shows greatly the reduction in permeability causing the decrease in fluid mobility if polymers are used as thickeners [23, 56].

Polymer solutions are classified as non-Newtonian fluids for all concentration ranges of commercial interest because their flow behavior is too complex to be characterized by the single parameter, viscosity. In porous media where the friction becomes pronounced, shearing force is the controlling factor if viscosity is to be conserved. *Rheology* is basically the study of the change in form and flow or deformation of matter, embracing elasticity, viscosity, and plasticity [56]. When a fluid is subjected to a shearing force, it deforms or flows. There is a resistance to this flow, which is defined as the ratio of the shearing force (shear stress, τ) to the rate of flow (shear rate, γ). In laminar unidirectional flow the terms shear stress and shear rate are used to indicate the applied force, f, and the response of the fluid. A certain force per unit area, f/A, is required to maintain a constant-velocity gradient, u/y. For *Newtonian fluids*, i.g., many liquids and low molecular weight fluids, the ratio of shear stress to shear rate is constant and it is called viscosity and it is independent of τ or γ, or it is called shear rate- independent (Newtonian) viscosity;

$$\mu = \frac{\tau}{\gamma} \qquad (2.5)$$

where:

μ = Newtonian viscosity

$\tau = f / A$ = shear stress

$\gamma = u / y$ = shear rate

In general for polymer solutions, the viscosity-shear rate relationship exhibited a Newtonian behavior at low shear rates and a power-law behavior at high shear rates. Non-Newtonian fluids, however, can not be characterized by a viscosity, as above, because the ratio of shear stress to shear rate is not a constant. The flow behavior of these non-Newtonian fluids may follow one of several complex flow models. Polymer solutions are generally classified as pseudoplastic fluids under most conditions. If the ratio of shear stress to shear rate is considered as an "*apparent viscosity, η*" for a pseudoplastic fluid, the Power-Law model shows that the viscosity decreases as shear rate increases. Thus, the experimental parameters of any viscometer model, spindle, and speed all have a profound effect on the measured viscosity (apparent viscosity) of any non-Newtonian fluid. This viscosity is accurate only when explicit experimental parameters are furnished and adhered to.

A *non-Newtonian fluid* is broadly defined as one for which the relationship of (τ / γ) is not a constant value. In other words, when the shear rate is varied, the shear stress doesn't vary in the same proportion or direction. So non-Newtonian flow is a mechanical proposition. As non-symmetrical objects (molecules) pass by each other - as happen during flow - their size, shape, and cohesiveness will determine how much force is required to move them. At another rate of shear, the alignment of the objects may be different and more or less force may be required to maintain motion. Non-symmetrical objects such as large molecules (macromolecules), colloidal particles, and other suspended materials like clays, fibers, and crystals are subject to the same behavior [30, 56].

There are several types of non-Newtonian flow behaviors characterized by the way a fluid's viscosity changes in response to variations in shear rate. The most common types of non-Newtonian fluids can exist as: (1) pseudoplastic, (2) dilatent, (3) plastic, (4) thixotropic, or (5) rheopectic. The last two fluids are time-dependent. Pseudoplastic fluids will display a decreasing viscosity with an increasing in shear rate, a phenomenon experienced by large number of polymer solutions. The most common type of the non-Newtonian fluids is the pseudoplastic type which include paints, emulsions, and dispersions of many types including polymer solutions. This type of flow behavior is sometimes called " *shear-thinning behavior* " [30, 57, 127].

Dilatent fluid, on the other hand, characterizes by an increasing viscosity with an increase in shear rate. Dilatency, although rarer than pseudoplasticity, is frequently observed in fluids containing high level of deflucculated solids such as clay slurries, candy compounds, corn starch in water, and sand/water mixtures. Dilatency also classified as "*shear thickening*" flow behavior. Plastic fluids behave like solids under static conditions. That means a certain amount of force must be applied to the fluid before any flow is induced; this force is called the " yield value." Tomato catsup is a good example of this type of fluid; its yield value will often make it refuse to pour from the bottle until it is shaken or struck, allowing the catsup to gush freely. Thixotropic and rheopectic fluids will display a change in viscosity; a decrease and an increase respectively, with time under conditions of constant of shear rate. Such behaviors are sometimes encountered in polymer solutions. Rheology of polymer solutions are reviewed by several researchers including: Schulz et. al, 1991[30], and Van Poollen et. al, 1980 [27].

Generally, Copolymer structure has a marked effect on solution properties and thus behavioral characteristics of water-soluble copolymers utilized in EOR [95]. Water-soluble copolymers alter the rheological behavior/properties of aqueous fluids to a great extent [127]. In oil-field applications one of the most important property is solution viscosity imparted by water soluble polymers when added to aqueous fluids. The most interesting feature in the rheology of hydrophobic associative polymers is the unique response to shear rate and salt content. They maintain or expected to maintain their viscosity with increasing salt concentration by means of hydrophobic associations [4]. In oil industry it is believed that the presence of surfactants with associated polymers, if mixed, causes a decrease in the extension of association and hence a reduction in apparent viscosity, this behavior needs to be verified. Thus new polymers have to be synthesized and tailored for use in EOR operations.

Hydrophobic association is usually reversible. This means that during unfavorable conditions or high shear rates, where aggregates are disrupted into individual molecules, the aggregates can reform their structure and the solution can regain its viscosity once the cause is left (reversible response) [95]. Such mechanism does not exist in polymer-surfactant flooding method. By this way, irreversible mechanical polymer degradation, which occurs for high molecular weight samples when subjected to high stress, is totally avoided. The reversible association /dissociation process gives rise to a particular rheological behavior as a function of shear rate or shear time [4]. Such properties are of great technological importance especially in applications of water-based systems which involve viscosity control. It is observed in previous studies that the ability of the associative copolymers to maintain large hydrodynamic volume (HDV) in the presence of mono- and divalent electrolytes is the most critical property for use as mobility control agents [9]. HDV is the volume occupied by the solvated chains. Large HDV is the principal factor in achieving high thickening ability and hence improved viscosity [184]. The structure of the candidate copolymer or its HDV has to be tailored to allow good permeation through the reservoir rocks without polymer adsorption, entrapment, or shear degradation.

Wang et. al [9], observed a relative increase in viscosity of hydrophobically modified polysodiumacrylate when sodium chloride (NaCl) was added to the aqueous polymer solution, a feature particularly suitable for successful EOR process. The same kind of observation was obtained by Bock et al. when HA random tetra-polymers containing N-vinyl-pyrrolidine synthesized for EOR applications [4]. A series of terpolymers as HAP's was prepared by Ezzel et al. [14], in an attempt to develop macromolecules that can maintain or increase the viscosity of aqueous system in the presence of mono- and/or divalent electrolytes. N-(4-butyl)phnylacrylamide (4BPAM) was used as hydrophobic monomer. The incorporation of water-soluble (acrylamide) and water-insoluble (4BPAM) monomers into a polymer backbone was accomplished using a micellar polymerization method where aqueous solution of sodium dodecylsulfate was used as a surfactant above it's critical micelle concentration (CMC) to solubilize the hydrophobic monomer. A water-soluble initiator ($K_2S_2O_8$) was used to induce free-radical polymerization. The results indicate that all the systems display typical polyelectrolyte behavior at low salt concentration and maintain their viscosity with increasing salt concentration by means of hydrophobic association above a critical polymer concentration C* [22]. By increasing the ionic strength of an aqueous solution containing a modified polymer, a strong viscosity increase can be obtained instead of the decrease classically observed with polyelectrolytes.

Newman, Charles and McCormick [33], mentioned that copolymers of acrylamide with sodium 2-acrylamido-2-propanesulfonate (NaAMPS) and 3-acrylamido-3-methyl-butanoic acid (NaAMB) maintain viscosity in high concentrations of divalent salts (M^{++}, M^{+++}) and do not phase separate in the presence of Ca^{2+} at temperatures up to 100 C°, temperature reservoir reaches 90C°. However, unlike NaAMPS, the NaAMB homopolymers will phase separate at 70C° in high concentrations of $CaCl_2$. This difference in some homopolymers over copolymers has been attributed to a weaker binding of the divalent ion to the sulfonate moiety in NaAMPS and the possibility of intra-molecular ion complexation of the divalent ion to the pendent NaAMB side chain, preventing formation of insoluble ionic bonds. Also, hydration of the polyelectrolyte near phase separation was combined with the homopolymer (polysodiumacrylate, NaAA) in the presence of divalent ions. Thus, polyacrylates and hydrolized polyacrylamides exhibit large viscosity losses and may phase separate in the presence of divalent counterions such as Mg^{2+} , Ca^{2+} , and Ba^{2+} [33].

The rheological properties of polymer solutions play an important rule in determining their effectiveness. Depending on the process in oil field operations, polymers can encounter various chemical species, including: salts (mono-valent and multivalent types), alkalis, alcohols, and surfactants. But if we restrictedly apply polymer flooding, polymers would encounter only salts and alkalis. The presence of such chemicals may significantly alter the chemical and physical nature of the polymer molecule and consequently the viscosity and other properties of the polymer solution will change. So the effects of these additives should be studied for any successful EOR operation using agents as polymers [38].

Studies of the rheological behavior of the hydrophobically associative and/or modified polymers can help in guiding the choice of the type and the length of the hydrophobic blocks that need to be incorporated in the polymer molecule to produce aggregates of size enough to give the required viscosity. Molecular weight and size of the polymer is related to the viscosity by Stokes law and the self- avoiding-walk model [128]. The viscosity and rock permeability are related to the mobility control of the flood.

2.4.1 Rheological/Viscometric Studies of Block Copolymer Solutions

Hydrophobically associating (HA) block copolymers, a class of associative polymers, are expected to substantially increase, unlike other polymers, the displacement fluid viscosity through association in oil flooding operations. Generally, copolymer structure can impart divers properties to aqueous medium over homopolymers. Small polymer concentration can yield incredible thickening results if proper synthesis routes and conditions are followed. Hill, Candau, and Selb [8] studied the synthesis and solution properties of *hydrophobically associating amphiphilic polyacrylamides* based-polymers and emphasized on the influence of the method of synthesis on solution properties. Ethylphenylacrylamide was chosen as a hydrophobic monomer and sodium dodecylsulfate as a surfactant in micellar copolymerization technique. They concluded that it is possible to control the association degree and therefore the rheological properties to polymers with high viscosification efficiency. Thomas et al. and McCormick et al., in two reviews, investigated on the same copolymers and claimed that blocky structure is evident from photophysical studies [7, 92]. Valint and Bock also reported on the synthesis and characterization of diblock copolymers of poly(tert-butylstyrene-b-styrene) followed by selective sulfonation of the styrene block to eventually establish water solubility. They found that polymer composition and architecture both influence solution rheological properties to a great extent. Viscosity enhancement was found to be attributed to polymer intermolecular association through the hydrophobic blocks similar to the micellization of surfactants [3].

Dowling and Thomas studied the photophysical effects of water-soluble acrylamide-styrene block copolymers on polymer solutions using cetylebromide (CTAB) as a surfactant in the micellar copolymerization. They concluded that styrene blocks impart hydrophobic micro-domains to aqueous copolymer solutions [7]. Higgins et al. [35], and Siqueira et al. [34] studied solution properties of diblock copolymers of poly[styrene-b-(ethylene-co-propylene)], P(ST-b-PEP), and poly(styrene-b-butylemethacrylate), P(ST-b-BMA), *in selective solvents*, n-dodecane and 2-propanol respectively. They showed that there exists an overlap concentration C* above which the viscosity increases in several order of magnitudes. All experimental findings are explained in terms of micelles in which the styrene blocks are effectively hidden in the cores and the hyrophilic blocks form the outer shell. So as it is usually the case for many amphiphilic block copolymers below the characteristic concentration C* , where systems exhibit Newtonian behavior, above this concentration copolymers behave shear thinning. Such type of behaviors would be suitable for the synthesis and characterization of polymers for EOR use.

Cogan and Gast [36] presented a dynamic light scattering study of polystyrene-polyetheleneoxide diblock copolymers in cyclopentane, a selective solvent for polystyrene. They concluded that addition of water has a profound effect on the micelles. It promotes monodisperse spherical micelles in solutions of large aggregates as well as in solutions containing only single chains. Further addition of water results in a solution of swollen micelles, i.e. a polymeric microemulsion. At very low copolymer concentration, saturated micelles exhibit a sharp increase in hydrodynamic size and hence an enhancement in viscosity. Also Winnik et al. [37] employed fluorescence spectroscopy on polystyrene-polyetheleneoxide diblock copolymers association in water. They found that this association process has a profound effect on the macroscopic properties of the solutions, such as viscosity.

In the previous studies researchers ascribed the increase in solution polymer viscosity to many different reasons. But the reduction in solution viscosity was mainly attributed to the presence of factors, i.e. surfactants, alcohols, high temperature, and divalent cations. Hill and co-workers, in two different communications, reported the negative effect of adding surfactants (SDS) to associative polymer solutions on viscosity [6,8]. Also Schulz et al.[4, 184], reported on copolymers of acrylamide and surfomers (surfactant macromolecules) instead of using an external surfactant during the synthesis. Apparently adding surfactants to the synthesized associative polymer solution has a reverse effect on solution viscosity explained by surfactant association with hydrophobic segments on individual polymer molecules which leads to suppression of inter-molecular associations of polymer molecules [15]. Inter-molecular forces, i.e. dispersion. dipole, or hydrogen bonding, play determining rule in the behavior of polymer solutions. This phenomenon, suppression of intermolecular forces, is not in favor of mixing surfactants with polymers during EOR operations, as it is the case in polymer-surfactant flooding method. So in order to develop an understanding of structure-property relationships, one needs much more detailed information at the molecular level.

Other associative polymers studied include: sulfonatedstyrene-butylstyrene block copolymers [106], copolymers of acrylamide with sodium-2-acrylamido-2-methyle-propane sulfonate [107], and block copolymers of methacrylic acid and p-n-,n-dimethyleaminostyrene prepared by living anionic polymerization [31]. From these studies a proper synthesis route and polymerization conditions would be necessary to meet successful enhanced oil recovery operations.

2.5 Studies on Amphiphilic Characters of Associative Polymer Solutions

Amphiphilic compounds or more briefly amphiphilies are characterized by possessing in the same molecule two distinct groups. Whenever water is the solvent, the groups are often designated as hydrophilic and hydrophobic portions, or head and tail respectively [8]. Amphiphilic compounds tend to concentrate at the interface as a monolayer at a water interface, with the tendency increasing as both the hydrophobic and the hydrophilic character of the amphiphile become more pronounced. However, in amphiphilic associative copolymers, the micellar interfacial layer is not a pure monolayer but rather a mixed one. At the interface amphiphilic compounds in general are arranged themselves so that the hydrophobe is removed from the water while the hydrophile remains in contact with the aqueous solution. This molecular orientation, which is very crucial to this work, is consistent in many experimental observations including the sharp reduction in surface and interfacial tension attaining by adding a small quantity of amphiphile, for economic purposes, to an aqueous phase. Because of this pronounced tendency for amphiphilies to accumulates as monolayer at an interface and to reduce the surface tension and the IFT, they are sometimes called surface active agents or more simply surfactants. The terms surfactants, amphiphilies, or amphiphilic compounds are used interchangeably in literature to denote surface active agents [22].

A surfactant molecule contains at least one polar hyrdophilic part and at least one non-polar hydrophobic unit, a hydrocarbon chain. Typical examples are soaps (i.e. sodium alkanoates) or phospholipids which form membranes. The coexistence of two opposite types of different behaviors (hydrophilic and hydrophobic) inside the same molecule is the origin of the local constrains which virtually lead to spontaneous *aggregation,* see Figure (2-1), into structures such as *micelles* observed with surfactants in solution of oil and water [4, 8]. micellar aggregation can be demonstrated by measurements of physical properties against surfactant concentration. The most obvious significant property is surface (or interfacial) tension. As surfactant concentration is increased, surface tension is lowered because of adsorption of surfactant molecules at the surface (or interface). The higher the concentration, the larger is the adsorption (adsorbed molecules are in equilibrium with bulk dissolved ones) and hence the lower the surface (or interfacial) tension. This surface activity is due to a well defined concentration called the *critical micellar concentration* (CMC) [22, 124]. Above which, tension remains nearly constant, expressing an almost constant concentration of molecularly dissolved molecules (monomers). The excess molecules aggregate into micelles in equilibrium with monomers. This phenomenon is illustrated in Figure 2-2.

The word micelle refers to aqueous solution. However, if micellar aggregation occurs in apolar media, a reverse or "inverted" micelles created. This phenomenon of micellar aggregation is technologically important in manufacturing many important chemicals. Similar behavior is expected for surface-active amphiphilic polymers because they can be considered as surfactant molecules bonded together covalently [15]. Surface active properties do not necessarily depend on the molecular structure of the compound or polymer. Sometimes the polymer does not have the characteristic of long chain aliphatic terminal groups that are typical of most surface-active agents, or relatively shorter alkyl groups on the comonomers which would not also suggest the surface active property of the polymer.

Most of the surface tension studies in the literature were conducted on low molecular weight compounds. Surface and interfacial tension studies of polymers are practically lacking, particularly studies related to the present work.

2.5.1 Surface/Interfacial Tension Studies of Amphiphilic Compounds

Peter Anton et. al [3], reviewed polysoaps where aqueous solutions of such polymers are characterized by low viscosity, single-molecule micelle formation (no multimolecular association) and hence no cmc, but high surface activity /solubilization power attributed to the formation of intramolecular hydrophobic aggregations and high amphiphilic character respectively. Such combination of properties are not together useful in EOR. Bektruov et. al reviewed hydrophobically associating polymers as polymeric surfactants and showed that they lower the surface tension of aqueous solutions [106]. Chou and Bae in 1989 investigated the efficacy of an oligomeric surfactant (a potassium salt) in EOR surfactant formulations for micellar/polymer flooding technique or as a primary agent for improving waterflood performance in oil recovery. The study concluded that the oligomeric surfactant provide significant results in favor of displacement process in oil flooding operations [10]. From this study **the first idea is originated** to use materials like polymeric surfactants or rather amphiphilic hydrophobically associating block copolymers to be used exclusively primarily as mobility control agents and at the same time surface active agents to provide proper mobility control and to increase the microscopic displacement efficiency during flooding respectively.

Ultra-low interfacial tension (IFT) in surfactants is usually associated with the formation of a middle phase microemulsion. Winsor [22], explained this phenomenon as type III phase diagram. Micellar two phase systems also exhibit ultra-low IFT [107]. The high interfacial activity in surfactant systems is attributed to the balance between the hydrophilic and hydrophobic forces by interactions of surfactant molecules. This balance causes molecules to concentrate at the interface lowering it's interfacial tension. This concept has been quantified, as developed by Winsor, P. A. [108], by introducing a quantity "R'' which is defined as *the ratio of solvent attraction between surfactant and oil to solvent attraction between surfactant and water*. This is expressed by

$$\mathbf{R = A_{co} / A_{cw}}$$

where A represents a type of cohesive energy.

Other contribution of interactions have been included in the definition of R ratio [22, 108]. The value of R has to be very close to unity prior to middle phase microemulsion and hence ultralow IFT or optimal solubilization by the amphiphile can be obtained. Molecular interactions/forces acting on amphiphilic compounds at the interface include: (1) Van der Waals forces, (2) hydrogen bonding, (3) hydrophobic interactions, (4) electrostatic forces, (5) repulsion forces, and (6) long range Van der Waals forces. External variables such as temperature, salinity, and oil type have influence on the value of R. Also, internal variables such as the structure of amphiphilic molecules, nature of hydrophilic and hydrophobic groups, and the size of both the groups [107, 109].

Therefore, for a given set of external and internal variables, the concept of hydrophilic and hydrophobic balance (i.e. R=1, optimal solubilization) can be applied to guide the choice of these groups contributed to a given polymer solution. It must be taken into account the thermal fluctuations in concentration within the solution that would change the value of R from point to point, so that unlimited micelle extension in practice may not occur, even in the range of relative concentrations where mean value of R is unity. In certain circumstances, however, the thermal fluctuations are not sufficient enough to disrupt long-range order, and a stable lamellar (i.e. R=1) arrangement of hydrophobic amphiphilic and hydrophilic layers may still persist. When the mean value of R is < 1 or > 1, the affinity of the surfactant layer will tend to become convex towered the water region for R < 1, since this inequality implies that the relative miscibility of the surfactant layer with the water region has increased while as with the oil region has decreased. The tendency for the interface to curve can be visualized by stating that when R<<1, the tendency will be to maximize the interfacial area of contact with water region while minimizing it with oil region [22, 23].

2.5.2 Surface and Interfacial Studies of Amphiphilic Block Copolymer Aqueous Solutions

The design of amphiphilic water-soluble block copolymer, as a likely candidate to be used in EOR operations, is mainly aimed to lower the mobility of the oil (gives lower mobility ratio), to reduce the IFT between oil and water, and to improve the microscopic displacement efficiency and eventually oil recovery. All these requirements and many others are not a simple task to achieve. However, work established so far help encourage investigating the subject to meet the objective. Hamad et. al [15], established that amphiphilic comb-like polymers have the ability to reduce the surface tension (ST) considerably at low concentration and remain constant furthermore. Although surfactants give an air-water surface tension of around 20 mN/m, they do give ultra-low IFT at the optimum conditions of salinity, hardness, temperature, and concentration. The degree of surface activity is a function of the polymer structure. So relating the IFT or ST to the structure of the polymer is going to be considered in the design process. The conditions that lead to ultra-low IFT for surfactant solutions will be used to guide the selection of polymer structures and solution conditions in this research.

Wesslen et al. [104], studied several types of water-soluble comb-shaped amphiphilic polymers and concluded that all the polymers studied have surface activity of 38-45 mN/m with CMC on the order of 1.5 gal/l. Polyacrylic acid's (PAA) surface tension has also been measured in NaCl solution at various ionic strengths, which is what is going to be done to polymer solutions in this study. Ishimuro et al. [88, 89], also showed that the surface activity of PAA solution increases and exhibits large time dependence with increasing concentration.

Ananthapadmanabhan et al. [42], established that new class of water-soluble celluosic polymer (a biopolymer) exhibits definitive surface active property at air/liquid and liquid/liquid interfaces than non-cellulosic polymers but these polymers suffer loss in stability by microorganisms. In another class of polymers, hydrophobically modified polymers also show more surface activity than unmodified ones. This activity is basically moderate relative to conventional surfactants that have high solubilization power and exhibit surface and interfacial activities in the range of (20-40) mN/m and (10^{-1} - 10^{-3}) mN/m respectively.

Bavlere et. al [32], studied the behavior of Alpha-Olefins (AOS's) sulfonates (surfactants) at high temperature, salinity, and hardness, together with their solubility in brine. Also chemical stability, phase behavior, and adsorption onto reservoir rocks are studied. Such kind of study is required for any material (polymer) to be a candidate for EOR application. The main advantage of AOS's is that they have an optimal phase behavior (high soluibilization parameters and low IFT) from low to high temperatures in the range of high salinities as it's encountered in reservoirs. Similar study was conducted on oligomeric surfactants by Chou and Bae [10], in 1989.

Peter Anton et al. [25], distinguished different classes of amphiphilic polymers in their rheological behaviors and surface activities. Relations between molecular structure and potential properties have been made. Particular attention has been paid to polysoaps over the other classes. Polysoaps are characterized by high solubilization capacity but by low viscosity attributed to the formation of intra-molecular hydrophobic aggregation which keeps the hydrodynamic volume small, a behavior not in favor of oil recovery.

Several researchers have investigated the behavior of block polyelectrolytes with the effect of additives such as NaCl, surfactants, and alcohols. Different systems have been made for different purposes. Asa Herslof et al. [110], studied the hydrodynamic effects in the NaCl/TTAB/Polysaccharide/Water system. The properties of which have been monitored by measuring the solution viscosity, surface tension, and phase equilibrium properties for increasing NaCl content. The results show that the viscosity is lowered upon the addition of salt or surfactant in general. That behavior was attributed to the contraction of segments in individual molecule and chain de-aggregation.

Surface and interfacial tensions of polyacrylamides (PAM's) and various types of surfactants have been recently investigated, Zhang et al. [13], in an attempt to elucidate the interactions between PAM and surfactants to be used in EOR as effective pusher fluids in surfactant/polymer flooding method. They concluded that the interaction is synergetic in some combinations and not in others where the interaction was dominated by hydrophobic interactions and hydrogen bonding for non-ionic surfactants. For ionic ones, electrostatic forces play a rule only at extreme pH values. Generally speaking, adding surfactants to homopolymer solutions creates incompatibility in reservoir fluids that would affect the mobility control, i.e. loosing the thickening ability of the fluids, poor sweep efficiency and premature breakthrough. These behaviors would change the properties of the system (oil/polymer/brine) in a manner that do not favor oil recovery. Incompatibility arises at the boundary between surfactant and buffer solutions where the surfactant and polymer solutions mix. Mixing can also take place because residual surfactant adsorbed on the rock surface may later desorb into polymer solution, and because large polymer molecules are excluded from smaller pores in the reservoir rock and. as a result, travel faster than surfactant. However, amphiphilic block copolymers are compatible with surfactants due to the presence of hydrophobic groups in both [13].

Zhu, Eisenberg and Lennox [1,2], studied the interfacial behavior of amphiphilic block copolymers upon varying block lengths of polystyrene/poly-4-vinylpyrridine. The effects of this variation on the properties of surface micelles have been elucidated by electron micrograph of Langmuir-Poldget films. They concluded that inter-molecular interactions leading to unique self-assembled morphologies, depending on the diblock composition can play determining rule in the effectiveness of amphiphilic block polyelectrolyte solutions by lowering the IFT property. The direct evidence of self-assembly into circular surface micelles at very low surface concentration of the diblock copolymers investigated is responsible for enhancement in interfacial activity. These surface micelles re-arrange themselves at high surface concentration and high surface pressures to form a quasi-2D thin film at the surface. Such class of block copolymers (amphiphilies) are characterized by low molecular weight but they are highly monodisperse.

All systems, investigated above, phase separate or aggregate in the solid state because of the existence of a very large value of a thermodynamic driving force, which makes these polymers unique. Moreover, the ability to control this value over wide ranges by regulating the hydrophilic/hydrophobic balance through a variation of the molecular parameters of the constituting blocks. Studies like such would provide an understanding of the factors controlling polymer-polymer and polymer-interface interactions from thermodynamic point of view.

A treatment of amorphous polymers differs from that for low-molecular-weight materials because of the long covalent-bonded structure that must be accommodated. A polymer molecule in solution is not a stationary piece of string, but instead is constantly coiling and uncoiling chain whose conformation in space is ever changing. In a very dilute solution the individual molecules can be considered as acting independently. Each molecule can be pictured as a string of beads with a tendency to coil upon itself to form a spherical cloud of chain segments having radial symmetry.

Furthermore, molecular orientations, monomer conformations and interaction energies would be easily amenable to study using film balance technique. Although the interfacial properties of low MW amphiphilies have been extensively studied using Langmuir film balance technique, block copolymers in such technique and others have been relatively little studied.

2.6 Polymer Synthesis and Characterization Studies

From block architecture point of view, two types of copolymers have been considered to be synthesized; series of diblock amphiphilic copolymers and series of multi-block amphiphilic copolymers. Various contents of hydrophobic groups are used during the synthesis in an attempt to optimize the copolymer structure-property relationship for EOR use. Homopolymers are also synthesized with the same synthesis conditions for comparison purposes. Then subsequent hydrolysis to the diblocks series has been performed to establish water solubility and then make it possible for characterization. FTIR and elemental analysis characterizations have been done with the purpose to characterize the polymer solutions [75]. The synthesized multi-block copolymers and d-block copolymers are classified as hydrophobically associating polymers (HAP's), since small quantity of hydrophobes (1-6 mol%) is used in the design strategy. Water-soluble polymers are generally used in many water-based applications such as: paints, drag reduction, cosmetics, paper making industry, water treatment, as well as in oil recovery operations.

2.6.1 Diblock Copolymer Studies;

Copolymerization of MMA with Vinyl Monomers

Series of diblock copolymers were synthesized using free-radical polymerization process in a heterogeneous medium. Di-functional free-radical oil-soluble initiators (AIBN & initiator made by DCI method) were utilized to produce di-block copolymers in this process. Subsequent base hydrolysis is performed on selected diblock copolymers to establish water solubility and suitability for EOR processes. Copolymerization of methylmethacrylate with acrylonitrile or vinyl-imadazole were performed in a heterogeneous media and initiated by an azo-initiator (AIBN). Hexane was used as a solvent in this process to yield di-block copolymers, poly(AN-b-MMA) or poly(VI-b-MMA).

2.6.2 Multi-block Copolymer Studies; (Copolymerization of Acrylamide with Hydrophobes)

Polyacrylamide that is heavily utilized in chemically EOR operations is usually prepared by free-radical polymerization process in an aqueous environment. Copolymerization of a hydrophobic monomer with a hydrophilic monomer (acrylamide) can result in an amphiphilic polymer. However, by definition, hydrophobic monomers, if incorporated, are insoluble in such an environment. So, a variety of alternatives have been suggested to overcome this problem: (1) the use of a solvent mixture in which both monomers are soluble (homogeneous copolymerization), (2) the solubilization of the hydrophobe into micelles dispersed in the water continuos medium (micellar copolymerization), and (3) the use of a fine suspension of the insoluble hydrophobic monomer using a suspending agent (polyvinylalcohol) to retard particle coalescence (suspension copolymerization). It was found, however, that only the micellar copolymerization route gave products with a high molecular weight (high thickening ability) and adequate hydrophobe incorporation for use as aqueous viscosifiers [6]. In this study, it is the main objective to build properties as high surface/interfacial activity and thickening power to the polymers that would be a proper design for chemically EOR processes.

2.6.2.1 The Reasons for Choosing *Micellar Process* over Microemulsion/Emulsion Copolymerization Processes:

This novel process initially reported by Evani and Turner et al. And modified by Candau et. al [6, 8, 61-64], the hydrophobic monomer (styrene was used in their study) is solubilized within the surfactant micelles (sodium dodecyl sulfate, SDS), whereas the hydropholic comonomer (acrylamide) is dissolved together with the water soluble initiator (potassium persulfate) in the aqueous continuos medium. SDS was used at concentrations between 4 and 20 times its CMC. The reaction mixture is optically transparent but it is actually a microheterogenous system of ordered domains.

Below are outlined the major differences between this process and the more conventional polymerizations carried out in the presence of a surfactant, i.e., emulsion or microemulsion process:

- In an aqueous emulsion polymerization, the amount of surfactant is low with respect to that of the hydrophobic monomer. On the contrary, in the present micellar process, the surfactant over hydrophobe ratio ([SDS]/[ST]) is quite high (typically in the range 15/1 to 17/1 by weight).
- A direct emulsion copolymerization implies a low water solubility of the monomers; i.e., the monomers are essentially located in the dispersed phase (large monomer droplets and small micelles). The situation is quite different in the micellar copolymerization, since the major part of the monomeric species, i.e., acrylamide, is soluble in the aqueous continuos phase; the hydrophobic monomer located within the micelles represents only a very small fraction of the total monomer feed, hydrophobically associating polymerization ($\cong$ 2-7 wt %).
- In the micellar process, the two monomers are segregated at the beginning of the polymerization into two distinct phases due to their very different solubilities, styrene hydrophobicity is very high. Such a situation affects the mechanism of the copolymerization.
- In the micellar process, the copolymerization reaction occurs in both the continuos and phase and dispersed phase. Therefore, although this process was

called "*micellar copolymerization*", it involves in fact a combination of a micellar polymerization and a solution polymerization.

- In the micellar process, a macromolecular chain never penetrates completely inside a micelle as opposed to the emulsion polymerization. Also the interfacial micellar layer is a region where both monomer species are in close proximity.
- The final reaction mixture in micellar process is not a latex (i.e., a fluid dispersion of insoluble polymer particles in water), but a homogenous, clear, and strongly viscous polymer solution. Besides, the copolymerization of a hydrophilic and a hydrophobic monomer by an emulsion process gives a latex functionalized with hydrophilic groups because of the reverse proportion of the two monomers.

Series of non-ionic multi-block copolymers $-[A-B]_n-$ are going to be synthesized via a novel micellar co-polymerization technique which itself differs significantly form microemulsion polymerization technique. Sodium dodecylsulfate (SDS) and hexadecyletriethyleammoniumbromide (CTAB) are going to be used as surfactants to solubelize the hydrophobes in the inter/intra micellar polymerization reaction to produce a homogenous aqueous micellar medium. Water-soluble free-radical initiator, potassium persulfate ($K_2S_2O_8$) is going to be utilized in the micellization process in different quantities to produce polymers with various molecular weights. Polymerization conditions will be varied to study the various effects on the finished polymers and eventually to design polymers with high thickening ability and surface activity.

Copolymerization of a hydrophobic monomer with a hydophilic monomer can result in an amphiphilic polymer, the specific nature of which can be controlled via polymerization parameters, temperature, type and level of hydrophobe, type and level of surfactant and level of initiator as well as polymer recovery technique. The dual hydrophilic/hydrophobic nature provides unique solubilization characteristics and modifies physical properties of the bulk polymer. Acrylamide copolymers provide a means to achieve diverse fundamental properties to be used in many industrial applications. Acrylamide is mainly used extensively in petroleum processes because it can be polymerized to high molecular weights, $5.0*10^6$.

2.6.3 Elemental and FTIR Analysis to Block Copolymers

Characterization and identification of synthesized polymers can be performed using various methods such as elemental analysis, FTIR spectroscopy, NMR spectroscopy, light scattering, size exclusion chromatography, viscometery, etc. Elemental and FTIR analysis are going to be utilized among others to know the composition and the structure of the recovered polymer respectively.

2.7 Analysis of Literature

The analysis of the literature reveals that water-soluble block copolymers can be efficiently synthesized for EOR application using two different techniques among other available techniques. But block copolymers with high thickening abilities can only be prepared by micellar copolymerization technique. However, block copolymers of polyelectrolyte nature can also be prepared by first copolymerization of appropriate monomers and then modifying the recovered polymers by, for example, base hydrolysis to establish water solubility.

The main *advantages* of micellar copolymerization process over other processes are:

1. It can produce water-soluble polymers with multi-blocky structure,
2. Does not produce a latex but a transparent clear viscous solution,
3. Can result in high-thickened aqueous solution using small dose of

hydrophobe,

4. Produces polymer solutions of high foaming ability,
5. produces systems of low cost,
6. Results in high hydrophobe incorporation to polymer main chain,
7. Represents a proper way to study polymer structure-property relationship,
8. Can be a better way to synthesize multi-blocks of copolymers,
9. Produces polymer solutions with various response to shearing force,
10. Represents a way to study the rheology of the polymer solutions,
11. Being an especially attractive polymerization technique, and
12. It yields an aqueous polymer solution with reversible associations upon shearing.

The main *advantages* of heterogeneous process are summarized as follows:

1. It can be a way to synthesize diblock copolymers,
2. Block polyelectrolytes can be obtained by doing hydrolysis to the recovered polymers,
3. Heterogeneous process yields high viscous material,
4. Azoinitiators, if used in a heterogeneous media, produce various polymer structures, and
5. Rheology of the finished hydrolized polymers can be studied in aqueous media.

After this analysis of literature, it is concluded that only the amphiphilic block copolymer structure produces regular micelles that can exhibit surface activity and also be made appropriate for EOR application. Other copolymer structures such as random or graft don't exhibit high thickening and surface activity as much as block copolymer. That is mainly because of the lack of producing hydrophobic aggregates.

It is concluded that only amphiphilic block copolymer structure would be effectively suitable for designing materials of both high thickening abilities and at the same times high surface and interfacial activities. Also the choice of hydrophobes and their levels would determine the solubility of the polymers. Proper synthesis routes should be followed to get polymers with desired properties. Polymerization conditions should be altered to induce various structural behaviors. Proper reagents should be chosen to help establish desired properties. Different polymer architectures would provide various solution behaviors and hence various formulations to different applications.

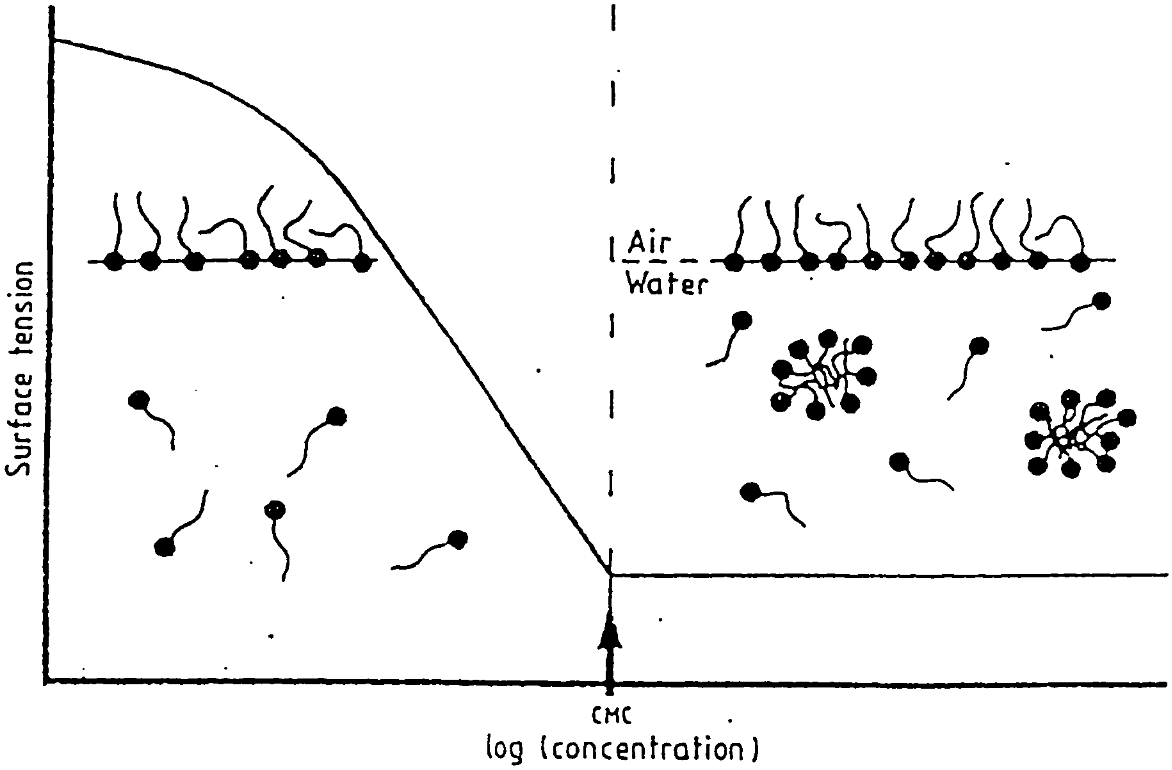


Figure 2-1 ; Surface tension between air and water as a function of surfactant concentration for an aqueous micellar solution, Dots stand for hydrophiles, tails stand for hydrophobes.

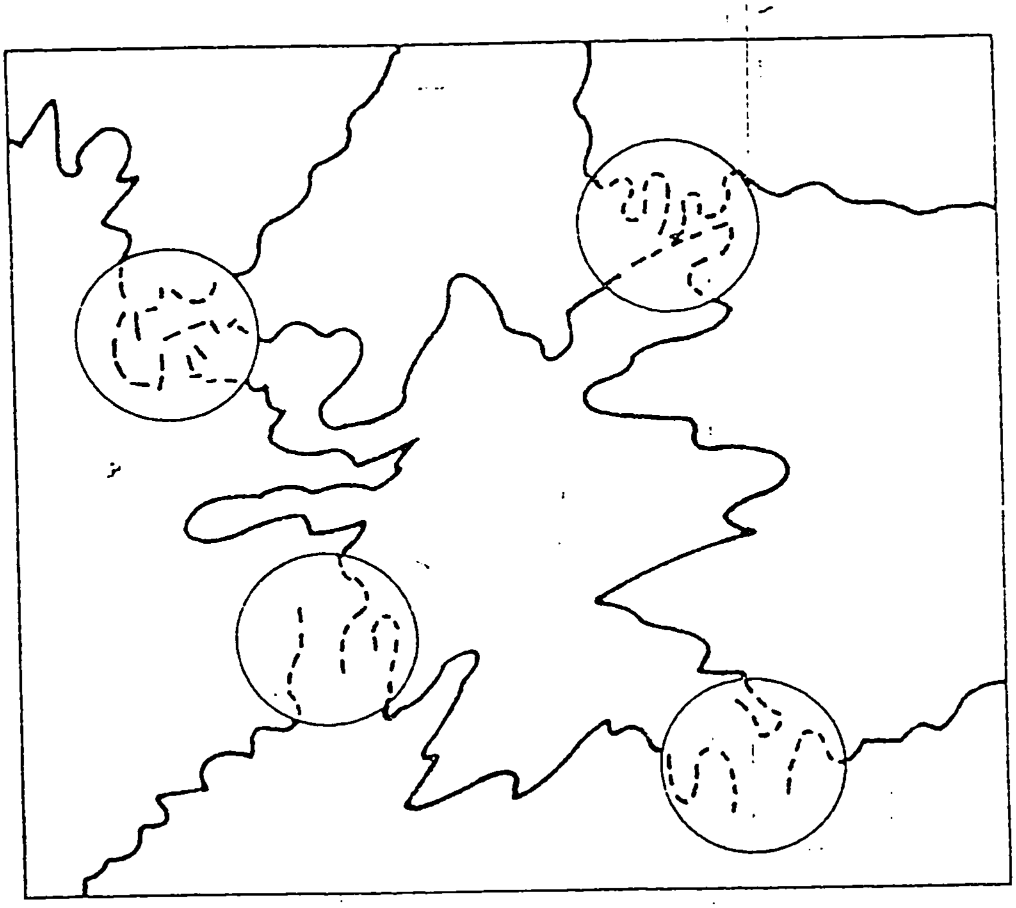


Figure 2-2 ; ABA Block copolymer structure.

CHAPTER THREE

POLYMER SYNTHESIS AND CHARACTERIZATION APPROACH

3.1 Introduction

Synthesizing polymers for a particular use is not a simple matter. Appropriate materials, monomers, initiators, solvents and other reagents, should be delicately chosen to meet required properties. Moreover, reaction conditions/parameters, polymer recoveries and solution preparations have to be modified/initiated to meet the requirements for the final use. Polymer solution characterizations and measurements suitable for achieving required properties have to be designed and properly implemented. For example, high molecular weight polymer is dependent on the ratio of the rate constants. Monomers possessing large propagation rate constant, k_p, and small termination rate constant, k_t, values provide faster rates of polymerization and higher molecular weights. Also chain transfer constants should be low for achieving high MW, as it is the case in water.

Generally, almost all the polymerization reactions carried out in this research were primarily performed using the experimental set-up shown in Figure 3-1, at the end of this chapter, with some modifications when needed.

Appropriate amounts of monomeric species, solvents, initiators, and other reagents, i.e. nitrogen, or formamide, as it is tabulated in Table 4-1, 4-2 and 5-1 are introduced in a three-necked flask equipped with a high speed mechanical or magnetic stirrer, rupper taps, a thermometer, and a reflux condenser. The reaction is initiated by subjecting the reaction mixture to stirring and heating effects which are maintained at proper temperatures and pressures throughout the course of the reaction. At the end of the reaction, the polymer is recovered through series of precipitation and re-dissolution steps. Then the polymer is purified/washed and then vacuum-dried and made it ready for characterizations. Elemental Analysis and Foruier Transition Infra-Red (FTIR) spectroscopy are performed to characterize the copolymers (di-blocks and multi-blocks) obtained at the end of each synthesis.

Rheological measurements for block copolymers are then performed using a Brookfield digital viscometer equipped with co-axial cylinder measuring system, appropriate spindles, and temperature controller. Data acquisition computer system is hooked to the viscometer for data analysis purposes. Normally rheological properties are affected by temperature, shear rate, fluid measuring conditions, sample previous history, sample composition and additives, and special characteristics of some dispersions and microemulsions.

Finally surface and interfacial tension measurements to copolymer solutions are performed to investigate the solution behaviors of the polymers subjected to different environments using a high precision tensiometer K12 equipped with a microprocessor and other auxiliaries. Plate and ring tools made from platinum are used during the measurements of both surface and interfacial tensions of copolymer solutions respectively.

3.2 Components of the Set-ups and Instrumentations Used in the Study

3.2.1 Polymerization Set-up for the Reactions

The experimental set-up which was used for all the polymerization reactions include a 500-ml four-necked flask equipped with a thermometer, mechanical or magnetic stirrer, thermometer, nitrogen inlet and outlet, reflux condenser, and addition funnel. High-speed stirrer is required for uniform mixing throughout the course of the reaction. The thermometer helps to measure the temperature of the reaction components, which has to be fixed at a certain value not to allow any transfer reactions to certain compounds during the course of the reaction that has to be set too. The reflux condenser is used to condense back the vapors coming up from the reaction vessel during the reaction process.

The cooling agent (ethylene glycol) was used to cool the inside surface of the vessel allowing the hot vapors to condense and return back to the reaction mixture for further conversion. For controlling the temperature at the bottom of the vessel, an oil bath thermostated in the normal way with the aid of contact thermometer and immersion heater is introduced under the reactor to establish a uniform heating media. Temperature control is essential in any polymerization reaction since the rate and degree of polymerization are strongly dependents on temperature. Exothermic polymerization reactions are expected for all the free-radical polymerization reaction designed.

Prior to any polymerization reaction, a vacuum distillation to each monomer is performed in order to free the inhibitors mixed with the reagents before carrying out any polymerizations. Multi-functional azo-initiators are first synthesized to be used for making di-block copolymers while free-radical water-soluble initiators are used in making multi-block copolymers. Other reagents are used as received without any further purification. Distilled and deionized water is used heavily in all the polymerization reactions and polymer solution preparations.

3.2.2 Rheological Measuring Instruments:

I. The Brookfield Digital Viscometer with Data Gathering Program (Model DV-II) and Other Accessories

The Brookfield Thermosel System consists of a Brookfield digital viscometer associated with related accessories to accurately measure the viscosity of liquids at ambient and elevated temperatures. Coaxial cylinder geometry equipped with a thermosel is used to measure the viscosity. The temperature of liquids in the cylinder is controlled by a solid state, triac output, proportioning controller which mainly maintains the spindle, chamber, and sample material at the desired temperature. The system is designed for measuring liquid viscosities over a temperature range of up to 300 °C (572 °F). The low limit of temperature control is 15 °C (27 °F) above ambient temperature. The designed viscosity range is from 5 centi-poise (cps.) to 8,000,000 cps. depending upon the viscometer, SC4, and UL adapter spindles utilized for specific type of analysis designed for the sample fluid in hand as shown in Figure 3-2.

The Brookfield UL adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube which has a removal end cap. The adapter has been developed for use along with Brookfield viscometer models to allow accurate and reproducible viscosity trials to be made in ranges below those normally measurable by a particular viscometer, as low as 1.0 Cps. At 60 RPM motor speed, the LVT model has a full scale range of 1-10 Cps with UL adapter. Along with its correct cylindrical geometry, it provides extremely accurate viscosity measurements and shear rate determinations. With the cap removed the open ended tube can be used in a beaker or tank. With the cap in place the closed tube holding a 16 ml sample can be immersed in a temperature bath very conveniently [57].

The working temperature range is from -10 °C to 100 °C. All immersed parts are made of stainless steel material to prevent corrosion in their life time. The removal cap of the low density polyethylene can be considered disposable for one time used required. The Brookfield viscometer is granted to be accurate within ± 1% of the full scale of the spindle/speed combination in use. It also has a sensitivity and reproducibility of ± 0.2 %. The accuracy of a particular viscosity reading is dependent upon the actual display reading. In general, the accuracy of the viscosity value will increase as the reading approaches 100. This is because the tolerance of ± 1% of the full scale viscosity applies to all readings, and represents a smaller percentage of measured viscosity as the actual reading increases.

The Brookfield digital viscometer (DV-II) is a laboratory instrument which can be utilized with all kinds of Brookfield accessories: UL adapter, small sample adapter, thermosel and heli-path stand. Also available with it these facilities: continuous display of basic viscometer reading in %, continuos display of calculated shear stress in dynes/cm^2, an Auto button for automatically zeroing the viscometer, an Autorange button for displaying full scale viscosity and shear stress range of any spindle/speed combination, and others for verifying special spindle entries, Hold button for freezing any display reading, Low button indicator for readings below 10% of the full range. The viscometer is programmed to accept all Brookfield spindles and spindle/chamber accessories [57]. These aspects are shown in Figure 3-3.

The Brookfield viscometer is of rotational variety. It measures the torque required to rotate an immersed element (the spindle) in a fluid. The spindle is driven by a synchronous motor through a calibrated beryllium copper spring; the deflection of the spring is indicated by a digital display. The degree of deflection is proportional to the viscosity of the fluid. Continuos readouts of percent full scale, viscosity and shear stress are provided by a means of the integral three-digit LED display. The minimum viscosity range is obtained by using the largest spindle at the highest speed while the maximum viscosity range is obtained by using the smallest spindle at the lowest speed. Measurements made using the same spindle at different speeds (RPM) are used to detect and evaluate the rheological properties of the test fluid.

The data gathering software is an easy to use and menu-driven program developed to facilitate data gathering and rheological analysis. It's designed for use with all viscometer's models and accessories of DV-II type. The digital viscometer is connected to a personal computer and printer to allow through rheological analysis for the sample, see Figure 3-4.

II. The Ostwald Capillary Viscometer

The most common simple instrument used for low viscosity liquids is the capillary viscometer (Ostwald's viscometer), as shown in Figure 3-5. Its main feature is that the liquid being tested flows under its own potential head. The calibration equation for such a viscometer is:

$$\frac{\eta}{\rho} = A \times t - \frac{B}{t^2} \qquad (3.1)$$

where B/t^2 is a correction factor for the kinetic energy losses at the entrance and exit to the capillary. For flow when the viscosity η, eta, is not constant but varies with shear stress τ, tow, or shear rate $\gamma^{\cdot}$, gamma, externally pressurized capillary and rotational viscometers are widely used.

These kind of viscometers have a short length of glass capillary tubing in which the capillary is one-to two-tenths millimeter in diameter and a few centimeter long, as shown in Figure 3-5, equipped with one or more bulbs on each end to hold the polymer solution conveniently. In operation, the polymer solution is forced up through the capillary by gentle air pressure to fill the bulb immediately above the capillary. Then it is allowed to flow back down by gravity. As the liquid level passes an upper marker line, a stopwatch is started; as it is passes a lower line, the watch is stopped. The elapsed time, called the *efflux time* for that solution, the time necessary for that volume of solution to flow through the capillary, is directly proportional to the viscosity of the solution. Efflux times of about a hundred are usual. The efflux-time measurements for a series of polymer solutions and their solvent are all that needed to evaluate the viscous drag of those polymer molecules.

3.2.3 General Procedures for Making Rheological Measurements (Operating the Brookfield Digital Viscometer)

Rheological behavior studies were performed by using a Brookfield digital viscometer equipped with coaxial cylinder measuring system and temperature controller and other accessories. The operating instructions were followed as explained in the viscometer's manual [57]. First of all the instrumentation was carefully placed on a firm level surface near 15 Amp., 115 Volt, 50 Hz. AC electrical service. The viscometer's stand was set up by attaching the rod extension to the bottom of the upright rod. The assembly part (upright rod & rod extension) was screwed into the base leaving the jam nut loose. The three leveling screws were then screwed into position on the base. The viscometer, digital part, was then attached to the stand by inserting it into the clamp, and positioning it appropriately on a firm level surface and centered between the stand legs. Then the assembly part was locked tightly to the stand base with the lam nut. The viscometer was then raised to the highest position on the stand. The whole setup is shown in Figure 3-2. Having the viscometer raised to the highest position on the stand, the alignment bracket was then attached to the rear of the viscometer pivot cup, securing it tightly with the knurled screw. with the use of the three leveling screws in the thermo-container base, the base level was positioned. The chamber was then inserted into the thermo-container using the extracting tool. The chamber was also rotated until it drops and locks in place prohibiting further rotation.

The temperature controller was then set on a level surface adjacent to the right of the thermo-container. The male plug (three-prong) was then inserted from the thermo-container braided cord into the socket on the back of the container. The four-inch stainless steel probe was inserted into the hole in the thermo-container located directly above the braided cord. The other end of the probe was then plugged into the connector located on the back of the controller. For removing the probe, the spring clip is just depressed and carefully the probe slided out. The above procedure is only followed by maintaining the thermo-container far below 100 °C.

The whole system should be aligned. So by looking down on the viscometer, the stand base was leveled by adjusting the three leveling screws until the bubble is centered. The viscometer was then lowered until the tips of the alignment bracket just touch the horizontal surface of the locating ring. The viscometer was then raised, positioning the tips of the alignment bracket about 1/16 inch above the horizontal surface behind the locating ring. Using both hands, the thermo-container base was gently slided until the tips of the alignment bracket just touch the locating ring. The coupling link was then connected to the spindle (the shearing body) and the coupling nut. The spindle was then lowered into the chamber and the link coupling nut was connected onto the viscometer's coupling nut using the left hand thread. The insulating cap was then placed over the sample s chamber inlet, thus capping the system for any external interference. The whole set-up is detailed in Figure 3-2. except that the Brookfield viscometer is replaced by a digital display.

Performing the viscosity measurements at this step is straightforward. With the instrumentation assembled and familiarization completed, the viscosity measurements can now be started peacefully. First of all the insulating cap and spindle were removed. The viscometer was then raised to the highest level in the stand. Then the sample chamber was removed, using the extracting tool, and was placed in an auxiliary holder. By the use of pipette, appropriate volume of polymer solution designated on the range data sheet was poured into the sample chamber. Using the extracting tool, the loaded chamber was put back into the thermos-container. The viscometer was then lowered and the thermos-container was properly aligned. The appropriate spindle was then inserted into the polymer solution in the chamber and was coupled to the viscometer. The insulating cap was then replaced.

The controller was turned on and the set point knob was adjusted to the desired set point temperature at which viscosity measurements are to be made. After this, the viscometer was also turned on and left running during the equilibrium period. The measurements were performed at different temperatures (25 °C, 75 °C, and 95 °C) for some selected polymers at lowest and highest shear rates (0.4 s^{-1} and 79.2 s^{-1}). After the thermos-container, spindle, chamber, and the test polymer solution sample has reached temperature equilibrium, which took about 10 minutes, *viscosity readings are taken at different speeds (RPM), shear stress and shear strain. Viscosity in (cps.) is obtained at different temperatures and shear rates.*

3.2.4 Measuring Instruments for Surface and Interfacial Activities of Copolymer Solutions

I. KRUSS Digital Tensiometer (Model K12)

The interfacial (liquid/liquid) and surface (liquid/air) tension measurements are very essential for characterizing any polymer solution to be used successfully in chemically EOR operations in flooding engineering field. The activity is checked by carrying out measurement of the dynamic forces exerted on a body whose precise geometry is known. The tensiometer consists of, as shown in Figure 3-6, a measuring instrument and a microprocessor control unit. The balance system situated in the head part of the instrument has an accuracy of 0.0001 gm. and 0.01 mN/m. It incorporates a servo-system for fully automated calibration and tarring. The solid metal housing provide the instrument with high stability and shock resistance that would be unnecessary to use a weighing table. Due to the rigid connection of the measuring body (*ring* or *plate*) to the balance system, a measurement is possible in both *push* and *pull* directions. A measurement in the push direction is necessary whenever the lighter phase has a higher affinity to the measuring body than the heavier phase. The temperature of the sample is optionally controlled using a circular bath, measured by a built-in pt-100 thermoresistor, and is displayed digitally. The force, F, which is detected when a measuring device of known circumference, L, is moved into the interface of two immicible phases (liquid/gas or liquid/liquid) is directly proportional to the surface or interfacial tension, σ, between the phases respectively.

$$\sigma \approx \frac{F}{L} \quad \text{in (mN/m)} \qquad (3.2)$$

The platinum ring can be used for measuring both surface and interfacial tension while the platinum plate is mainly used for surface tension measurements. To minimize temperature changes and air circulation inside the tensiometer, plexiglass doors have been installed to isolate the measuring area from surroundings. In the thermostat vessel, a magnetic stirrer which can be operated either manually or automatically is integrated by the processor. This feature allows reproducible starting conditions when measuring sample of the same solution at different concentrations. The combination of an electronic balance system and a microprocessor allows for fully automated measurements. There is absolutely no further need to correct the values obtained by the plate method because the microprocessor unit take care of that.

3.2.4.1 The Plate Measuring Method

The measuring body is a vertically suspended platinum plate of exactly known geometry. The plate's surface is roughened for good wetting property. The lower edge of the plate is brought into contact with the sample liquid.

The liquid (jumps) to the plate and pulls it into the liquid. The force F, caused by this wetting is measured by pulling out the plate up to the level of the liquid surface as shown in Figure 3-7. The measuring procedure is static which means that the plate can stay at zero level for a long period of time. Thus a continuos measurement of the surface tension is possible without the problem of forming a new surface all the time as it is necessary with the ring method.

An advantage of using the plate method is that the measured values do not need a correction. The surface tension of the liquid is just determined according to the wetting length l_b as

$$\sigma = \frac{F}{l_b * \cos\alpha} \qquad (3.3)$$

where α is the contact angle. The equation can only be used if this angle is zero and hence $\cos\alpha = 1$, which indicates the total wetting of the plate. This specific condition is compiled with the roughened clean platinum surface necessary for the measurement.

3.2.4.2 The Ring Measuring Method

The ring method characterizes with accurate, simple and fast measurement. No wetting contact angle effects, where measurements made at the interface. In ring measuring method, surface and interfacial measurements can be both carried out. The measuring device (a ring) is made form platinum resistant to corrosion and can be easily suspended vertically by a hook projecting from the headpiece of the instrument. The geometry of the ring has to be known for producing automatic results by the processor tensiometer K12. The wetting length of the ring is $l_b = 119.95$ mm and the mean radius is $R = 9.545$ mm and the radius of cross-section of the wire is $r = 0.185$ mm. The platinum ring is dipped into the sample liquid and immediately removed afterwards. The maximum force, F_{max}, which is necessary to pull the wetted circumference, l_b, of the ring through the surface of the liquid is

$$\sigma = k_{\max} \times \frac{F_{ef}}{l_b} \qquad (3.4)$$

where σ is the measuring tension.

The correction factor takes into account the weight of the liquid lifted by the ring. The main disadvantage of the ring method is the necessity of correction of the measured values. It does not only determine the force on the ring caused by the surface tension but also the weight force of the liquid volume of the lamellas at the bottom of the ring as it is indicated in Figure 3-8. Lecomte Du Nouy mentioned this method first in 1919. The automatic correction made by the tensiometer s microprocessor was based on the publication of Zuidema et. al [115]. The equations are interpreted using the tables of Harkins et. al [115, 165].

3.2.5 General Procedures for Doing Surface and Interfacial Measurements Using Both Plate and Ring Methods

Surface and interfacial tension activities of dilute polymer solutions were examined by using Kruss digital tensiometer K12 supplied with plate and ring measuring devices and dosimat unit. It was of primordial importance to calibrate the instrument before any measurement takes place.

3.2.5.1 The Plate Method

The standard measuring device for the plate method is a rectangular platinum-iridium plate of exactly known geometry incorporated in the processor. The Plate method can *only* be used for measuring surface tension. Before any measurement was carried out, the measuring device is cleaned with a suitable solvent (acetone) and distilled water then annealed/burned shortly to slightly red-heat in a Bunsen flame. The annealing was necessary to remove substances from the platinum surface which can not be removed by rinsing only.

The plate was then fixed into the measuring unit. This was done by sliding the plate carefully into the guiding mechanism, situated at the top part of the measuring area as can be seen in Figure 3-9. The plate was introduced to the limit stop into the clamping device with integrated guidance. The guidance of the clamping device was locked by turning in a clockwise fashion a small black wheel located on the left outside of the measuring unit housing. The locking was absolutely necessary in order to avoid damage of the force measuring system. Enough sample liquid (≈ 18 ml) was transferred to a glass container of known geometry and then placed on top of the thermostat vessel which itself is then lifted up by turning the wheel until the liquid surface is just under the edge of the plate.

The tensiometer processor, which is connected to both the measuring unit and the dosimate unit, has a feature of a digital display. The latter unit gives the tensiometer a feature of measuring series of solutions of different concentrations automatically. Series of measurements for a specific sample was preferred over single measurements to get more accurate results by taking the average values. After switching ON the tensiometer, several parameters were entered. The first menu was displayed; the options like plate method and series of measurements were pressed. Moreover, parameters such as sample number, maximum number of measuring values, interval, and standard deviation and other preset values were entered. At this point the plate was fixed in the measuring unit and the liquid surface was close to the edge of the plate. The plate was then dipped into the liquid 2 mm deep before automatic measurement started and then lifted up to the level of the liquid. The START button was then pressed to begin a fully automatic series of measurements. The end of the measurements was indicated by an acoustical signal. For any error during this procedure the STOP button can be pressed to terminate the measurement.

3.2.5.2 The Ring Method

The so-called ring method is a method for measuring accurately the interfacial tension (IFT) between a liquid of heavy phase (polymer solution) and another liquid of light phase or oil (n-decane) , with a metal ring. The method was mentioned first in 1919 by Du Nouy. It is the objective by this method to get the IFT of polymer solutions of different concentrations and conditions. If IFT is obtained, this would open many ways in the research. Pressure drop across interface, effectiveness of polymer flooding, and oil recovery effectiveness are among those advantages. In the interfacial tension measurement, the density of each phase was first obtained and entered to the processor at the beginning to make automatic IFT calculations.

Before doing any IFT measurement, the measuring device was cleaned by acetone then by hot and distilled water. The ring was then heated to a red-hot for a short time to get red of substances on the metal. The same procedure was followed as in measuring the surface tension by the plate method with view exceptions. Two techniques for the force measurement step at the interface of the liquids by the ring method were used. The measurement is in *pull direction* and *push direction* relative to the interface. After the ring is fixed and the liquid is transferred by a pipette, either of the two techniques can be chosen. But it was the push direction that utilized extensively.

For the measurement in the *pull direction*; the ring method, IFT measurement, series of measurements, and pull direction and other preset values were chosen from the menu displayed by the processor. The density of the light phase (n-decane) was given by the supplier Aldrich chemical company to be 0.729 gm/cm^3. But the density of the polymer solution was obtained by suitable means of measurements. After this the oil is transferred to the top surface of the polymer solution by using a pipette. Then the ring is dipped in to 3 mm by lifting up the thermostat vessel until the ring passed the interface. The tarring was started by pressing the START button after waiting enough time for the solution to reach equilibrium, otherwise erroneous results would be because of foams at the interface. Automatic measurements were started until the end of it as it was indicated by an acoustical signal. For repeating the measurement, pressing the START again would do the gob.

In the *push technique*, on the other hand, the ring has to be pushed from specific lighter phase into the interface. The measurement was started by choosing appropriate options as in the pull technique. All the required parameters were then entered and the heavy and light phases were introduced carefully to the sample container by a pipette. The heavy phase was first filled in up to 8 mm height (30 ml). Then the light phase (oil) was carefully, without any disturbances, overlaid about 7 mm height (25 ml) by using a pipette. Then the ring was dipped into the light phase (n-decane) by lifting up the thermostat vessel. The ring was stopped about 2 mm above the interface. The fully automatic measurement started after pressing START. The end of the measurement was indicated by an acoustical signal. For all interfacial measurements, a circular water bath was constantly used to maintain the temperature at 25 °C.

3.3 Materials Used for the Synthesis

Acrylamide monomer was used as received from Fluka Chemical Co. In synthesizing block copolymers, all liquid monomers such as styrene (ST), MMA, VI, acrylic acid, VP, AN, and 1-dodecene (C12) were first freed from inhibitors by vacuum-distilling at 30 °C before any copolymerization reaction takes place. Sodium dodecyl sulfate (SDS), hexadecyle triethyle ammoniumbromide (CTAB) and potassium persulfate initiator ($K_2S_2O_8$) were purchased from BDH Limited Pool, England. 2,2'-Azobis(2-methyl-propionitrile) (AIBN) was purchased from Aldrich Cemical Co. Formamide was purchased from Flucka Chemical Company.

Solvents and other reagents were used as received without any further purification. Methanol, dichloromethane, CCl_4, diethylether were used extensively through out the preparation of initiators and polymers. Deionized and distilled water were used extensively for all aqueous solutions. NaOH, acetone, and isopropanol were used in the hydrolysis reactions as received.

3.4 Polymer Synthesis and Conditions

3.4.1 Copolymerization in a Heterogeneous Media (Synthesizing Diblock Copolymers)

Hydrophobically Associating MMA Copolymers:

The experimental procedure used for synthesizing series of di-block MMA copolymers was extracted from Seymour method [41-43]. The detailed procedure is given in Chapter 4. Also azo-initiators and polyinitiators were prepared to be used in synthesizing di-block copolymers.

3.4.2 Copolymerization in a Micellar/Homogenous Media (Synthesizing AM/ST and AM/C12 Multi-block Copolymers)

Typical Synthesis of Hydrophobically Associating Polyacrylamides:

The general experimental procedure used for synthesizing series of multi-block copolymers by the micellar process was extracted from Candau et. al technique [8]. Reaction mixtures are shown in Table 5-1. Aqueous solutions of acrylamide (AM) were first charged in a 500 ml three-necked flask equipped with a reflux condenser. The solution was then degassed by gentle bubbling with nitrogen for 20 minutes while stirring. After complete dissolution, the surfactant, sodium dodecyl sulfate (SDS) or CTAB was added with gentle stirring for 10 minutes to avoid forming bubbles. The reagents should be added carefully and quickly by slowly keeping the nitrogen to deaerate the flask to avoid air to enter or forming bubbles. After 10 min. of dissolution, the flask inlets and outlets were covered with septum caps. After 15 minutes or more (i.e., depending on the amounts) of gentle stirring, the second comonomer, either styrene (ST) or 1-dodecene (C12), was added by injection with a syringe into the reaction mixture and stirring was continued for 1/2 - 1.0 hr depending on the amounts of hydrophobes until a micelleized homogenous clear transparent solution was obtained, otherwise expectation of copolymeriztion is less. The micelleization should be closely checked by eye-inspection. Then the whole setup with an oil bath underneath was placed on top of heater/stirrer plate and the temperature was controlled at 50 °C not more or less. Then the polymerization was initiated by charging with a syringe an appropriate amount of a water-soluble initiator solution, potassium persulfate ($K_2S_2O_8$). The reaction mixture was left under moderate stirring for 48 hours to get a high yield. The reaction conditions for each experiment conducted is given in Table 5-1, Chapter 5, where detailed study is provided there.

The polymers were then recovered through several precipitation /dissolution cycles. Usually the finished polymer solution is slowly poured into a constantly stirred five times excess of methanol. The solid polymer recovered is then again washed several times with methanol to removed all traces of water, surfactant and residual unreacted monomers. Then the polymer is vacuum-dried in an oven at 60 °C for 24 hr. Finally the polymer was crushed into fine powder and then dried again for 6 hr.

3.5 Aqueous Solution Properties of Copolymers

3.5.1 Rheological Measurements of the Polymer Solutions

Fine powder of solid samples of di-block or multi-block copolymers were dissolved in deionized water under mild agitation (magnetic stirrer) at room temperature making stock solutions of concentrations (0.01, 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 wt %). The rheology of dilute and semidilute solutions of proper concentrations in terms of viscosity-shear rate profile was investigated by using a Model LV *Brookfileld viscometer* with U.L. adapter. The viscosity of the polymer solutions were measured with and without brine (1.0 to 10.0 wt % NaCl) to investigate the effects of salt on the polymer.

Temperature was regulated at 25 °C ± 2. Various shear rates were used ranging from 0.4 to 79.2 1/sec.

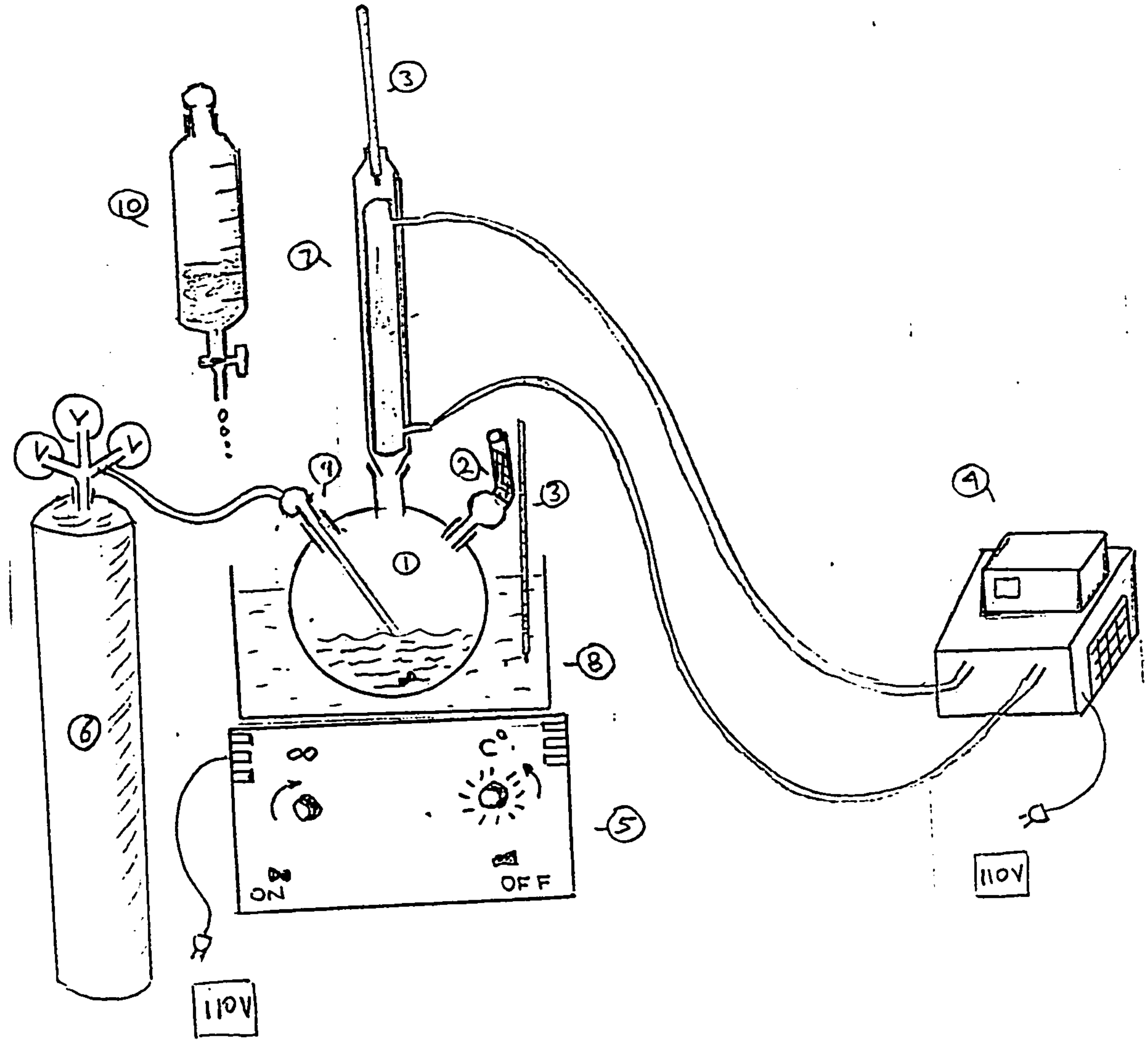
3.5.2 Surface and Interfacial Measurements of the Polymer Solutions

Solid samples of di-block or multi-block copolymers were dissolved in deionized water under mild agitation (magnetic stirrer) at room temperature making stock solutions of concentrations (0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0 wt %). n-decane was used as an oil phase in the IFT measurements. The surface tension and interfacial tension (IFT) were measured using *Kruss digital tensiometer* equipped with a microprocessor and dosimate. The surface activity of dilute and semidilute solutions of proper concentrations with and without addition of brine (0.0 to 10.0 wt % NaCl) was investigated. Temperature was regulated at 25 °C ± 2, in most of the measurements unless stated elsewhere.

3.6 Copolymer Characterizations

Testing a product is as important as making it. Identification of the recovered polymers made possible by performing *Elemental Analysis and FTIR spectroscopy* to exactly know the structure and functional groups present in the polymer, respectively. The results of the characterized polymers are given in Tables 4-4 , 5-2, and 5-3. Elemental analysis was mainly used to determine the percent content of elements; carbon, hydrogen, nitrogen and oxygen, present in the copolymers. The analysis was conducted in K.F.U.P.M central laboratory in the Research Institute.

Foruier Transition Ifra-Red (FTIR) spectroscopy was conducted in the chemistry department in K.F.U.P.M using Perkin Elmer spectroscopy. These methods can be extremely useful when working with hygroscopic copolymers such as those used in enhanced oil recovery since assessment of rheological behavior is dependent on accurate concentration measurement.



Three-neck flask
Moisture absorber (Cl Co3)
Thermometer
Cooling system
Temperature and stirring controller
6- Nitrogen cylinder
7- Condenser
8- Water or oil bath
9- Nitrogen purging
10- Dropping funnel

Figure 3-1; Schematic Diagram of most Copolymeriztion Reactions Conducted for all Experiments.

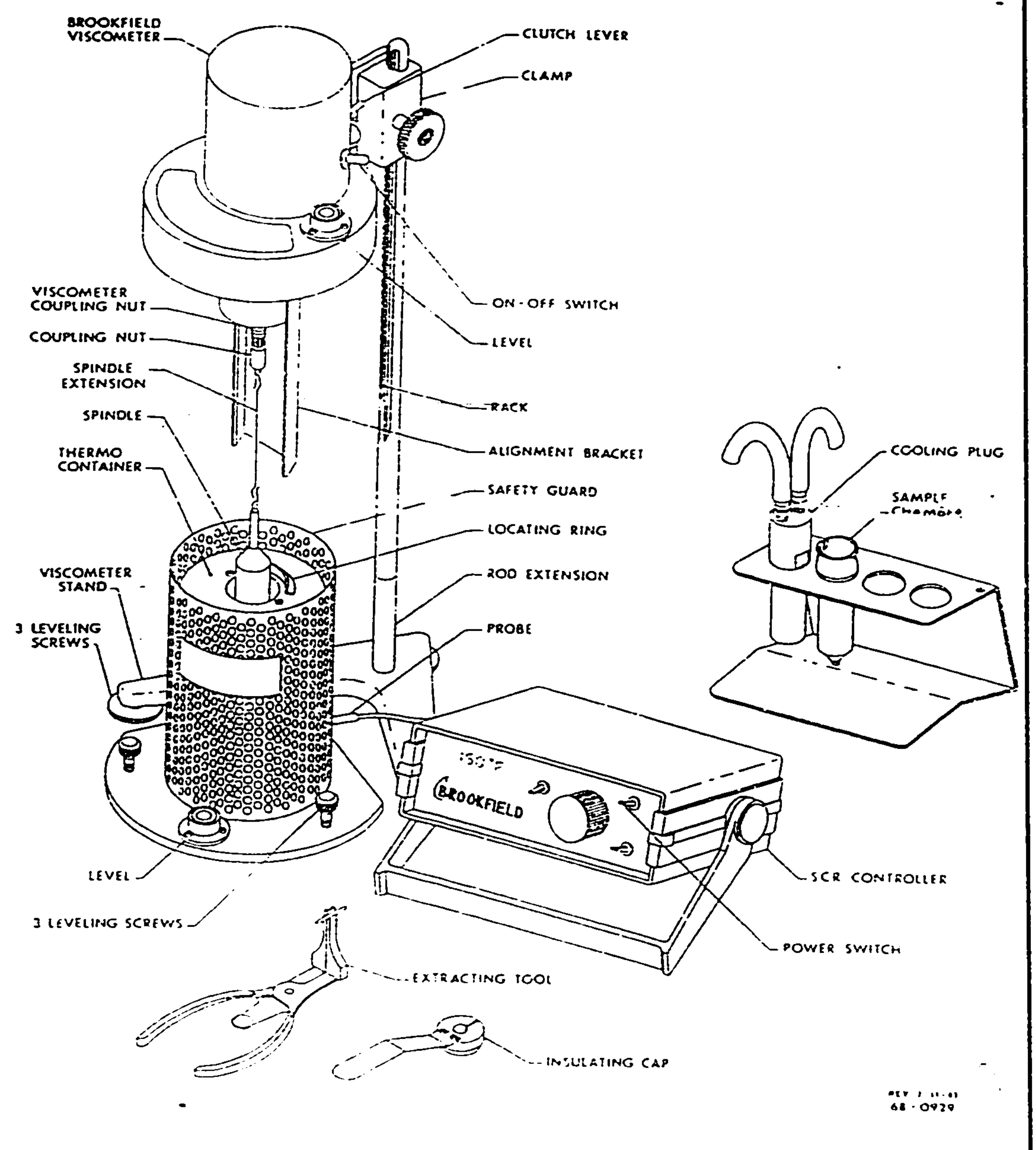
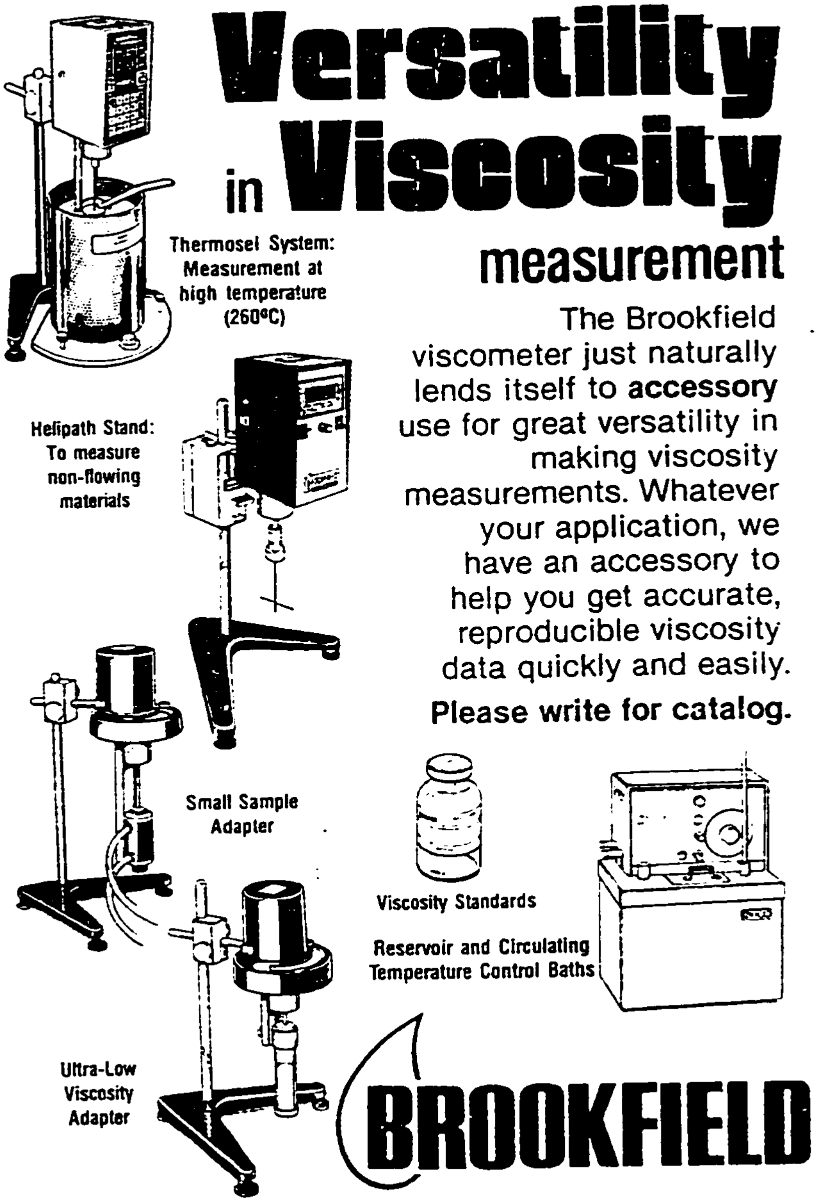


Figure 3-2; Brookfield Digital Viscometer (Model DV-II)



Versatility in Viscosity measurement

Thermosel System: Measurement at high temperature (260°C)

Helipath Stand: To measure non-flowing materials

The Brookfield viscometer just naturally lends itself to **accessory** use for great versatility in making viscosity measurements. Whatever your application, we have an accessory to help you get accurate, reproducible viscosity data quickly and easily.

Please write for catalog.

Small Sample Adapter

Viscosity Standards

Reservoir and Circulating Temperature Control Baths

Ultra-Low Viscosity Adapter

BROOKFIELD

Figure 3-3; Brookfield Spindles, etc.

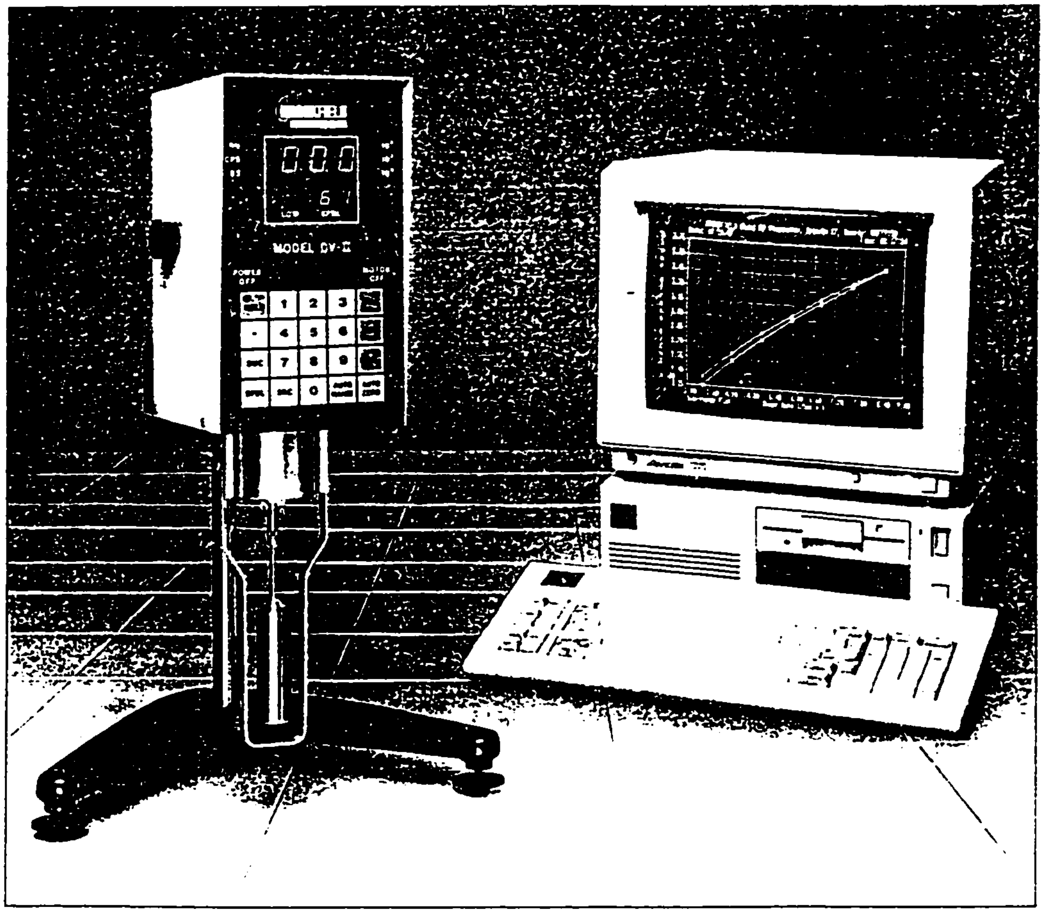


Figure 3-4; Data Gathering Terminal and Software.

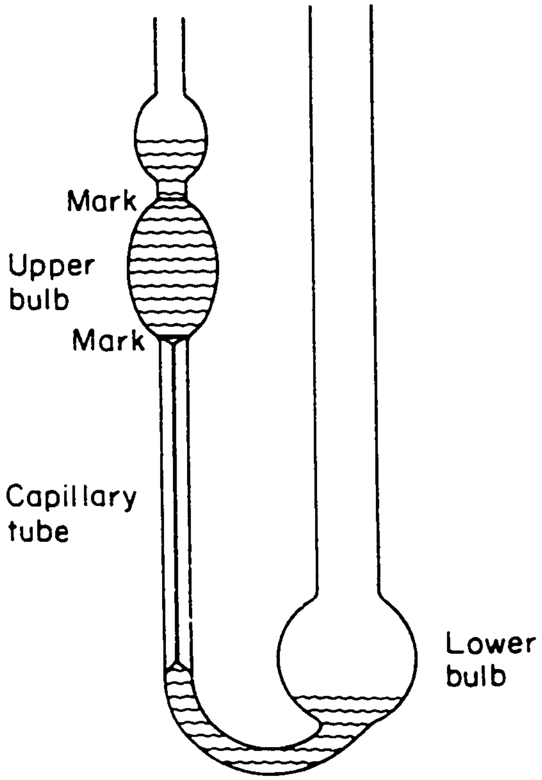


Figure 3-5; Ostwald Viscometer

Time t is measured for fluid to flow out of upper bulb (between marks).

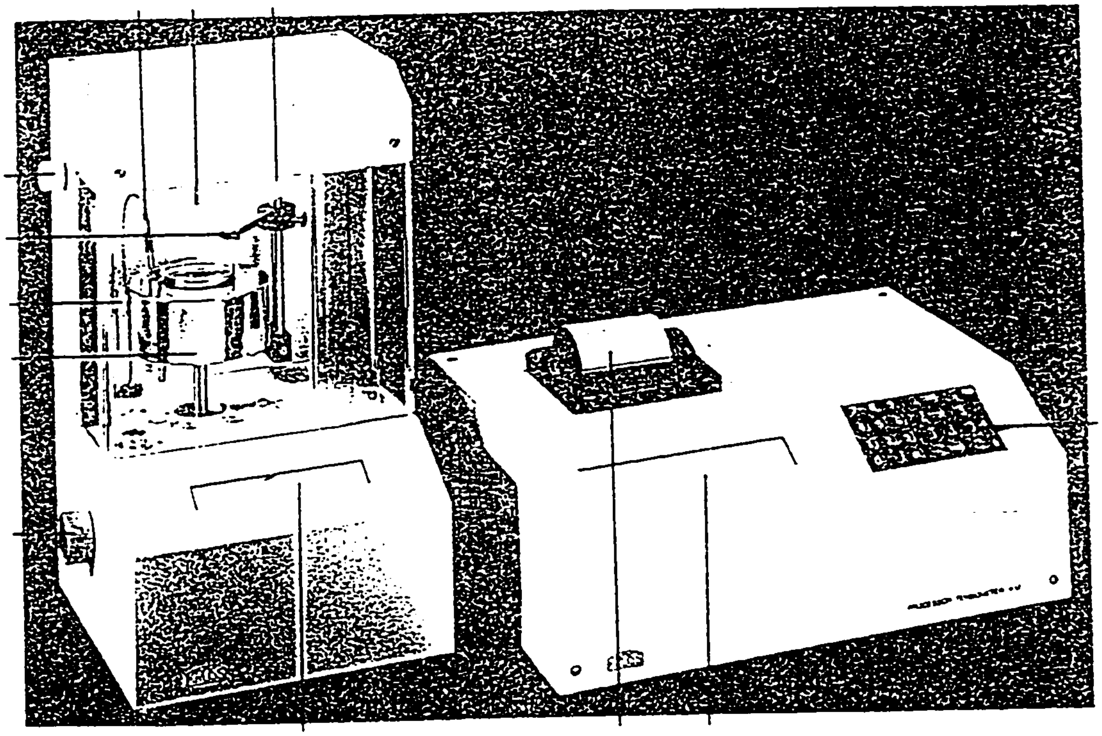
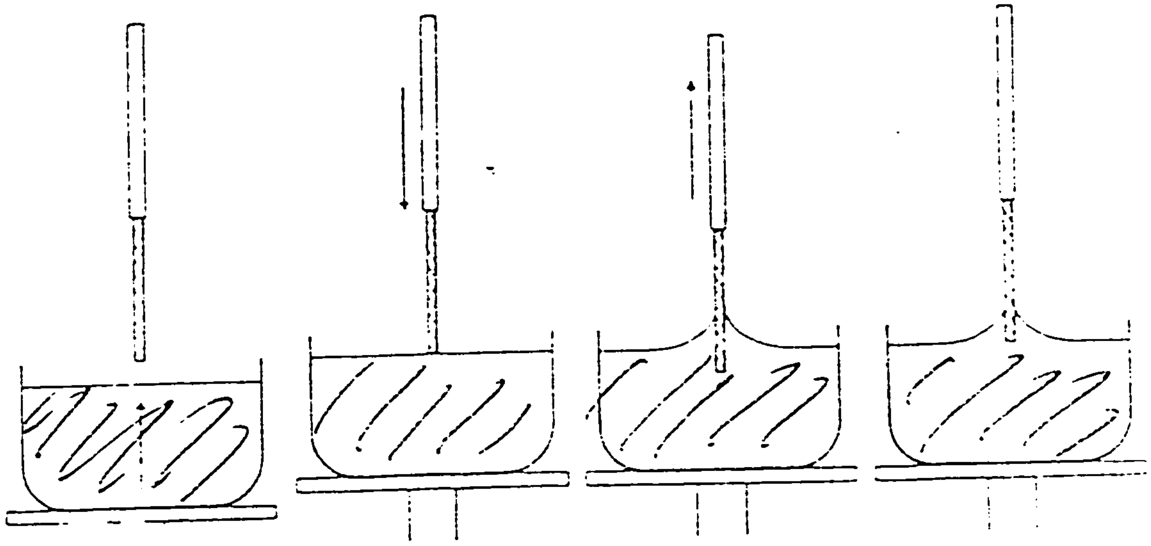


Figure 3-6; KRUSS Ring and plate Tensiometer.



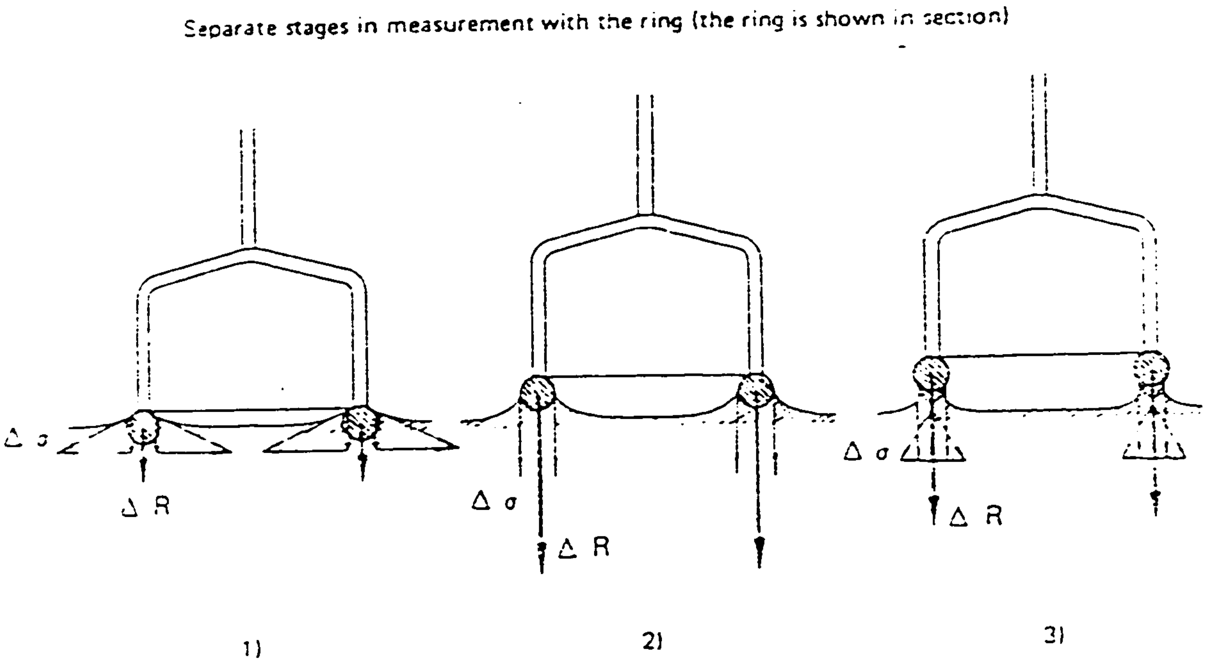
Separate stages in measurement with the plate (the plate is shown in section)

Test vessel is raised towards the lower edge of the plate.

The lower edge makes contact and the plate is drawn into the liquid by surface tension.

The plate is drawn up to the zero level by the tensiometer.

Figure 3-7; Separate Stages in Measurement with the *PLATE* technique.



The vessel is raised towards the lower edge of the ring.

The lower edge makes contact and the plate is drawn into the liquid by surface tension

The plate is drawn up to the zero level by the tensiometer.

Figure 3-8; Separate Stages in Measurement with *RING* technique..

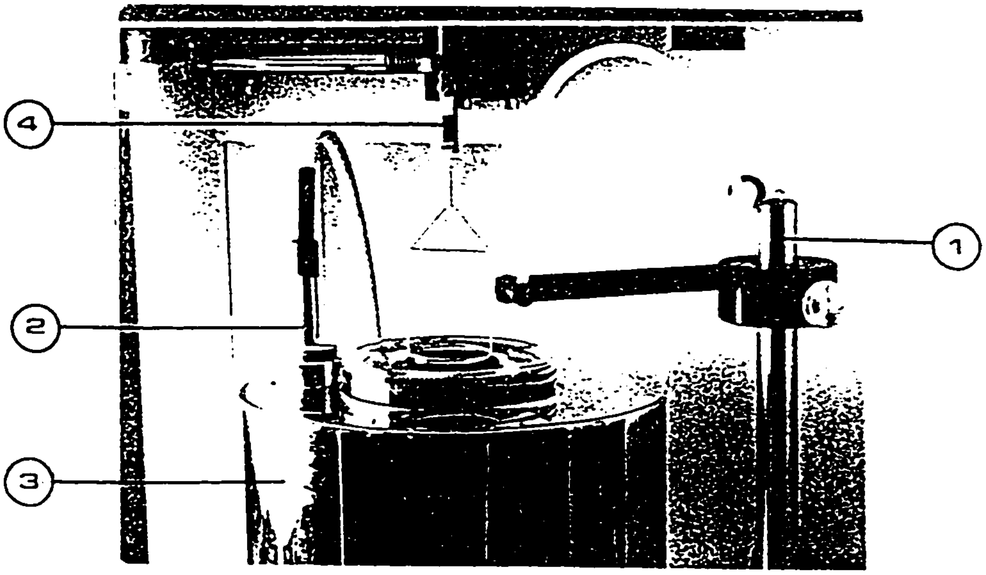


Figure 3-9; The measuring unit of the tensiometer,

(1) guidance and stand for the dosiomat tube,

(2) Pt-100 thermoelement,

(3) Thermostat vessel, and

(4) Ring and plate guidance

CHAPTER FOUR

AMPHIPHILIC DI-BLOCK COPOLYMERS OF METHYL-METHACRYLATE WITH VINYL COMONOMERS:
SYNTHESIS AND AQUEOUS SOLUTION PROPERTIES

4.1 Introduction

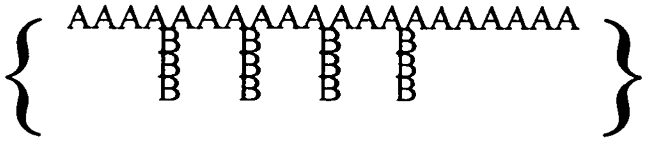
Amphiphilic diblock copolymers have recently become the subject of extensive research due to their self assembly capabilities and microphase separation behavior because of the formation of microheterogenous solution or microdomains. These copolymers are in general interfacially active and act as compatiblizing agents for two-phase separated materials. Amphiphilic polymers find use in many technical applications due to their ability to enrich at interfaces, thereby stabilizing interfacial structures. Diblock copolymers, if properly synthesized, can also be used as mobility control agents that are of high interest in chemical industries of water-based systems, i.e. EOR by polymer flooding. Water-soluble diblock copolymers modified with relatively small amounts of a hydrophobic comonomer, hydrophobically associating polymers, have become the object of considerable interest in many applications because of their interesting rheological behaviors in dilute solutions; i.e. an increase in the zero-shear viscosity due to inter-molecular interactions, and their amphiphilic character generally imparts desirable properties at the interface in colloids.

Polymeric or associative thickeners typically used as mobility control agents in oil recovery processes suffer from a variety of deficiencies, such as shear instability and brine intolerancy. Block copolymers containing both hydrophobic and hydrophilic segments have been shown to form high MW aggregates in solutions as micellar type structures resulting in high efficient shear stable thickeners [29]. Diblock copolymers, which consists of a block of polymer A covalently bonded to a block of polymer B can behave as surfactants if proper structural designs are followed [22, 34-36]. Also simple polymers can often be modified to have an amphiphilic nature similar to surfactants [38]. Amphiphilic materials may result when a hydrophobic block, such as polystyrene (PST) or polymethylmethacrylate (PMMA), is covalently bonded to a hydrophilic block like polyvinylimadazole (PVI) or polyacrylic acid (PAA). For the purpose of such designing, the hydrophobic part should be relatively small for achieving solubility. In such synthesis several chemical polymerization processes can be utilized, i.e. homogenous, heterogeneous, or post modifications [8, 96].

In diblock copolymers, two different homopolymer chains are linked to form a single linear polymer molecule. Since each of the blocks retains some basic properties of the homopolymer from which it originates, in particular with respect to polymer/polymer, polymer/solvent, and polymer/surface interactions, diblock copolymers can display amphiphilic behavior, both in melts (mesomorphic structures), solutions (micelles) and at interfaces (selective adsorption). For the latter reason, block copolymers are increasingly being used as stabilizers of hydrophobic particles in hydrophilic media and vice versa. The idea is that one block (the anchor) adsorbs on to the particle surface, where as the other block sticks out into the solution, thereby providing a steric barrier which prevents the particles from approaching each other too closely.

Water-soluble diblock copolymers are prepared in this study by chain growth or free-radical solution polymerization, as it is commercially synthesized, of appropriate monomers or by post reaction procedures [53,211]. Block copolymers can also be prepared by ionic or any other polymerization where each of which has definite features. Distribution of the units along the backbone can be accomplished by several ways. In nearly all procedures, proper sequencing can be obtained by carefully controlling monomer reactivity, concentration, order of addition, and reaction conditions, i.e. initiator dose, temperature, and reaction media. There are several *classes of copolymers:*

ABABABABABABABA	Alternating copolymer,
AABABBBABAAABAAABBA	Random copolymer,
~~AAA—(A)$_x$—AABBB—(B)$_y$—BBB~~	**Di-Block copolymer,**



and, Graft copolymer

A description of copolymer structure requires the specification of composition, i.e. the relative amounts of comonomers of A and B into the chain; and linearity. Copolymers are most often classified according to their; thus the major classes of copolymers are: statistical (random) copolymers, alternating copolymers, graft copolymers, and *block copolymers*. In block copolymers, long linear sequences distribution of monomer A are joined to long linear sequences of comonomer B. Sequence distribution of monomers in block copolymers can be: Di-, Tri-, or Multi-, depending on the synthesis conditions.

It is well recognized that block copolymers produced from monomers which form noncompatible blocks exist in a variety of special arrangements in both the solid and dissolved states. With the amphiphilic nature of block copolymers composed of hydrophilic and hydrophobic blocks in the same molecule, they are expected to be capable of functioning as high molecular weight detergents that can associate when dissolved in suitable solvents into micellar type structures. Gallot and co-workers [46], demonstrated that poly(styrene-diblock-4vinylethylprinidiumbromide), where the latter monomer is hydrophilic, gave micellar structures that had molecular weights (MW) ten times higher than the an associated polymer molecules when dissolved in water/methanol mixture. These high MW structures were found to be due the formation of aggregates of the insoluble polystyrene blocks, which were stabilized by the water-soluble vinylprinidium blocks [29].

It has been shown in the literature [24] that since some polymers are insoluble in their monomers, insoluble trapped free radicals are produced when a vinyl monomer ,i.e. acrylonitrile, is polymerized in the bulk. Macroradicals are also produced when styrene (ST) is polymerized in alcohols and when other vinyl monomers are polymerized in poor solvents. That the rate of polymerization of MMA and that of the copolymerization of ST and maleic anhydride was faster in poor solvents than in good solvents and that has been observed in previous works.

It is known that heterogeneous solution polymerization takes place when the Hildbrand solubility parameter values of the solvent and polymer differ by at least 1.8 units. The presence of macroradicals in the precipitated polymer has been demonstrated by electron spin resonance (ESR) techniques. Block copolymers of MMA and acrylonitrile were obtained by the addition of acrylonitrile to MMA macroradical in methanol, ethanol, 1-propanol, and hexane at 50 °C. It has been shown also that block copolymers can be obtained by the addition of styrene to acrylonitrile macroradicls, by the addition of styrene or MMA to vinyl chloride macroradicls, and by the addition of any vinyl monomer to a suspension of a macroradical in a poor solvent providing the difference in the solubility parameter values of the monomer and the macroradical are not greater than 3.1 Hildbrand units [41]. For poly(MMA-b-AN) block copolymer, it was found that the rate of formation decreased in poor solvents as the difference between solubility parameter of solvent and macroradical increased. The block copolymer sample prepared at 50

°C. and above were dissolved in benzene which is a nonsolvent for AN homopolymer but a good solvent for MMA and the block copolymer.

Block copolymers of selected macroradicals that have been synthesized by polymerizing MMA in poor solvents were: poly(MMA-b-acrylic acid), poly(MMA-b-AN), poly(MMA-b-ethylmethacrylate), poly(MMA-b-styrene), poly(MMA-b-vinyl acetate), and poly(MMA-b-vinylpyrrolidone [42]. It was found that the length of growing chain in the coils is diffusion controlled. Therefore, the MW of PMMA prepared *in hexane* is essentially independent of the concentration of initiator. Although living ionic techniques was proven to most versatile procedure for the preparation of well-defined block copolymers, it was found that the preparation of poly(MMA-b-ST) were not successful besides it is an expensive technique.

While the pioneer block copolymer was produced by addition of chloroprene to MMA macroradicals by Bolland and Melville in 1963, most block copolymer polymerization are nowadays produced by anionic synthesis, Ziglar catalysis, and step growth or chain growth. There has been increasing activity in synthesizing block copolymers, as seen before, since they offer the potential for obtaining products that incorporate desirable properties of two or more homopolymers. There are several different approaches to synthesizing polymers with long blocks of two or more different monomers [39]. All the methods require considerable theoretical understanding and manipulative skills to obtain well-defined products for specific end use [18].

Copolymerizations of vinyl monomers such as MMA, acrylonitrile, vinyl-imadazole, acrylic acid, or styrene, by free-radical polymerization were reported by several workers [41-43]. It was generally admitted that the overall kinetics of vinyl polymers in heterogeneous medium can be interpreted in terms of an occlusion of the free radical end-groups of the growing chains by the polymer's chains themselves. Some of these radicals are trapped and remain inaccessible to the most reagents unless swelling agents are added or unless the temperature is increased in order to uncoil the polymer molecules.

It is experimentally evident that the presence of trapped radicals in a polymeric chain offers a possibility of preparing block copolymers if another monomer is added in such conditions that the end free radical become accessible for further addition [11]. Bamford and Jenkins [203], have shown that polyacrylonitrile prepared by photopolymerization at 25°C. adds further acrylonitrile, vinyl acetate, vinylidene chloride, acrylic acid, acrylamide, methyl acrylate, MMA, or styrene monomer by heating it up at 60 °C. Hiemeleers and Smets [40], prepared and studied several polymers in heterogeneous medium with the influence of ultra-violet (UV) light. They concluded that the formation of these block copolymers was a direct consequence of the presence of trapped radicals in precipitated polymers, i.e. polyacrylonitrile. Inversely, it was impossible to obtain any block copolymer from polyvinyl chloride. Morishima also has studied the photopolymerization of some polyelectrolytes [58].

Diblock copolymers may be also synthesized by introducing peroxy-groups into a preformed polymer, during or after polymerization, and subsequently initiating the reaction of a second monomer by the peroxidized polymer. Such technique has been used by Ceresa R. J., in 1960 [39], and produced several combination of block copolymers. The high molecular weight achieved for bulk-polymerized poly(MMA-b-AN) of the order 10^6 is such that intermolecular entanglement produce pseudo-crosslinks which are undesirable in this research. If the polymer contains fewer crosslinks the synthesized block copolymer is soluble but branched.

Seymour et. al. [43], studied the synthesis of acrylonitrile (AN) block copolymers. It was found that poor yields of poly(MMA-b-AN) were obtained when AN was added to MMA macroanions, but good yields of poly(ST-b-AN) were obtained by anionic techniques. Poor yields of block copolymers were obtained when nonpolar monomers such as styrene, methyl acrylate, MMA, ethyl acrylate, and vinyl acetate were added to a slurry of AN macroradicals, but these yields increase in the presence of n,n-dimethylformamiode. Poly(MMA-b-AN) with blocks of increasing length were produced by heating MMA macroradicals in 1-propanol with increasing amounts of AN. Acrylonitrile has higher water solubility than MMA.

In a series of studies of block copolymerization of trapped radicals, Minoura and Ogata in 1969 [50], reported that (acrylonitrile-styrene), (vinyl chloride-styrene) and (vinyl chloride-methyl methacrylate) block copolymers can be synthesized by employing trapped radicals in PAN or PVC formed in a heterogeneous media by tri-n-butylboron in air as an initiator. The trapped polymer radicals were activated an addition of dimethylformamide as a solvent. In their study, they have concluded that in the process, the PAN trapped radicals were more active than the PVC radical. The viscosity of poly(VC-b-ST) was measured and found that the intrinsic viscosity increases with increasing conversion. Viscosity behavior of polyacrylamide, alkaline, and surfactant solutions have been inestigated for EOR purposes [5].

Block copolymerization of MMA and polyethylene oxide (PEO) has been studied by Minoura and Nakano [44], by employing high-speed mechanical stirring at 30,000 RPM at 50 °C. They explained that the higher the molecular weight, the better for block copolymerization because degradation occurs easily. Block copolymers of ethylene oxides with other monomers have also been studied by Zdrahala et. al. [45] with the purpose to investigate their chemical compositions, dilute solution behaviors and viscosity, and other peculiar properties including morphologies and solubilities. Many other studies have been conducted to get block copolymers of ethylene oxides [65,66,74,76,82,180,190,191,210]. These polymers can have a future for EOR purposes if properly designed, an area need to be studied.

A group of new polymers of modified polyethylene oxide has been synthesized by introducing different alkyl groups (C_{10}, C_{11}, C_{12}, ..., C_{18}). It was found that water-soluble polymers have surface-active properties and viscosification to polymer's aqueous solutions. Moreover, it was found that these polymers are thermally and mechanically stable and useful in increasing oil recovery during water flooding operations [47].

Copolymers have found considerable utilization in day-to-day application. For example, Spandex (used in sportwear) is a block copolymer of polyurethane (which is a stiff chain) and polyester (a flexible chain). Copolymers of styrene and acrylonitrile are classified as high performance or engineering plastics. Saran, which used as a film and filament, is a copolymer of vinyl chloride and vinylidene chloride with a high content of the latter constituent. polystyrene-block-polybutadiene is a typical rubber. Ethylene-propylene copolymers show good resistance to ozone, heat and oxygen. There are two general types of ethylene-propylene copolymers. One variety is saturated and requires vulcanization before use in automotive parts such as bumpers and chassis. The second type is commonly referred to as ethylene-propylene-dine terpolymers. They are used in the production of appliance parts, as seals and gaskets, and in wire and cable insulation.

There are mainly two procedures for *the synthesis of polymers*, namely addition polymerization and condensation polymerization. *Addition polymerization* involves the sequential addition of monomers one by one to a chain end. This sequential addition requires the creation of an active site. There are three distinct mechanisms based on the type of active site: free-radical, anionic, and cationic.

Strong acids, anionic polymerization, initiate cationic polymerization by strong bases, and free-radical polymerization by easily cleaved molecules such as peroxides and azo-compounds. The initiation and termination steps, which occur in copolymer synthesis through addition polymerization, bear much resemblance to the initiation and termination steps in homopolymerization. The difference, if any, lies in the propagation step, which entirely determines the copolymer composition. The sequence of the different monomer units depends on factors such as monomer and radical activity, polarity, and steric factors.

As a result of self-assembly, block copolymers have considerable application potential. Micellization and solubilization are also two phenomena associated to block copolymers with other molecules and have significant contribution to many behaviors in solutions. The incompatibility between the A and B blocks is the basic driving force for aggregation. The aggregation minimizes the unfavorable interactions between A blocks and the B chains with the aqueous media [48,60-64].

4.2 The Synthesis of Methylmethacrylate (MMA) Copolymers with Vinyl Co-monomers

The advent of block copolymerization gave rise to an entirely new concept for the design and control of polymer properties. Some properties of the homopolymers could be maintained nearly unchanged in a block copolymer system. Furthermore, the added benefit of some new property usually due to the block copolymer morphology arises that belongs to neither of the homopolymers. The motivation of the work of this research was then to hopefully obtain block copolymers of amphiphilic character with thickening and interfacial properties.

In *this work*, synthesis of diblock copolymers of MMA with other vinyl monomers was carried out with the aim of investigating their solution viscosity and interfacial tension properties. Free-radical polymerization was chosen with the use of azo-initiators to induce polymerization at controlled environment. Monomers were freed from inhibitors by vacuum-distilled reaction prior to each polymerization [84].

This study is concentrated on the behavior of block copolymers in solution. The blocks, which are made up of different monomer types, are usually incompatible with one another and hence they prefer to exist in a demixed state rather than in a mixed state. This is a characteristic common to most amphiphilic polymer molecules and is in contrast to the behavior exhibited by species of low molecular weight. In systems consisting small molecules, the large negative free energy contribution from the entropy of mixing usually offsets the unfavorable positive free energy of interaction between the molecules. as a result the existence of the dissimilar molecules as a mixture is thermodynamically favored over that as demixed pure phases. Such a large negative free energy contribution from the entropy of mixing is absent when two polymer molecules mix. Consequently, only those polymer molecules that are chemically very similar prefer to mix. Most polymers, as a general rule, are mutually incompatible with one another. In the case of a diblock copolymer, the incompatibility among the two blocks give rise to the interesting phenomena of microdomain formation in pure block copolymers and of self-assembly in solutions. In the pure state or in solution, the two incompatible blocks are either partially or completely segregated from one another. For example, when AB diblock copolymer is present in solvent S which is selective for B (the term "selective solvent" refers to the solvent being a good solvent for one the blocks and a poor solvent for the other block in the copolymer), the copolymer spontaneously organizes itself in such a way that the resulting microstructure consists of a core region made up of A blocks and a surrounding shell region consisting of B blocks and the solvent S. This multimolecular structure is referred to as a *micelle*. Such a microstructure generated by block copolymers in solutions, resembles in all essential aspects, the well will known micellar aggregates formed from a variety of low molecular weight *surfactants*.

Free radical copolymerization is first carried out by creating a free radical active site or radical generating species, such as peroxide or azo-compound as well as iniferters, e.g., involving photolabile sulfur-carbon bonds, on a given polymer, which then initiates polymerization of the second monomer. Heating generate radicals which then initiate the polymerization. The use of polymers with end-groups that can be converted into radicals by organometallic compounds is another feasible approach to making block copolymers through radical polymerization. Free radical polymerization can be carried out on a large variety of monomers, which are *not amenable to anionic polymerization.*

However, conversions obtained are not very large and the resultant copolymers are usually polydisperse in structure and molecular weight. Anionic polymerization, on the other hand, yields monodisperse copolymers, but the method is restricted to monomers such as styrene, butadiene, isoprene, and methyl styrene. Anionic copolymerization is usually carried out at very low temperatures (-70 °C) in a nitrogen atmosphere, using ultra pure reagents and solvents which is sometimes troublesome. Besides these factors, both the cost and the risk/hazard involved are added to the complexity of the method.

Free radical polymerization can be a suitable method for the preparation of block copolymers. For example, block copolymers may be prepared by coupling macroradicals, or by generating new radicals in the presence of a second monomer by photolytic or mechanical degradation. As an alternate, difunctional initiators may be employed[84]. These are usually diperoxides or peroxide-azo containing molecules, and thus can be decomposed in to steps by temperature control. The first cleavage initiates polymerization and production of a macroperoxide or macroazo-molecule. The second cleavage is in the presence of a second vinyl monomer, and a block copolymer results. Also block copolymers may be prepared by addition of a second vinyl monomer to occluded "living" macroradicals. Thus by use of the proper technique block copolymers have been reported prepared by free radical polymerization [51-54].

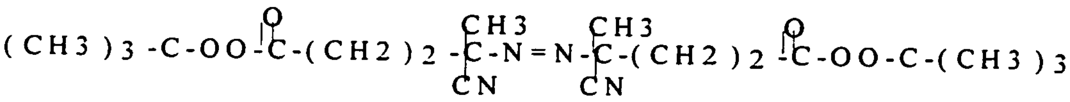
4.2.1 Polyfunctional Initiators

Di- and polyfunctional initiators are of great interest because of their capacity to generate free radicals stepwise giving the possibility of using them in direct procedures to obtain block copolymers of different structures. In polyinitiators, e.g., polyaxo derivatives, the initiating groups are in the chain rather than the end groups. The general formula for such initiators is -(-R-N=N-R-N=N-)-, where R may be of low molecular weight, or R may be a precursor sequence of the block copolymer.

Preparation of di-tert-butyl-4,4'-azo-bis-(4-cyanoperoxyvalerate): (RS604)

Many azoperoxides are derivatives of 4,4'-azo-bis-(4-cyanovaleric acid) compound or ACV, an important azoacid from which other types of hetrofunctioal initiators have been prepared in literature. They represent the building block of other polyfunctional initiators due to the easy attachments of functional groups at each end.

Simionesscu et al. [52,54], synthesized azoperoxide bifunctional initiator by two different methods. A synthetic method (CDI method) was modified in this study in an attempt to synthesis a new sequential free radical initiator which has a structure,



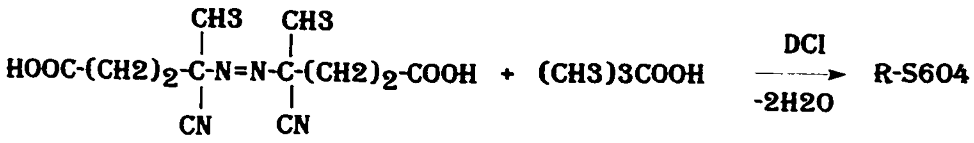
$$(CH_3)_3\text{-C-OO-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-N=N-}\overset{CH_3}{\underset{CN}{C}}\text{-}(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-OO-C-}(CH_3)_3$$

RS604 initiator with MW = 454, mp. = 95C.

Because of the difference in stability of azo-group and per-ester group on the compound, block copolymer synthesis can be carried out in two separate stages of polymerization as seen in DCI method. The initiator (RS604) has an azo-group at the center and per-ester groups at each end of the molecule.

DCI Method:

In a three-neck flask equipped with a magnetic stirrer and dropping funnel placed on water (ice) bath maintained at 0°C. as seen in Figure (3-1), 12 gm of DCI or dicyclohexylcarbo-di-imide and 70 ml of tetrahydrofuran (THF) were introduced first. Then a solution of 5.4 gm of ACV in 75 ml THF prepared separately was added. The mixture was treated for 15 minutes with 30 ml chloroform ($CHCl_3$) and 6 gm of t-butyl-hydroperoxide $[(CH3)_3\text{-COOH}]$ solution drop wise from the dropping funnel where t-butyl-hydroperoxide is in excess. The stirring was maintained for 48 hr in the absence of light. The dicyclohexyl urea separated from the very beginning (solid powder) and was finally filtered off. After evaporating the solvents (THF, $CHCl_3$) under vacuum, the residue (oily liquid) was washed with 5 % $NaHCO_3$, 5 gm into 100 ml distilled water, several times. Then the residue was extracted as : (1) adding dichloromethane (organic solvent) to the mixture, (2) filtering the mixture solution, (3) shaking the remained solution vigorously. Two layers were left in the funnel, the organic layer and aqueous layer. Then the organic layer was removed after settling by gravity. Again dichloromethane was added and the procedure was repeated. Distilled water was added twice for washing the material left. The wet material in the flask was then poured into another flask containing $CaCl_2$ to dry it. The contents were left a day shielded from light and then was filtered off. Viscous material of a bi-functional initiator was obtained. Water and acetone was added to the viscous material to make it rigid. and then filtered. Fine crystals (1.9 gm) of azo-initiator RS604 was obtained after drying in an oven at 30 °C.



$$HOOC\text{-}(CH2)_2\text{-}\overset{\overset{CH3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}N{=}N\text{-}\overset{\overset{CH3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}(CH2)_2\text{-}COOH + (CH3)3COOH \xrightarrow[-2H20]{DCI} R\text{-}S604$$

(ACV)

Reaction in DCI method.

In this work, with the attempt to synthesize a block copolymer of styrene and methyl methacrylate (MMA), the azo-group of the initiator will be decomposed first at 60 °C in order to initiate the styrene monomer and produce the polystyrene polymeric initiator with the perester groups at both ends of the polymer chain. Such chains are going to initiate the polymerization of the second monomer, MMA.

4.2.2 Polymerizations and Copolymerizations

Polyinitiators can be used to prepare block copolymers by radical polymerization in two step procedure. In the first step the polyazo compound is partially decomposed in the presence of a monomer (ST) to prepare an azogroup-containing prepolymer. Decomposition of the remaining azogroups in the presence of the a second monomer results in a block copolymer.

a. Preparation of Styrene Polymeric Initiator: (macroinitiator) or (BP 7)

In a three-neck flask, 10 ml of destabilized styrene (freed from inhibitor) and 0.035 gm of the initiator (RS604) and 10 ml benzene were charged separately. The dissolution was speeded up by shaking the bottle while blowing nitrogen to expel air as in Figure 3-1. The tightly capped bottle was then clamped and contents were stirred on a thermostated water bath at 60 °C. This temperature was sufficient to activate the azo-group in the initiator molecule yet leaving the perester group intact. After the required time period of polymerization (4 hr), the bottle was quickly cooled and the contents were diluted with benzene 10 ml, then coagulated with drops of methanol. The precipitates were filtered using suction. Coagulations and filtrations were repeated twice after which the polymer was vacuum-dried in an oven at 60 °C. until it reaches constant weight. The procedure was adapted from Piirma and Chou work [53].

Preparation of MMA Copolymers (Diblocks):

b. Preparation of Poly(styrene-block-MMA) Using Macroinitiator:

As an example; 0.08 gm of polystyrene polymeric initiator (macroinitiator) and 30 gm of benzene were charged in a three-neck flask equipped with inlets and outlets to deaerate the solution by nitrogen. After the contents were completely dissolved, 10 ml of MMA was added and the solution mixture was deaerated by nitrogen for 15 minutes. The flask was then tightly capped with a punched cap and sealed with gasket. The polymerization was maintained at 60 °C. for 24 hr. Then the contents were slowly coagulated with a three-fold quantity of methanol to obtain finely divided precipitate. HCl was then added in a small quantity to increase the pH solution. The mixture was then vacuum-filtered and washed with dichloromethane twice, after which it was vacuum-dried in an oven at 60C. for 12 hr. Procedures from Piirma and Chou work [53] were followed with some modifications.

As another example; the same procedure was followed, except that the reaction was in a bulk media and in the presence of heat, to obtain a block copolymer labeled (BP12). The initiation was achieved by light and heat at 60 °C. Table 4-2 shows the reaction conditions.

Di-Block Copolymers Based on SEYMOUR Method

c. Preparation of Poly(MMA-b-acrylonitrile) by UV Irridiation:

In a Pyrex tube, 5 ml of a freshly distilled MMA was added to 5 ml hexane which also contained 0.05 gm of azo-bis-isobutyronitrile (AIBN). The bottle contents were first degassed in a vacuum system prior to irradiation by ultraviolet light (UV) from an annular type phtoreactor equipped with lamps emitting at 350 nm at 25 °C. At the end of reaction time (8 hr.), MMA macroradicals were expectedly obtained. Then the block copolymer was prepared by transferring the slurry of MMA macroradicals in an inert atmosphere to small bottle containing 25 ml of freshly distilled acrylonitrile. The bottle was sealed and the mixture was heated to 50 °C. for 72 hr. The procedure of Seymour and Hepuzer [42,43,51] was applied with some minor modifications.

d. Series Preparations of Poly(MMA-b-acrylonitrile) copolymers:

The procedure of Seymour et. al [41-43] was followed in preparing diblock copolymers. Hexane was chosen (a poor solvent) to solvate the materials because its solubility parameter value differ from that of the MMA stable macroradical by more than 1.8 Hildbrand units.

As an example; 25 ml of freshly distilled MMA was polymerized in the absence of oxygen and in the presence of 0.3 gm of AIBN with 50 ml hexane in a reflux apparatus fitted with dropping funnel, oil bath and mechanical stirrer for homogenous heating, and nitrogen inlet/outlet deaerating the contents. The same materials were charged at the same conditions in another flask except that 0.7 gm of AIBN was used instead and the polymer obtained labeled P9/II L. Block copolymers (P9/II L and P9/II R) were synthesized by the addition, to both flasks, of 25 ml or

(62 mol%) of freshly distilled acrylonitrile (AN) in an inert atmosphere. Table 4-1 shows the reaction conditions.

Adding dichloromethane and then methanol in high quantities, two-fold washed the block copolymer (P9/II R) completely. Vacuum-filtration and washings were repeated twice and then the polymer recovered was vacuum-dried in an oven at 60 °C. But the block copolymer (P9/II L) was washed by three-fold methanol. The precipitate was washed again and then dried in an open atmosphere for some time and then vacuum-dried at 60 °C for 12 hr.

Moreover, block copolymers of poly(MMA-b-AN) of different doses and varied amounts of initiator (AIBN), as shown in Table 4-1, were synthesized with the same polymerization conditions as described earlier in an attempt to get polymers with different molecular weights.

Table 4-1; Copolymerization conditions for the synthesis of di-block co-polymers of poly(AN-b-MMA) in a heterogeneous medium

Sample code	Hexane; Ml	[MMA]* ; mol%	[AN]♦ ; mol%	[AIBN]; gm
P9/ II R 38AN-0.3AIBN	50	38.1 (25 ml)	61.9 (25 ml)	0.3
P9 /II L 38AN-0.7AIBN	50	38.1 (25 ml)	61.9 (25 ml)	0.7
P11/ I 38AN-0.2AIBN	25	38.1 (25 ml)	61.9 (25 ml)	0.2
P11/ II F2 76.5AN-0.15AIBN	25	23.5 (12.5 ml)	76.5 (25 ml)	0.150

* Water solubility of Methylmethacrylate at 20° is 11.5 g/l, density = 0.936 gm/cc, FW=100.12 g/mol

♦ Water solubility of Acrylonitryle @ 20 °C is 93 g/l, more soluble than MMA, density = 0.806 gm/cc, FW_{AN} = 53.06 g/mole, 0.3797 moles in feed

e. Preparation of Poly(MMA-b-Vinylimadazole):

It is known that vinyl imadazole (VI) is water-soluble in all proportions. It has been mentioned previously that block copolymers can be synthesized successfully when a vinyl monomer, such as VI, is added to the suspension of a macroradical like MMA macroradical in a poor solvent, e.g. hexane, providing that the difference in the solubility parameter values of the monomer and macroradical are not greater than 3.1 Hildbrand units.

As an example: 3 ml freshly distilled MMA and 10 ml of hexane as a solvent were charged in a three-neck flask deaerated with nitrogen. Then 30 mg of AIBN was added to the contents. After 10 minutes, the time required to produce MMA macroradicals, the other monomer (5 ml VI) was added with caution. The reaction was kept under 70 °C through out the polymerization for 48 hr. The product had a brownish/orange color and very viscous and was found soluble in methanol. Addition of potassium hydroxide (KOH) gave white precipitate with no more brownish color. It was found that the reaction mixture insoluble in dichloromethane. Then the precipitate was washed with two-fold of di-ethylether. Finally the polymer was recovered purely by repeated precipitation and dissolution cycles. Then it was washed again and vacuum-dried in an oven at 60 °C. for 12 hr. and labeled BP15. The yield was very small (1.5 gm), and the hydrolysis afterwards was not successful. so another experiment was conducted.

As another example: In a five-fold scale, the previous experiment was repeated to increase the yield for enough characterization. In a flask, 15 ml of freshly distilled MMA was added to 50 ml hexane and the contents were purged with nitrogen for 15 minutes. Then 150 mg of AIBN was added to induce initiation step. The contents remained under stirring for another 15 minutes at 70 °C. After that 25 ml of vinylimadazole (VI) was added. The reaction mixture started to solidify early, after 20 hr., and was found soluble in methanol and isoporopanol but insoluble in water or di-chloromethane. A 100 ml of methanol was added to the solidified compound under mild heating to ease solidification. By this, the solvent hexane has been removed. Then the contents of the flask were just poured to 1000 ml of distilled water for getting a precipitate. Another 50 ml methanol was added to the reminder of the flask and found soluble in isopropanol and insoluble in methanol. Then 150 ml of isopropanol was added to remove all the reminder in the flask. Then it was kept for some time under mild heating. The solid material was brokendown into small pieces. Di-chloromethane was then added in small quantity. The solid material was transferred to a beaker containing the previous material. The beaker was kept under mild heating for some time. Then its contents was filtered under vacuum several times. The material recovered spread on piece of paper and left for drying. It was expected to recover 25 gm of the polymer. Then the material was vacuum-dried in an oven at 50 °C. for 8 hr. Then it was crashed into powder. The weight of the polymer recovered was 27.5 gm (86 %) enough to perform characterizations, e.g. Foruier Transition Infra-Red (FTIR) and Elemental Analysis.

Master Table 4-2; Synthesis Conditions of Di-Block Copolymers of MMA by Heterogeneous Copolymerization

Sample Code	Structure	MMA, X_1; Ml	X_2; ml	Initiator; gm or MG	Solvent; ml	Temp.; °C
BP8'	Poly (MMA-b-ST)	10	10	0.08 gm PSTI	(30 gm) benzene	60
Bulk P12	Poly (MMA-b-ST)	10	10	HEAT	-	60
P9/II R	Poly (MMA-b-AN	25	25	0.5 gm AIBN	50 ml Hexane	50
P9/II L	Poly (MMA-b-AN	25	25	0.7 gm AIBN	50 ml Hexane	50
UV-P10	Poly (MMA-b-AN	5	25	0.05 gm AIBN	5 ml Hexane	25
P11/I	Poly (MMA-b-AN	25	25	0.2 gm AIBN	25 ml Hexane	50
P11/IIF	Poly (MMA-b-AN	12.5	25	0.036 gm AIBN	25 ml Hexane	50
BP15	Poly (MMA-b-VI)	3	25	30 MG AIBN	10 ml Hexane	70
BP45	Poly (MMA-b-VI)	15	25	150 MG AIBN	50 ml Hexane	70

where X_2, second monomer dose; **ST,** Styrene; **AIBN,** azo-bis-isobutyronitrile
PSTI, Polystyrene polymeric initiator

Preparation of Copolymers of Poly(MMA-b-AN):

Freshly distilled methyl- methacrylate was polymerized in the absence of oxygen and in the presence of 1.5% recrystallaized azobisisobutyronitrile as a 10% solution in the freshly distilled solvent at a specified temperature such as 50 °C.

Block copolymers were produced by the addition of freshly distilled acrylonitrile to a suspension of the macroradical in hexane as a solvent. The rate of polymerization was monitored by observing aliquot yield data. The block copolymers were filtered, solvent washed and vacuum-dried.

4.3 Polymer Modifications

Most of the MMA copolymers recovered were not water-soluble in all proportions. Some, however, were marginally soluble. For any aqueous solution behavior characterization study to take place, i.e., for EOR purposes or water-based systems, the polymers should be made water-soluble by appropriate modifications. Base/Acid hydrolysis, quaternization, or sulfonation are among the techniques suitable to produce a water-soluble product through modifications. Polymer modifications are generally intended to impart different desired properties to the modified material such as enhanced thermal stability, increased solvent stability, multiphase physical responses, biological resistance, compatibility or degradability, impact response, flexibility, rigidity, etc. Base hydrolysis was chosen to hydrolyze selected polymers for the purpose of studying their solution behaviors, e.g. viscosity and ST/IFT activity.

4.3.1 Base Hydrolysis to Di-Block Copolymers

Hydrolysis will be always an alternative technique to modify polymers and copolymers commercially. Polymethacrylates have always been hydrolyzed; however, the hydrolysis of methacrylates generally requires more drastic reaction conditions than that of acrylates. Unless careful control over hydrolysis process is exercised, incomplete reaction as well as chain degrading may take place. The procedure is of the same value, since the molecular weights and tacticity of certain esters can be determined with comparative ease. Well defined polyacrylic ester, for example, on hydrolysis are thought to retain the characteristics of the backbone, thus offering information on the molecular weight and tacticity of the resultant polyacids. If on reesterfication of the polyacid the original polyester is regenerated, the procedure has a measure of self-consistency. Generally, atactic and isotactic polymeric esters are more rapidly hydrolyzed than the corresponding syndiotactic resins.

The alkaline hydrolysis, as expected, will frequently resin in rigid gels, particular if a dilute alkaline solution is added to the polyester solution to permit good dispersion of the alkaline solution. If the concentration of alkali is too high, the polyacrylate salts will tend to precipitate. Isotactic polymethyl methacrylte with Mv of 1,250,000 can be hydrolyzed to the extent of 49% within 1.5 hr whereas the conventional polymer of Mv 100,000 is hydrolyzed 50% in 140 hr. Syndiotactic and atactic polymethylmethacrylate also hydrolyze slowly. In general it was observed that as hydrolysis proceeds, the polymer becomes swellable in water at low degrees of conversion. Only when hydrolysis has reached approximately 15% of the ester groups, does the polymer, which now might be considered a copolymer of methylmethacrylate and sodium methacrylate, becomes water-soluble. At any rat, however, a water-soluble potassium polyacrylate or sodium polyacrylate could be obtained with appropriate procedures.

a. Preparation of Sodium Poly(methacrylate-block-acrylonitrile) :

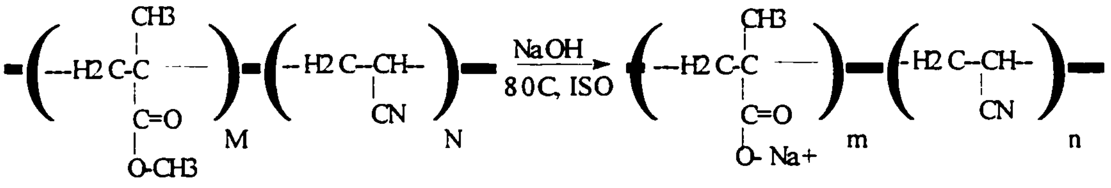
(derived from parent copolymer, P9/IIR)

As an example: to a cooled solution of 9 gm (0.225 mole) of sodium hydroxide pellets (NaOH) in 10 gm (0.555 mole) of water and 200 ml of isopropanol, as a hydrolyzing medium, was added to 9 gm of conventional polymer P9/IIR. The mixture was deairated by passing nitrogen through isopropanol was chosen as an appropriate medium to facilitate and wet the chains. The mixture was heated to 83 °C. for 140 hr. (6 days) for complete hydrolysis and then cooled.

After 140 hr. of hydrolysis, reaction was stopped and then 200 ml of isopropanol/acetone mixture was added after cooling. Then the mixture was washed several times with 30ml distilled water to remove excess NaOH. The mixture was then vacuum-filtered and the filtrate was vacuum-dried for 4 hr. at 40 °C. The solid material was then crashed to powder and again vacuum-dried for another 4 hr. It was found that traces of NaOH still exist, excess weight. So the powder was washed with 100 ml methanol which is soluble with NaOH, and then the mixture was vacuum-distilled. A mixture of methanol and sodium acetate was further added and the solution mixture was stirred under worming for 1/2 hr to extract NaOH. Then the mixture was vacuum-filtered and weighs 13 gm. Then 100 ml of distilled water was added to the filtrate under mild heating till it got viscous and homogenous. The solution mixture was then decanted into 600 ml methanol to get a precipitate, white color polymer. The washing was repeated twice. Then the precipitate was isolated by vacuum-filtration and dried in an oven at 60 °C for 2 hr. After two hours of drying the recovered hydrolyzed polymer weigh 8.5 gm. Then it was crashed and dried for 4 hr. in an oven at 60 °C.

b. Hydrolysis of the Copolymer (P9/II L):

Another example of hydrolysis is as follows; 9 gm of purified poly(MMA-b-AN) P9/II L was added to 9 gm (0.225 mole) NaOH in 10 ml of water and 200 ml of isopropanol in a rounded-bottom flask, fitted with a reflux condenser. The reaction mixture was then stirred and heated to 83 °C. Before the reaction started, it was deairated by bubbling nitrogen. After 140 hr. (> 6 days) of hydrolysis, the hydrolysis was thought to be complete. It was found that the mixture, a white homogenous solution, is soluble in water or methanol. Then 30 ml of distilled water was added under mild heating and left overnight for complete dissolution. Then the contents were decanted to a bottle containing 300 ml isopropanol and left under mild agitation for precipitation. Two cycles of dissolution/precipitation were repeated. Some acetone was added to harden the precipitate which was then broken-down into small pieces. The polymer (precipitate) was then vacuum-dried in an oven at 60 °C. for 2 hr. Another 100 ml of isopropanol was added to the polymer and left under mild heating for few minutes to make it brittle. Then the polymer is washed again with 60 ml of distilled water and left for dissolution. The aqueous solution was decanted to a beaker containing 300 ml of isopropanol under stirring. Then 200 ml of acetone was added to the precipitate to make harden it and left under mild heating for 8 hr. The solid polymer was broken-down into small pieces and left fort drying. Then it was transferred into a beaker containing 150 ml of isopropanol and left under mild heating for 2 hr. The recovered polymer was then acetone-washed and vacuum-dried for 4 hr. Further washing with distilled water and then methanol was performed to get red of excess NaOH. The solid polymer was then crashed to fine powder and vacuum-dried in an oven at 60 °C. for 8 hr. The expected structure of the hydrolyzed copolymer takes the scheme as shown below.



Hydrolysis Reaction Representation.

c. Preparation of Sodium Polymethacrylate-block-Polyvinylimidazole: [Na-polyMA-b-polyVI] (sample used BP45)

Another example of hydrolysis is as follows; A solution of 12.2 gm of NaOH pellets in 13.5 ml distilled water was charged in a 100-ml round-bottomed flask fitted with a reflux condenser. Then a solution of 12.2 purified polymer in 270 ml isopropanol was added to the flask which is under nitrogen purging. The reaction was then started under stirring and heating at 83 °C. After 140 hr. (more than 6 days) of hydrolysis, the reaction stopped and cooled. Then the contents was filtered to eliminate isopropanol and then washed with 300 ml distilled water and left under mild stirring and heating. Another 200 ml of distilled water was added because the mixture was very viscous and has some hydrogels. More distilled water was added (400 ml) to the mixture and kept overnight to settle. The hydrogels were then gravity-separated and the upper layer was transferred to another flask. Six-fold of isopropanol was then added to the solution to get a salt precipitate by settling for 2 days. The contents were vacuum-filtered while isopropanol being added from above the crucible funnel. White precipitate was separated from the filtering after shaking and settling under mild heating over a water bath. This process was repeated several times until the white stuff (the polymer salt) was completely separated from the black. Then the salty solution was left overnight under propanol and then vacuum-filtered. Then the contents were transferred to small rounded-flask and propanol was freed. The white stuff was then vacuum-dried in an oven at 60 °C for 2 hr. while the black one was discarded. Therefore, only 1.75 gm was recovered as white salt after several purifications to use the hydrolyzed polymer later on for solution property analysis. Hydrolysis conditions are mentioned as depicted from Table 4-3.

The black stuff was washed with 200 ml propanol to extract any salt but unfortunately it was jelly may be because of chain cross-linking due to prolong hydrolysis. Aqueous gel formation was expectedly attributed to the aggregation of extended linear coil micelles in which the hydrophilic ends become entangled as the temperature rises due to dehydration. The hydrolyzed polymer was then characterized by FTIR spectroscopy.

BP8' and BP12 polymers, however, exhibited resistance to hydrolysis. They both have been acidically hydrolized by sulfuric acid but without any success. Other polymers were also hydolized without any success. The lack of water solubility to other diblock copolymers (BP8', BP12, BP10, P11/I, and P11/IIF2) could be due to the fact that they are not hydrolyzed to a high enough degree because of steric hindrance to reaction, or the molecule has become too hydrophobic in nature, as is the case of samples BP8' and BP12. However, these polymers were completely soluble in organic solvents such as methanol and dichloromethane.

Table 4-3; Hydrolysis Conditions for Selected Copolymers at 83 °C.

Sample Code	Isopropanol ml	NaOH; gm	H_2O; ml	Polymer; gm	Recovered polymer; gm	Hydrolized polymer* structure
P9IIR or HD2&	200	9 gm (0.225 mol)	10	9	8.5	Na-polyMA -b-polyAN
P9IIL or HD6	200	9 gm (0.225 mol)	10	9	8.0	Na-polyMA -b-polyAN
BP45 or HD8	270	12.2 gm (0.305 mol)	13.5	12.2	1.75	Na-polyMA -b-polyVI

& HD stands for hydrolized polymer

* Hydrolized polymers obtained were fully water-soluble

Reaction temperature: 83 °C.

4.4 Polymer Characterizations and Identifications

4.4.1 Elemental Analysis

Elemental Analysis (EA) meant to characterize polymers was performed right after they were successfully synthesized to determine the elements constituting each copolymer (*composition*): carbon, hydrogen, oxygen, and nitrogen contents as in Table 4-4. It was conducted at the central analytical laboratory (CAL) of the K.F.U.P.M research institute. Carlo Euba model 1106 elemental analyzer was used for the determination of elements. Routinely, for solid samples, the elemental analyzer accuracy is within ± 0.3%.

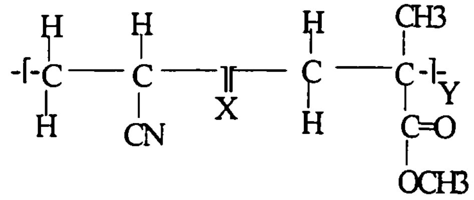
As an example for the analyzer: A standard compound, di-nitro-phnylhydrazone ($C_{12}H_{14}N_4O_4$), contained 51.79%C, 5.07%H and 20.14%N gave 51.62, 5.06 and 20.09 for the respective elements.

Table 4-4; Elemental Analysis of the copolymers of MMA

Sample ID	%C	%H	%N	%O
BP8', P(ST-b-MMA)	73.6	7.9	ND*	15.9
BP12, P(ST-b-MMA)	90.1	7.9	ND	ND
P9/IIR, P(AN-b-MMA)	61.5	7.4	7.6	19.8
P9/IIL, P(AN-b-MMA)	59.2	8.1	ND	30.3
P10UV, P(AN-b-MMA)	57.7	7.9	ND	29.2
P11/I, P(AN-b-MMA)	61.9	7.2	9.9	17.9
P11/IIF2, P(AN-b-MMA)	61.2	7.2	10.1	18.6
BP15, P(VI-b-MMA)	55.4	6.7	16.6	13.6
HD2, Na-polyMA-b-polyAN	11.7	2.9	ND	-
HD8[a], Na-polyMA-b-polyVI	42.3	5.7	11.1	24.4

ND: not detected , a : In HD8 there were no sulfur present.

As an example: To know the composition of P11/IIF2 polymer or (% MMA and % AN), the following calculation was performed.



Structure of poly(AN-b-MMA) copolymer

To get $\frac{Y}{X}$%, and then the % MMA and % AN, we know that MW_{AN}= 53 g/mol and MW_{MMA} = 100 g/mol, and %N=10.1, then

$$\frac{\mathrm{x}}{\mathrm{x}+\mathrm{y}}=\frac{(14)(1)(x)}{(53)(x)+(100)(y)}=\frac{10.1}{100}$$

based on Nitrogen; $\dfrac{14}{53+100\dfrac{y}{x}}=0.101$

$$\frac{y}{x}=\frac{MMA}{AN}=0.856$$

Basis = 1; % MMA = y/(x +y) = (y/x)/(1+y/x) = 46,
and hence % AN = 54

Another an example: Elemental analysis was also done to the sample HD8 as shown in Table (4-4). It was found that
% Na-PMA = y/(x +y) = (y/x)/(1+y/x) = 38.77,
and hence % VI = 61.23

Similarly, Na-polyMA-b-polyAN copolymer composition has been obtained from elemental analysis and % AN and % NaPMA were calculated.

4.4.2 FT-IR Analysis

Fourier Transform Infra-Red spectroscopy (FT-IR) for some of the copolymers (see Appendix C) were done by Perkin-Elmer spectrometer in an attempt to characterize the copolymers synthesized earlier. The IR spectra (absorbance vs. wavenumbers) of the hydrolized copolymer (HD2 in Table 4-4) showed a sharp peak at 2220 cm^{-1}, as shown in Figure (4-1) end of this chapter, indicating the presence of the nitrile group -CN and hence confirming the incorporation of polyacrylnitrile into the copolymer chain while the PMMA blocks were completely hydrolized to Na poly(metacrylate) blocks confirmed by the presence of carboxylate groups.

The copolymer BP15 or polyMMA-b-polyVI has also been characterized by FT-IR analysis using Perkin-Elmer spectrometer (400-4800 cm^{-1}). The IR spectra of the polymer showed a sharp peak or band at 1727 cm^{-1} indicated the presence of carbonyl group from PMMA and also at 1648 cm^{-1} indicating the presence of N=C or PVI in the block copolymer structure. The band showed at 1148 cm^{-1} is an indication of C-O in the copolymer. The IR spectrum of this polymer in hand is shown in Figure (4-2). The IR spectra of the comonomers of MMA and VI are shown in Appendix C for comparison.

Moreover, FT-IR analysis has been done to other MMA copolymers such as BP10, P9IIR, P9IIL, and P11IIF2 as indicated in Appendix C. The IR spectra showed a sharp peak at 1730 cm^{-1}, indicating the presence of the ester carbonyl group from PolyMMA. Also the band at 2220 cm^{-1} indicates the presence of nitrile group -CN and confirmed the incorporation of PAN into the block copolymers. The FTIR spectra of MMA copolymer P9IIR is shown in Figure (4-3) along with the major absorbence bands for convenience.

Block copolymer of polyST-b-polyMMA was also analyized by FT-IR Perkin-Elmer spectrometer (400-4800 cm^{-1}) and its IR spectra, as shown in Figure (4-4), for sample BP8' which showed a sharp peaks at 1733 cm^{-1} and 1494 cm^{-1} indicating the presence of both carbonyl and aromatic groups in PMMA and PST in the copolymer, respectively. Finally IR spectra of the polyinitiator RS604 has also obtained, Figure 4-20 Appendix C, from the same instrument and it showed a sharp peak at 1590 cm^{-1} indicating the presence of azo group -N=N- in the polyinitiator chain.

The FTIR spectra of the monomers MMA and VI are shown in Figure 4-5, while the IR spectra of the other monomers such as ST and AN are shown in Figure 4-6 for comparison purposes.

4.5 Aqueous Solution Properties of Copolymers

The solution properties of the MMA copolymers have been studied with many different conditions. Solution viscosity behaviors and, surface and interfacial tensions of the solutions were investigated with respect to temperature, polymer concentration, salinity and shear rate. For this study, concentrated stock solutions were first prepared at least 24 hr before analysis. Then solutions of desired concentrations were later prepared by dilution from the appropriate stock solutions with deionized water. Deionized and distilled water were used extensively. Proper concentrations of NaCl were also prepared for investigating the effects of adding NaCl to the polymer solutions.

4.5.1 Viscosity Behavior of the Copolymer Solutions

(Rheological Behavior in Aqueous Solutions)

Solution viscosity of the polymers that successfully and completely hydrolized were determined using a digital Brookfield viscometer with UL adapter accessories at shear rates ranging from 0.4 to 73.4 s^{-1}. The procedures mentioned earlier in Chapter (3) were followed. All the viscosities of the copolymers having concentrations, 0.5 wt %, 1.0 wt %, 1.5 wt %, and 2.0 wt % were measured at temperatures 25 °C, 45 °C, 75 °C, and 95 °C. Also polymer concentrations of 0.01 wt %, 0.05 wt %, and 0.1 wt % were prepared to investigate the dilute solution behavior of polymer at different shear rates.

Dilute and semi-dilute aqueous solution regimes of synthetic water-soluble (hydrolized) polymers; HD2, HD6 and HD8; are of interest in this part where the examination of structure-property relationship is needed. It should be noted that relatively high viscosities and pseudo-plastic behaviors, as depicted in Figures 4-7 to 4-9 and Tables 4-5 to 4-7, are observed for these hydrophobic block polyelectrolyties (charged polymers). The solution properties and ultimate performance of these polymers as mobility control agents are dictated by molecular structure.

The micellization process of the hydrophobic blocks in a polar media results in small colloidal structure referred to as *micelles* at a critical polymer solution concentration or CMC. The amphiphilic polymer molecules are arranged in a micelle with their hydrocarbon portion pointed toward the interior of the micelle and their ionic ends outward toward the aqueous phase. The number and the size of the micelle depend on the polymer concentration. The transformation of the solution to the colloidal state as the polymer solution exceeds the CMC occurs to minimize the free energy of the solution (heat is liberated) and is accomplished by a sharp drop in the surface tension of the solution. Electrical conductivity, ion activities, viscosity and other solution properties also show marked changes at CMC. Both spherical and rod-like micelles can be formed in the micellization process but rod-like exhibit high viscosity than spherical micelles.

a. Effect of shear rate and concentration:

Tables 4-5 to 4-7 and Figures 4-7 to 4-9 display the effects of shear rate and polymer concentration on the viscosity of the *block polyelectrolytes*, i.e., block copolymers of long soluble ionic block length (as a corona in a regular micelle) and a short insoluble block length (as a core in the regular micelle)in an aqueous solution, sodium polymethacrylate-block-polyacrylonitrile and sodium polymethacrylate-block-polyvinylimadazole (HD2, HD6 and HD8). For the three polymers considered, an almost shear rate independent viscosity is observed when the shear rate is high, i.e. 39.6 and 79.2 S^{-1}, as depicted in Figures 4-7 to 4-9. Generally as shear rate increases, the solution viscosity slightly decreases which is a case of less shear-thinning effect but the situation is different at low shear rates where there exist a strong shear thinning behavior, since the physical interchain associations are disrupted, an advantage to polymer flooding operations where the shearing is high during injection at the start but not afterwards. The solution shear viscosity of the polymers considered, however, is restored when the shearing force is removed.

Furthermore, Figures 4-7 to 4-9 show an increase in viscosity as the polymer concentration increases from 0.01 wt % to 0.1 wt % and 0.5 wt % to 2.0 wt % for the concentration range considered of the three polymers. At 2.0 wt % (20,000 PPM or 20,000 mg/l) of HD2 polymer concentration, The polymer exhibits the highest response in solution viscosity, 1800 cps., among the other polymers due to strong intermolecular hydrophobic association into multimolecular micelles that increases the HDV of the coil. HD8 polymer, however, maintains its viscosity at high shear rate, 79.2 s^{-1}, than HD6 polymer. It is readily observed that the degree of association were lower in the case of the diblocks HD6 and HD8.

As expected the behavior of such polymers in deionized water (no other additives were added at this point) which is a solvent selective for one of the blocks is significantly worth investigating since these polymers when dissolved in water behave as high molecular weight species. At critical polymer concentration they start to rearrange their single chains in such away that they associate or aggregate hydrophobically (HD2 and HD6) to minimize their exposure to water by forming regular micelles of nonpolar dense core and polar, diffuse outer shell (coronas) formed from the soluble blocks. Micelles can have different forms, spherical or rodlike shapes. The latter would be characteristics of high solution viscosity.

The low viscosity in HD6 polymer compared to others is mainly attributed to an increase in intra-molecular aggregation over inter-molecular aggregation keeping the hydrodynamic radius small. However, HD2 polymer exhibits lower intra-molecular association over the *polyelectrolyte effect*, i.e., chain expansion caused by the electrostatic repulsion in pure water or aqueous solution of low salt concentration. It should be noted that generally high viscosities (compared to unassociated polyelectrolytes) and pseudoplastic behaviors are observed for these polyelectrolytes in deionized water.

Table 4-5, The viscosity-shear rate relationship for block copolymer of Na-polymethacrylate-block-polyAN or HD2 for specified polymer concentrations.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt %, in Cps	η_a of 1.5 wt %, in Cps	η_a of 1.0 wt %, in Cps	η_a of 0.5 wt %, in Cps	η_a of 0.1 wt %, in Cps	η_a of 0.05 wt %, in Cps	η_a of 0.01 wt %, in Cps
0.3	0.4	1800	1000	260	240	200	150	120
0.6	0.8	250	200	150	130	85.2	70.1	65.1
1.5	2.0	120	110	85.1	42.1	38.1	32.1	26.1
3.0	4.0	93.1	90.1	48.1	32.1	20.1	18.1	10.2
6.0	7.9	77.1	61.1	30.1	29.1	11.5	10.0	8.02
12	15.8	65.1	50.1	25.2	18.0	7.26	6.76	4.26
30	39.6	60.2	41.2	20.1	16.2	5.01	3.52	3.41
60	79.2	45.1	32.2	18.5	14.8	4.84	2.96	2.86

2.0 wt % ~ 20,000 PPM = 20,000 mg/l

Table 4-6, The viscosity-shear rate relationship for block copolymer of Na-polymethacrylate-block-polyAN or HD6 for specified polymer concentrations.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt %, in Cps	η_a of 1.5 wt %, in Cps	η_a of 1.0 wt %, in Cps	η_a of 0.5 wt %, in Cps	η_a of 0.1 wt %, in Cps	η_a of 0.05 wt %, in Cps	η_a of 0.01 wt %, in Cps
0.3	0.4	240	210	200	130	96.1	65.2	45.3
0.6	0.8	105	100	95.2	65.1	55.6	44.3	32.6
1.5	2.0	50.1	48.1	42.1	24.1	20.1	18.6	15.7
3.0	4.0	38.1	29.1	24.0	13.5	12.1	10.6	9.86
6.0	7.9	24.5	22.5	19.5	9.52	8.62	7.51	6.34
12	15.8	20.2	17.7	14.3	8.52	6.89	5.88	4.61
30	39.6	19.7	15.2	11.0	7.66	5.21	4.32	3.10
60	79.2	18.5	14.6	10.7	7.01	4.32	3.15	2.12

2.0 wt % ~ 20,000 PPM = 20,000 mg/l

Table 4-7, The viscosity-shear rate relationship for block copolymer of Na-polymethacrylte-block-polyVI or HD8 for specified polymer concentrations.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt %, in Cps	η_a of 1.5 wt %, in Cps	η_a of 1.0 wt %, in Cps	η_a of 0.5 wt %, in Cps	η_a of 0.1 wt %, in Cps	η_a of 0.05 wt%, in Cps	η_a of 0.01wt%, in Cps
0.3	0.4	920	812	230	200	130	120	100
0.6	0.8	345	400	155	115	80.2	55.1	50.1
1.5	2.0	184	174	84.2	80.2	46.2	28.1	14
3.0	4.0	107	101	60.1	51.1	33.2	14.0	8.01
6.0	7.9	80.1	68.5	42.1	40.6	23.5	11.5	5.01
12	15.8	72.8	60.1	38.7	26.1	14.8	7.52	4.01
30	39.6	66.5	51.8	33.7	20.0	9.90	5.31	3.81
60	79.2	47.3	43.1	31.1	16.9	6.26	4.96	2.70

η_a; Apparent viscosity RPM; Revolution Per Minute

b. *Intrinsic solution viscosity of the copolymers:*

The intrinsic viscosity is a direct measure of the hydrodynamic volume of the isolated polymer molecule, and hence viscometery can provide direct information of the effect on polymer conformation of variations in experimental conditions (temperature, degree of ionization when salt is added, nature and concentrations of added small molecule solutes, etc.). Dilute solution measurements can yield $[\eta]$, an indication of the hydrodynamic volume HDV of an isolated polymer chain in solution. The Mark-Houwink-Sakurada (MHS) parameters, a and K, governing the relation between $[\eta]$ and MW, i.e. $[\eta] = Kx(MW)^a$, also provide information upon the polymer conformation, while at the same time supplying the means by which the MW of samples can be estimated by viscometry.

As can be readily observed from Table 4-8 and Figure 4-6 that the reduced solution viscosity of HD2 is much higher than the other copolymers. However, due to non-linearity of reduced viscosity profile with respect to polymer concentration c, where Huggins relationship shows a dramatic upturn in the η_{red} vs. c plot at low polymer concentration making accurate determination of $[\eta]$ impossible, an inherent viscosity (η_{inh}) or Kraemer's equation is used instead of Huggin's equation to determine the intrinsic solution viscosity of the copolymers in the dilute regime.

Kraemer equation: $$\frac{\ln(\eta/\eta_s)}{C} = [\eta] - k''*[\eta]^2*C \tag{4.1}$$

where $[\eta]$ is the intrinsic solution viscosity

and k'' is the Kraemer's coefficient calculated in Table 4-8.

Table 4-8; Reduced viscosity$^{\&}$ for copolymer solutions of HD2, HD6 and HD8 in deionized water at 25 °C and $\gamma = 0.4\ s^{-1}$

Polymer conc.; g/dl or wt %	HD2 $\eta_{red,}$ dl/g	HD6 $\eta_{red,}$ dl/g	HD8 $\eta_{red,}$ dl/g
0.01	11900	4430	9900
0.05	2980	1284	2380
0.1	1900	951	1290
0.5	478	258	398
1.0	259	199	229
1.5	666	139	541
2.0	899	119	459

& η_{red} = reduced viscosity =$(\eta-\eta_s)/(\eta_s \times C)$
η_s = solvent viscosity = 1.0 cps.

Due to data inconvenience, Kraemer's relation is used instead of Huggin's equation.

Table 4-9; Inherent viscosity* for block copolymer solutions of HD2, HD6 and HD8 in deionized water at 25 °C.

Polymer conc.; g/dl ~ wt %	HD2 $\eta_{inh,}$ dl/g	HD6 $\eta_{inh,}$ dl/g	HD8 $\eta_{inh,}$ dl/g
0.01	478.75	381	460
0.05	100.21	83.5	95.7
0.1	52.983	45.65	48.67
0.5	10.961	9.73	10.6
1.0	5.561	5.29	5.44
1.5	4.605	3.56	4.5
2.0	3.748	2.74	3.4

- η_{inh} = inherent viscosity =$(\ln(\eta/\eta_s))/C$
- η_s = solvent viscosity = 1.0 cps. at 20°C
  and C = polymer concentration)g/dl)

By linear regression analysis of the data in Table 4-8, the following parameters were obtained from Kraemer equation (4.1) and MHS^{30y} relationship can be used for MMA copolymers to give some insight on the molecular weight of the copolymer from its intrinsic viscosity;

as the intercept = $[\eta]$

and the slope = $-k''x[\eta]^2$

$$[\eta]/dl/g = 7.1x10^{-5}\ MW^{0.73} \qquad (4.2)$$

at 25°C

Table 4-10; Kraemer's and MHS's Parameters ([η], k'', and Mw) for Copolymers in the Dilute Solution Regime.

Polymer	$[\eta]$, ml/g	MW, $x10^{-5}$	k'', $x10^{3}$
HD2	182	6.1	3.6
HD6	147	4.5	4.4
HD8	174	5.6	3.8

It is evident from the results (cf. Table 4-10) that HD2 copolymer shows higher intrinsic viscosity than others while HD6 shows the lowest. A high intrinsic viscosity in HD2 means that the polymer maintains its viscosity at high dilution solution. We believe that these high $[\eta]$ may reflect residual intermolecular association persisting at very low concentration of copolymer. The higher values of k'' and the lower intrinsic viscosities reflect a reduced solvent quality, surface tension, as depicted in Table 4-15. The lowering in $[\eta]$ reflects the contraction of the polymer coil because of intra-molecular hydrophobic interactions which are stronger upon increasing the hydrophobic level. It is concluded that the viscosity of all block polyelectolytes studied considerably depends on the block copolymer concentration rather than the extent of hydrophobic association.

The molecular weight of the copolymers can be regarded as an estimation rather than the true values due to the possibility of intra-molecular interactions causing a more compact polymer coil at low concentrations with such polymers.

c. *Effect of temperature:*

Tables 4-11 to 4-13 show the effect of temperature on the solution viscosity of the copolymer. As it is the case for many polymer solutions, a decrease in viscosity with increasing temperature is observed. All the copolymers examined experience a decrease in hydrodynamic radius on heating. Only lowest and highest shear rates, conducted by the instrument, were chosen in studying the temperature-shear rate-viscosity relationship. It is evident from Tables 4-11 to 4-13 and Figures 4-14 and 4-15 that the block polyelectrolytes maintain some of their thickening ability at high temperatures, > 90 °C, which is usually encountered during injection to oil reservoirs.

Table 4-11, The viscosity-temperature-shear rate relationship for the copolymer of sodium polymethacrylate-block-polyacrylonitrile or **HD2** for polymer concentration of 2 wt % at lowest and highest shearing.

Shear rate, S^{-1}	η_a, in Cps, at 25 °C.	η_a, in Cps, at 45 °C.	η_a, in Cps, at 75 °C.	η_a, in Cps, at 95 °C.
0.4	1800	1440	1150	920
79.2	45.1	39.5	34.1	30.0

Table 4-12 The viscosity-temperature-shear rate relationship for the copolymer of sodium polymethacrylate-block-polyacrylonitrile or **HD6** for polymer concentration of 2 wt % at lowest and highest shearing.

Shear rate, S^{-1}	η_a, in Cps, at 25 °C.	η_a, in Cps, at 45 °C.	η_a, in Cps, at 75 °C.	η_a, in Cps, at 95 °C.
0.4	240	192	150	120
79.2	18.5	15.0	11.5	9.2

Table 4-13, The viscosity-temperature-shear rate relationship for the copolymer of sodium polymethacrylate-block-polyvinylimadazole or **HD8** for polymer concentration of 2 wt % at lowest and highest shearing.

Shear rate, S^{-1}	η_a, in Cps, at 25 °C.	η_a, in Cps, at 45 °C.	η_a, in Cps, at 75 °C.	η_a, in Cps, at 95 °C.
0.4	920	730	580	465
79.2	47.3	37.5	30.0	24.0

d. *Effect of sodium chloride (NaCl):*

In order to asses the effect of brine (NaCl) on the solution viscosity of the copolymers, a range of NaCl concentration was considered, 1.0 wt % to 10 wt %, as a function of apparent viscosity. Figures 4-10, 4-11, 4-15 and Table 4-15 show the effect of salt on the viscosity of the copolymer solutions; HD2, HD6 and HD8; at two shear values, 0.8 and 79.2 s^{-1}.

For instance, at 0.8 s^{-1} shear rate, the addition of NaCl solution to the polymer solution readily lowers the viscosity of the polymer solution of HD8 and HD6 polymers with approximately the same rate. However, in HD2 copolymer the solvent quality much decreased particularly at low salt content. All the three samples show salt tolerance beyond 10 wt % above which the solution begins to show little turbidity. At shear rate of 79.2 s^{-1} HD2 copolymer, among the three samples, exhibits only 15% reduction rate in solution viscosity while HD6 copolymer exhibits least salt tolerancy that others.

As it is the case for non-ionic polymers, i.e. polyacrylamide, adding salt to its solution does not affect its solution quality, invariant behavior. However, for polyelectrolytes (ionic charged polymers) the thickening ability of the polymer solution is drastically reduced as that is mainly attributed to charge screening effects (so called polyelectrolyte effect) where electrostatic interactions and charge repulsion are significantly reduced (screened), bringing down the hydrodynamic volume of the polymer coil and hence the solution viscosity. But for block polyelectrolyte micelles, the interaction is much less significant due to hydrophobic association.

From all the results, it is evident that HD6 copolymer exhibits high lowering rate in thickening ability with adding salt (28.5 %) at 79.2 s^{-1}, a phenomenon explained by electrolyte interaction behavior. For all the copolymers studied, one can readily observe that the block copolymer electrolyte systems display typical polyelectrolyte behavior at low salt concentration and maintain their viscosity with increasing salt concentration, no drastic reduction in viscosity, by means of hydrophobic association. Addition of increasing amounts of NaCl lowers pseudoplasticity as depicted in Figures 4-10 and 4-11.

For nonassociating polyelectrolytes, addition of inorganic salts should bring about changes to the behavior of polymer solutions. The screening of charge repulsion tends to reduce drastically the solution viscosity. However, when viscosity enhancement due to interchain association prevails over polyelectrolyte effect, addition of NaCl salt result in an increase in solution viscosity of the polymer system (polymer/water/salt) particularly in the case of inter-molecular hydrophobic association. But when the intra-chain association in pure water is high enough, addition of salt leads to a more compact network which rapidly collapses to random coil configuration, no chain expansion is occurred [9].

Taking into account the above considerations, one can interpret the results, as EOR is concerned, in Table 4-15 and Figures 4-10 and 4-11 as that relatively little hydrophobic intermolecular associations have been maintained over intarmolecular aggregations as in HD2. However, a reduction in solution viscosity is interpreted as a predominance of polyelectrolyte effect over hydrophobic associations. Therefore, classical viscosity reduction of polyelectrolyte solutions in the presence of salts can be successfully prevented or rather highly reduced if hydrophobic blocks or segments are incorporated to the polyelectrolyte blocks or main chain. All the observations suggest that effective hydrophobic association was not enhanced by the addition of salts for hydrophobically associating ionic block polymers [29] as reported by Fredrick in his work, in 1984.

A similar observations has been first experimentally noticed by Strauss et al. And reported by Morishima [58], who show the existence of intramolecular micellization in amphiphilic polyelectrolytes and of critical content of hydrophobic residues. They called such amphiphilic polyelectrolytes " polysoaps ". Such polymers are characterized by high soluibilization power but exhibit very low solution viscosity [19,25].

4.5.2 Surface Activity of the Copolymer Solutions

Copolymer solution properties have also been examined by conducting measurements of the surface (air/liquid) tensions at different polymer concentrations; 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 wt %. The measurements were carried out at room temperature regulated at 25 °C. The surface tension were measured using a platinum plate method of plate-ring tensiometer where the plate was suspended from an electrobalance into the sample solution in a glass container with known geometry. The detailed description of the procedures is given in Chapter 3. Furthermore, different NaCl concentrations ranging from 1.0 to 10 wt % were taken and then mixed with polymer solutions making desired concentrations where the surface tension of the brine solutions was then determined at 25 °C.

The results of the measurements are summarized in Table 4-14 and demonstrated in Figures 4-13and 4-16 which show the effects of polymer concentration on the surface tension of copolymers; HD2, HD6 and HD8. As depicted in Table 4-14 and Figure 4-13 for HD2 copolymer, a decrease in surface tension is observed with increasing polymer concentration over the whole range and that is due to more micellization. HD2 copolymer shows more surface activity than the other two. As the polymer concentration increases, the surface tension decreases because of the extent of adsorption of more molecules at the air-aqueous polymer solution interface [116]. The increase in adsorption is attributed to the reorientation of the amphiphilic structure of the polymer and consequently causes reduction in the surface tension [117]. The surface tension of the block polyelectrolytes studied has shown to be decreasing with time as depicted in Figure 4-16 and that could be attributed to the surface equilibrium in reorientation process of hydrophobic moieties and additional adsorption from the bulk phase to the interface. As observed in previous studies, extensive equilibrium times are required due to slow diffusion and conformational changes of the polymer coil [118]. *Conformations* are usually refer to the different arrangements of atoms and constituents in a molecule that result from rotations around single bonds, such as the fully extended planer zigzag, randomly coiled, extended coil, compact core in a micelle, helical, and folded -chain arrangements.

Another behavior has also been examined regarding the effects of adding salts (NaCl) on the surface tension of the copolymers HD2, HD6 and HD8 for 1.5 wt % as polymer concentration. The results of the measurements are depicted in Table 4-15 and Figure 4-16. The results show that a further decrease in surface tension with an increase in salt content up to 10 wt % salt. HD8 copolymer exhibits the highest surface activity (35 mN/m) at the highest NaCl concentration (10 wt %) as depicted in Table 4-15. It is expected that as the polymer solution concentration increases, the surface activity of the brine block polyelectrolyte would increase with different degrees of magnitudes.

Such an increase in surface activity or reduction in surface tension is explained by the formation of multi-molecular micelles through hydrophobic associations. The presence of salt enhances the aggregation or micellization behavior producing more micelles through micellization process. Such behavior has been confirmed experimentally by the decrease of CMC with the square root of salt concentration [61-64, 210]. The tendency of adsorption at the interface and hence lowering in surface tension is increased at the formation of multi-molecular micelles, i.e. clusters. Since study was only up to 10 wt % salt, it is expected as its the case for block polyelectrolyte regular micelles, that the higher salt content would be no longer micellization dependent. However, in the presence of only single chains as in homopolyelectrolyts where no micelles present , the salt effect is more pronounced. This can be explained by the fact that polymer chains in the corona of the micelles are already expanded by the steric exclusion and, because of the polyelectrolyte chains in their vicinity, are already at a somewhat elevated salt content. Effects due to salt addition are therefore less significant.

Table 4-14 ; Surface Tensions in mN/m of Ionic Di-block Copolymers @ 25 °C and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt %.

Sample code	Structure	at 0.01 wt %	at 0.05 wt %	at 0.1 wt %	at 0.5 wt %	at 1.0 wt %	at 1.5 wt %	at 2.0 wt %
HD2	Hydrolized Poly(AN-b-MMA)	68.62	66.70	58.79	57.67	57.30	54.10	48.73
HD6	Hydrolized Poly(AN-b-MMA)	70.86	68.61	63.65	52.88	46.16	51.02	49.06
HD8	Hydrolized Poly(VI-b-MMA)	66.20	65.71	64.43	58.73	55.83	51.48	50.18

* A stock solution of 2 wt % of each sample is used to make the solutions by dilution.
& The surface tension of distilled water at air-water interface was found to be 72.21 mN/m.

Table 4-15: Rheology and Surface Activity of Amphiphilic Ionic Diblock Copolymer Solutions of 1.5 wt % in (1.0 wt % to 10 wt %) NaCl Concentrations at 25 °C.

Sol. Poly. conc., 1.5 wt % ⇓	Effect of NaCl Concentration on polymer solutions, in (wt %) NaCl								
NaCl Conc., wt % ⇒	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample Code: **HD2** Surface Tension at 25 °C vs. salt %	54.10	52.34	49.10	47.17	45.98	44.82	43.06	42.86	41.01
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	1000	551	381	300	250	200	190	150	140
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	32.2	9.72	9.18	8.42	6.94	6.61	5.51	4.91	4.84
Sample Code: **HD6** Surface Tension at 25 °C vs. salt%	51.02	50.51	50.91	49.36	48.81	43.92	42.41	40.50	40.00
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	210	205	200	190	170	160	140	120	100
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	14.6	10.6	8.56	7.86	6.31	5.91	4.81	4.34	4.16
Sample Code: **HD8** Surface Tension at 25 °C vs. salt%	51.48	45.11	40.66	39.21	38.60	37.34	36.20	35.74	35.00
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	812	721	710	651	550	500	441	381	332
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	43.1	21.7	18.5	17.2	14.2	11.1	9.75	8.32	8.10

Note; a 1.5 wt % of HD8 copolymer shows good salt tolerancy at 10 wt % NaCl, 332 cps. at 25 °C.

4.5.3 Interfacial Activity of the Copolymer Solutions

Properties of the copolymer solutions also have been examined by conducting interfacial tension (IFT) measurements using platinum ring method of plate-ring tensiometer. The hydrocarbon, n-decane, was used as the light phase or oil phase in all measurements. The procedures were mentioned in detail in the previous chapter. The IFT of the aqueous solutions in n-decane were measured for two polymer concentrations, i.e. 0.5 wt % and 1.5 wt % at different NaCl concentrations ranging from 0.0 wt % to 10.0 wt %, for both polymers HD2 and HD8 that show relatively good interfacial activity at oil-solution interface. The solutions were left for two days to equilibrate and become freed from air bubbles, that would give erroneous results if not removed, before the measurements of the IFT was carried out.

What comes from the measurements of the interfacial behavior of polymer solutions, with different polymer concentrations and NaCl salt content, is summarized in Table 4-16 and demonstrated in Figures (4-17 and 4-18). As expected for block polyelectrolytes, the IFT decreases as the polymer concentration increases, but the presence of salt from 1.0 wt % to 10 wt % results in interesting solution behavior. It was found that adding salt (NaCl) to the polymer solution enhances the interfacial activity further more. This kind of behavior is attributed to the creation of more aggregations in the presence of salt. Such interesting behavior gives prospects for the applications of block polyelectrolytes, in range of salt content studied, with n-decane as the hydrocarbon phase [134-137].

Table 4-16 : The Effect of NaCl Concentration on the IFT of Aqueous Solutions of Ionic Di-block Copolymer HD8 and HD6 for 0.5 and 1.5 wt % Polymer Concentration at 25 °C.

NaCl conc, wt %	**IFT[a]**, (mN/m) of Copolymer Sample **HD6**, at Poly. Conc. of		**IFT**, (mN/m) of Copolymer Sample **HD8**, at Poly. Conc. of	
	0.5 wt %	**1.5 wt %**	**0.5 wt %**	**1.5 wt %**
0.0	21.12	11.56	19.60	10.09
1.0	10.35	7.25	6.65	4.73
2.0	8.51	6.82	5.96	4.50
3.0	7.43	5.23	5.10	4.00
5.0	6.18	4.81	4.52	3.87
6.0	5.83	4.43	4.12	3.54
7.0	5.15	4.01	3.93	3.27
9.0	4.21	3.51	3.21	2.51
10.0	4.01	3.28	3.10	1.87

[a] IFT at (deionized water/n-decane) interface at 25 °C. = 45.64 mN/m.

4.6 Discussions and Conclusions

Series of (amphiphilic) hydrophobically associating block copolymers and/or ionic block copolymers (block copolyelectrolytes) have been synthesized/modified and their solution properties were evaluated. Three series of such polymers have been successfully hydrolized to establish water solubility for aqueous solution evaluation. Generally the viscosites of the solutions of block polyelectrolytes studied in this work are high enough for use in EOR as mobility control agents.

Block polyelectrolytes, i.e., block copolymers of long soluble ionic block length (as a corona in a regular micelle) and a short insoluble block length (as a core in the regular micelle)in an aqueous solution, exhibit hydrophobic associations and hence an increase in hydrodynamic volume explained by an increase in solution viscosity above critical concentration. The micelles are very compact and posses a core consisting of an insoluble PAN moiety from which radiate the branches comprising the soluble polyelectrolytic chains. In conclusion, it can be said that the behavior in dilute solution of MMA block copolymers in a selective solvent for the sodium polymethacrylate chains is very strongly dependent of the insoluble polyacrylonitrile part even when the latter constitute only few weight percents of the macromolecular chain. A very hydrophobic short chain present at the extremity of long polyelectrolyte chain is sufficient to give rise to an intermolecular association. The main parameter, among others, of the polymolecular micelles (big particles) formed by these associated polymers is the length of the soluble blocks (their ionic strength, charge density, and type of counterion) and not the whole weight of the particles. However, the micellization process as well as the micelle behavior strongly depends on the solvent quality (salt concentration), temperature, and the length of insoluble blocks.

All the polymers show psuedoplastic behavior and good salt tolerancy with the exception that HD6 copolymer exhibits the least salt tolerancy where 28% reduction in viscosity has only experienced over the range considered. So as a whole the polymers exhibit moderate salt tolerancy up to 10.0 wt % without any significant change. The salt sensitivity of HD6 polymers at low concentration is attributed to its polyelectrolyte character. However, a 2 wt % (20,000 PPM or mg/l) produces 1800 cps in deionized water (0.0 wt % salt), a property very interesting for some applications. Also, a 1.5 wt % of HD8 in a brine aqueous solution (10 wt % NaCl) shows interesting salt tolerancy (330 cps.) among other copolymers as depicted from Table 4-15 (Master Table). See Appendix B.

Almost constant shear-viscosity exhibited by the polymers at high shear rate and shear thinning behavior at low shearing, characteristics favorable in polymer flooding operations. High shearing encountered around the injection well pore where the effective solution viscosity would be relatively low, thus requiring less power to be moved. But with decreasing shear, ahead of the injection, the viscosity would increase as the polymer solution penetrates more deeply into the formation. The polymer solutions drastically affected by the addition of salt where the brine causes a coil collapse and hence a reduction in viscosity. Since it is highly unlikely that the non-polar block is affected by the ionic strength, the observed coil contraction may be due to the transmission of the contraction of the polar micellar region upon the non-polar core. Obviously increasing concentration of the polymers studied as leads to an increase in polymer solution viscosity but the increase imparted is not enough if cost efficiency ratio is considered.

The viscosity of the polymer solution decreases with increasing temperature due to a decrease in solvent viscosity but after long time it levels off. The polar portion of the micelle appears to be affected by both the ionic strength and the temperature of the medium. Both cause a contraction of the polar region of the micelle. This is not an unusual phenomenon with respect to ionic strength in polyelectrolytes, but the effect of temperature increase at 50 to 70 °C may be caused by dehydration resulting in a contraction of the polar portion of the micelle. Also, the decrease in viscosity could be attributed to the disruption of supermolecular aggregates which exist as a result of entanglements in the polyelectrolyte chains. It was found that viscosity in water depends on polymer composition, microstructure, molecular weight, polymer concentration, ionic strength, hydrophobe level, temperature, and sample history.

The polymers also exhibit low surface tension and interfacial tension through reduction in interfacial activity with 1-decane where the activities could be compared to that of surfactant systems. The structure of the hydrophilic polyelectrolyte blocks affects the conformation of the chains and thereby the surface activity, which depends on how densely the amphiphilic polymer molecules, are packed and aligned at the air/water surface. A similar behavior for a polymer/oil interface. Strong foaming ability was realized in all the polymers. Moreover, the polymers exhibit no CMC or breakpoint resembling CMC in surfactants and that may be due to the concentration range considered [131-137]. However, it should be noted that, in general, critical micelle phenomena in block copolymer systems (polymer plus solvent) occurs at very much lower concentrations than in low molecular mass amphiphiles (monomeric surfactants) and is thus quite difficult to be determined experimentally because micelles are undetectable in dilute solutions [61-63]. Also low CMC value is a sign of high solubilization power. This is an excellence correspondence between the adsorbability of the macromolecules, their ability to reduce surface and IFT, and the value of CMC. In other words, the higher the tendency to form micelles and lower the CMC value, the more surface active the material would be [90].

The surface activity of vinyl-type synthetic homopolyelectrolytes is generally low, compared to surfactants, due the fact that their conformations are inadequate to separate their groups satirically to hydrophilic and hydrophobic parts at the air-water interface. But this is not always the case where it was found that in some tetra-alkylammonium salts with hydrophobic moieties the arrangement of hydrophobic gegenions at the interface and the ease formation of folded conformation also at the interface contribute much to the high surface activity. For many polyelectrolytes, surface tension begins to decrease above the critical concentration, C*, at which at which the lateral and attractive inter-macro-ion interaction occurs at the interface and the two-dimensional orientation by adsorption forms [87-89].

The results indicated that the magnitude of association on solution behavior and, in turn, on the CMC depends mainly on the length of the insoluble hydrophobic block and its content. The unique solution properties of MMA block copolymers can be exploited to meet industrial demands for specific formulations or applications. It is necessary to keep in mind that the behavior of block polyelectrolyte systems is considerably more complicated than that of copolymer micelles containing nonionic water-soluble blocks. Micelle behavior is strongly influenced by the polyelectrolyte nature of the outer shell, which, in turn, is affected by the presence and nature of the small ions, as well as the charge density along the chain and the degree of neutralization. Thus, we can conclude that the parameters of micellization of block polyelectrolytes are influenced by variables such as block length, salt content, and nature of the interface, temperature and concentration. These variables can not always be considered independently, since a change in one parameter can sometimes cause a change of the effect of another parameter on the property of the system. Therefore, a theoretical model is necessary to elucidate more on the behavior of such kind of micellization. An attempt has been made for some systems in the self-assembly of block copolymers [48].

Amphiphilic molecules of polyelectrolyte type can be used for enhanced oil recovery operations provided that they keep their viscosification efficiency high in water environment which contains small ions. Usually, the electrostatic nature of the interaction in an aqueous media is demonstrated, as for the hydrolyzed polymers synthesized in this research, by the decreased binding as the amount of NaCl is increased. PMMA-PAN, PMMA-PS, and PMM-PVI block copolymers have been converted into hydrophobic-hydrophilic copolymers of polyelectrolytic character using hydrolysis method. Their amphiphilic properties in dilute solution in selective solvent (i. e. water) for the sodiumpolymethacrylate parts have been confirmed to induce viscosification during shearing using viscometry. Under these conditions and due to the insolubility of the hydrophobic parts, several molecules of block copolymer can be associated to form micelles These particles are very compact and possess a core consisting of an insoluble moiety surrounded by the soluble polyelectrolytic chains. The main parameter of such a particle is the length of the soluble blocks and not the whole weight of the particle. The micellization process has been investigated as a function of the molecular characteristics of the copolymers, the temperature, the viscosification character, the interfacial activity, and the salt concentration. On the contrary, random copolymers and homopolymers do not exhibit association because of the structure of their molecules.

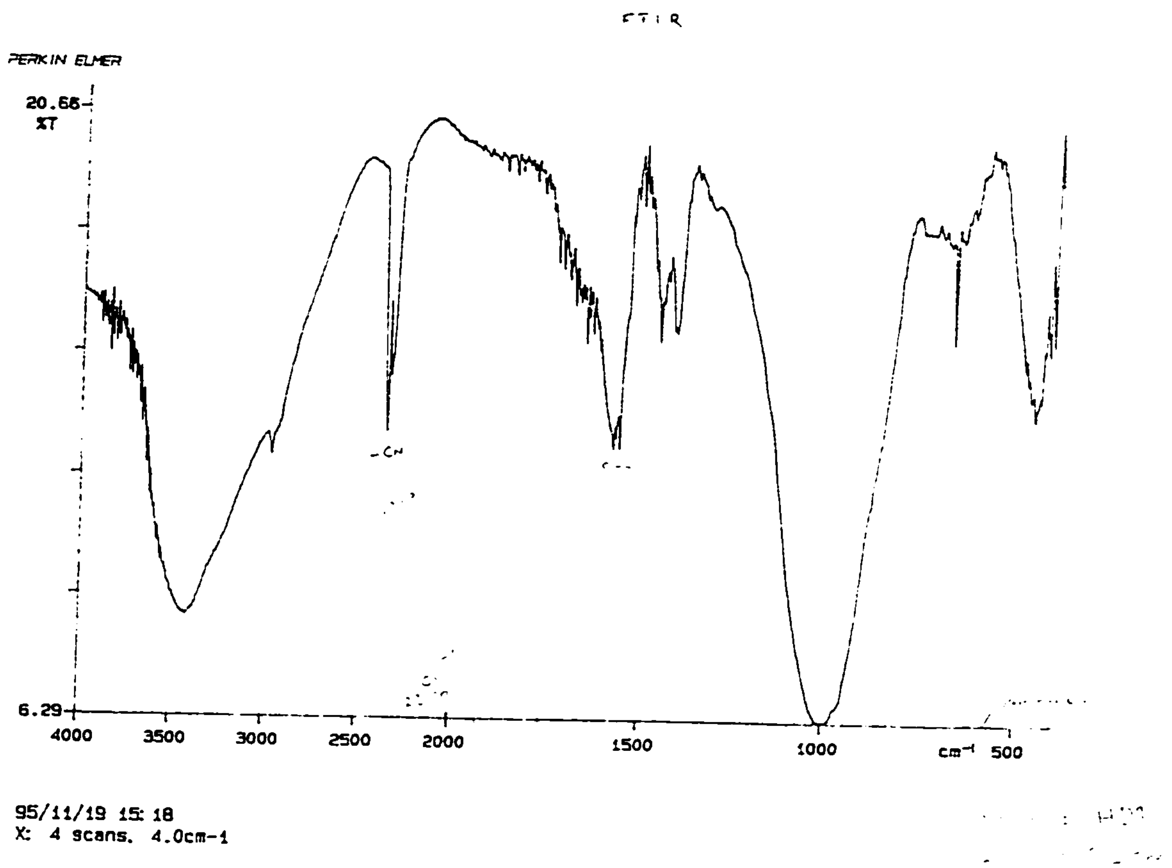


Figure 4-1: Foruier Transition Infra-Red Spectroscopy of sample HD2, or characterization of the hydrolized polymer Polymethylmethacrylate-block-Polyacrylonitrile using Perkin-Elmer spectrometer.

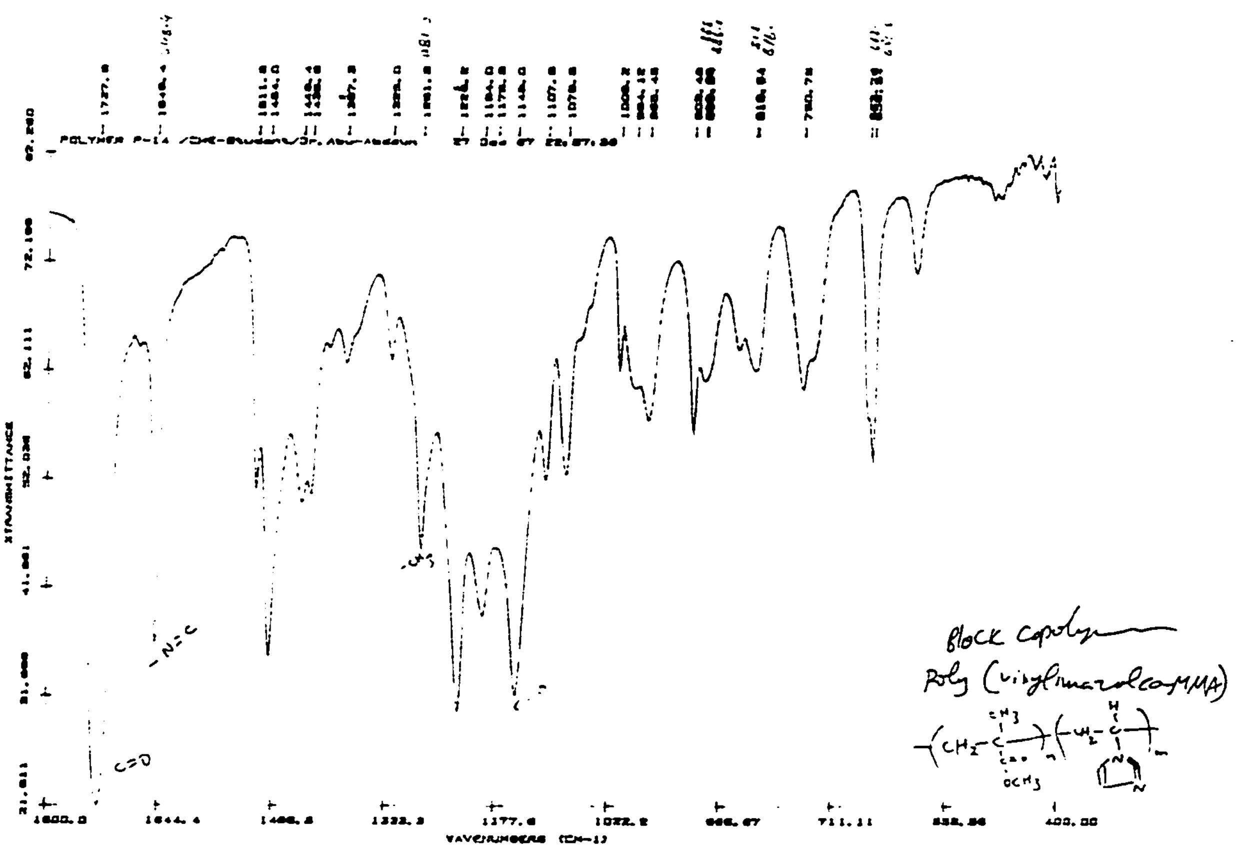


Figure 4-2: Foruier Transition Infra-Red Spectroscopy of sample P15, or characterization of the polymer Polymethylmethacrylate-block-Polyvinyl-emadazole using Perkin-Elmer spectrometer.

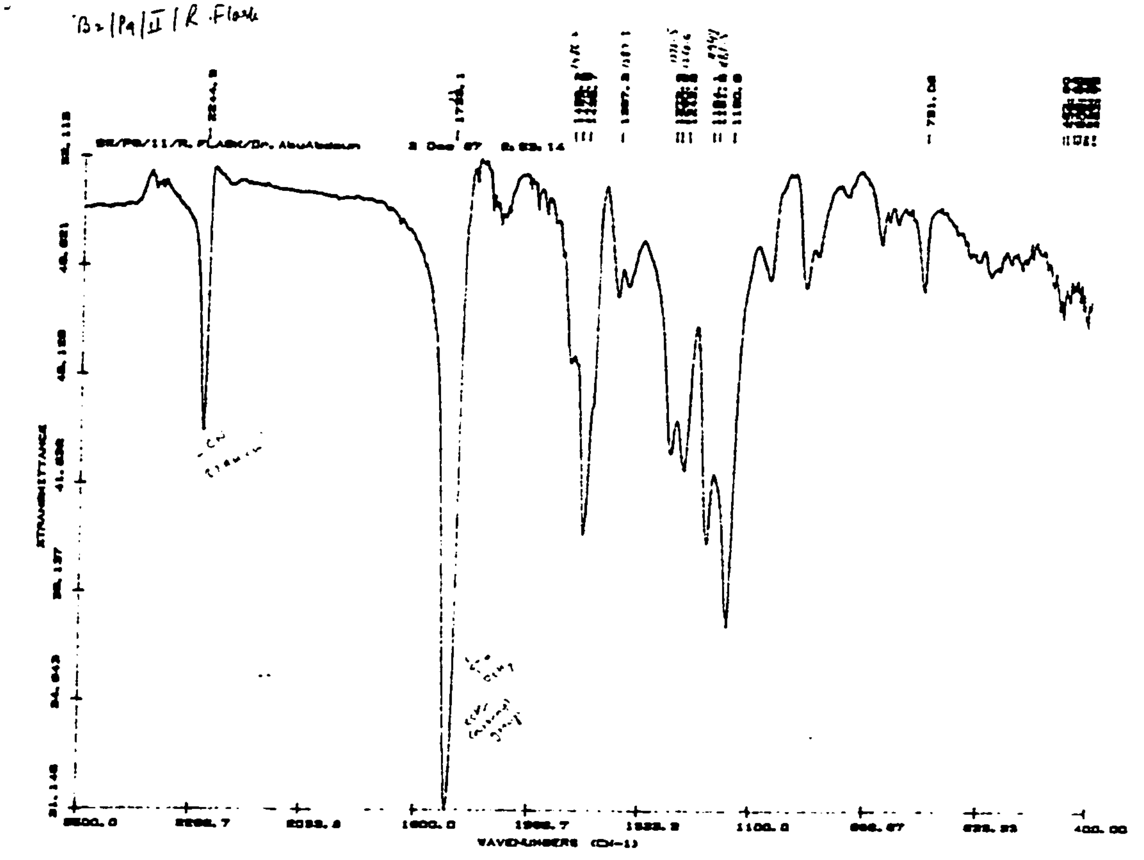


Figure 4-3: Foruier Transition Infra-Red Spectroscopy of sample P9IIR, or characterization of the polymer Polymethylmethacrylate-block-Poly-acrylonitrile using Perkin-Elmer spectrometer.

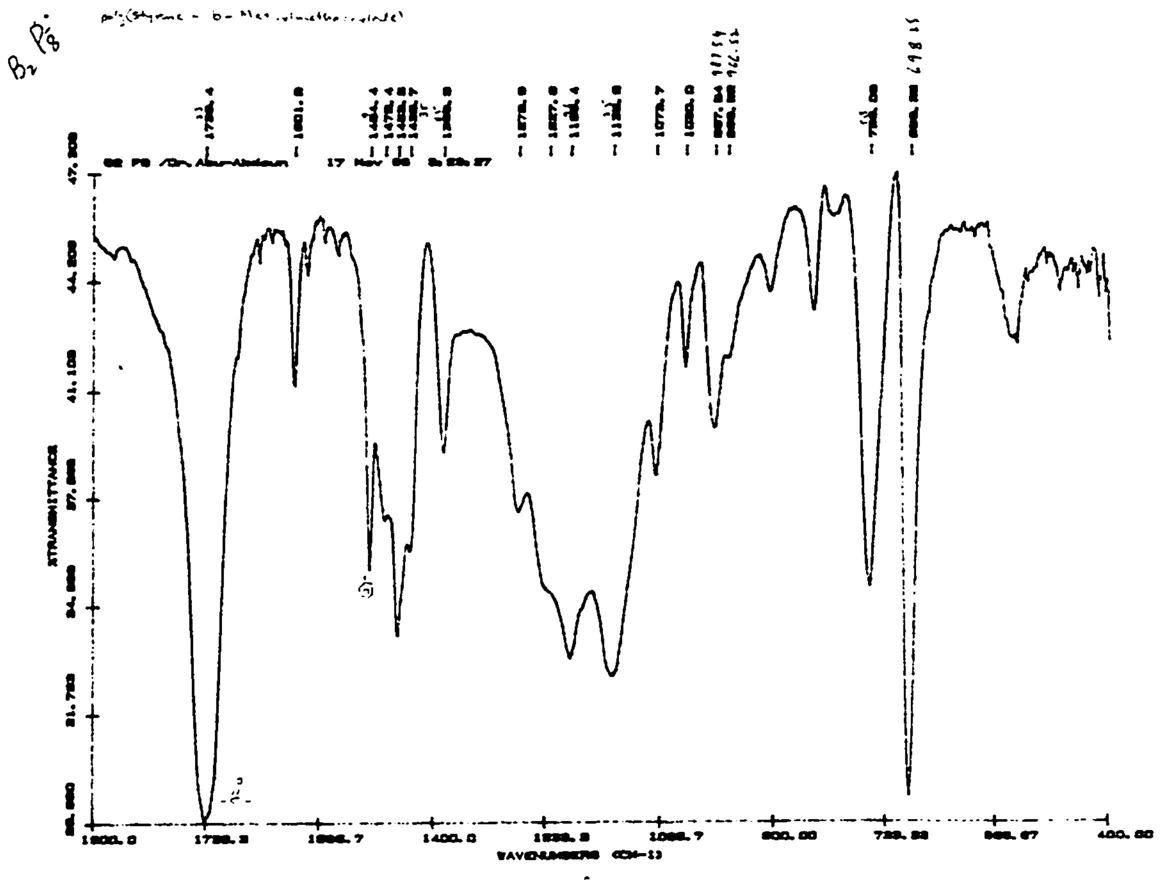


Figure 4-4: Foruier Transition Infra-Red Spectroscopy of sample P8', or characterization of the polymer Polymethylmethacrylate-block-Polystyrene using Perkin-Elmer spectrometer.

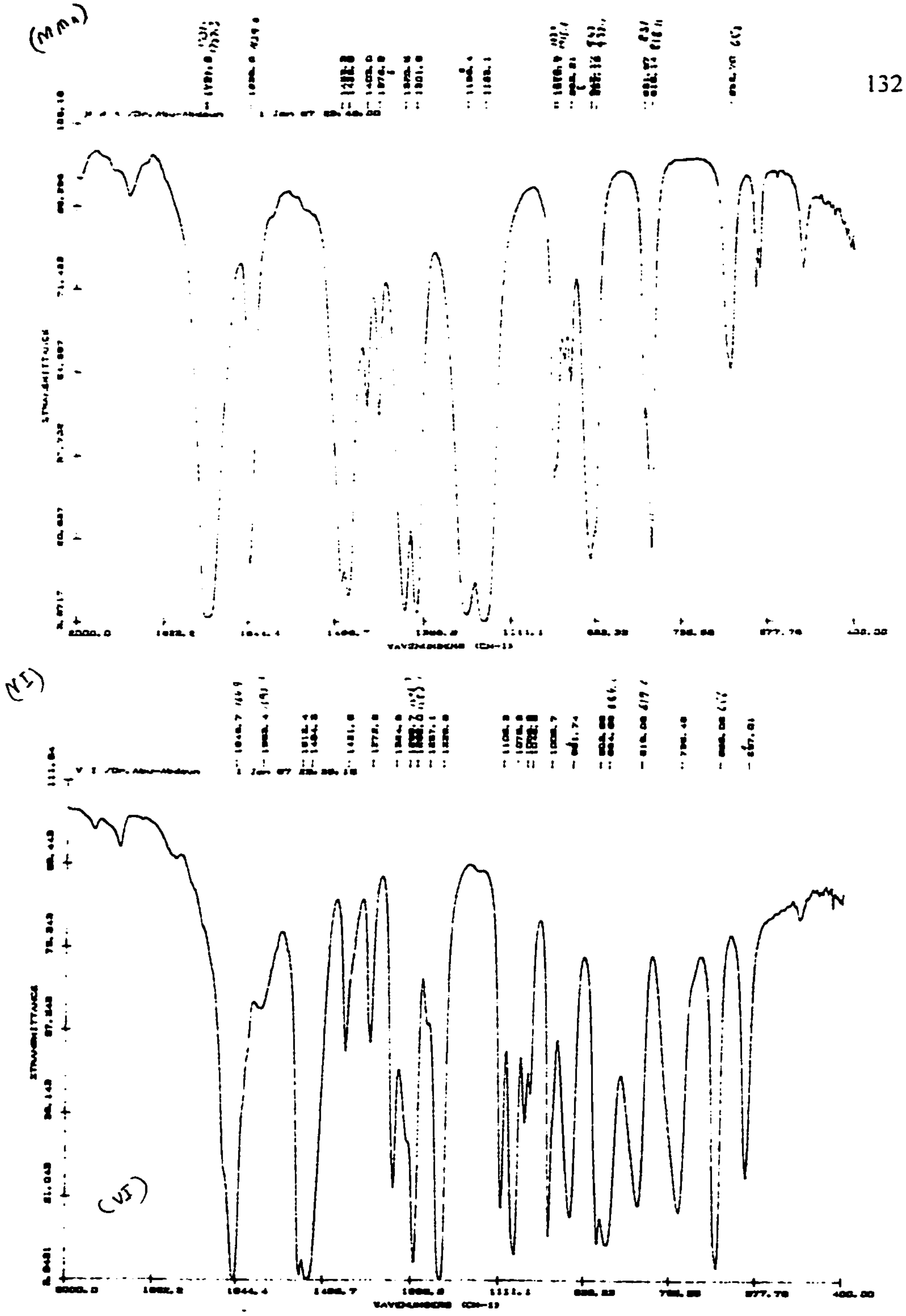


Figure 4-5a : Foruier Transition Infra-Red Spectroscopy of sample MMA and VI, or characterization of the monomers methylmethacrylate and vinylemadazole using Perkin-Elmer spectrometer in the range of 400 cm-1 to 2000 cm-1 as wavenumber.

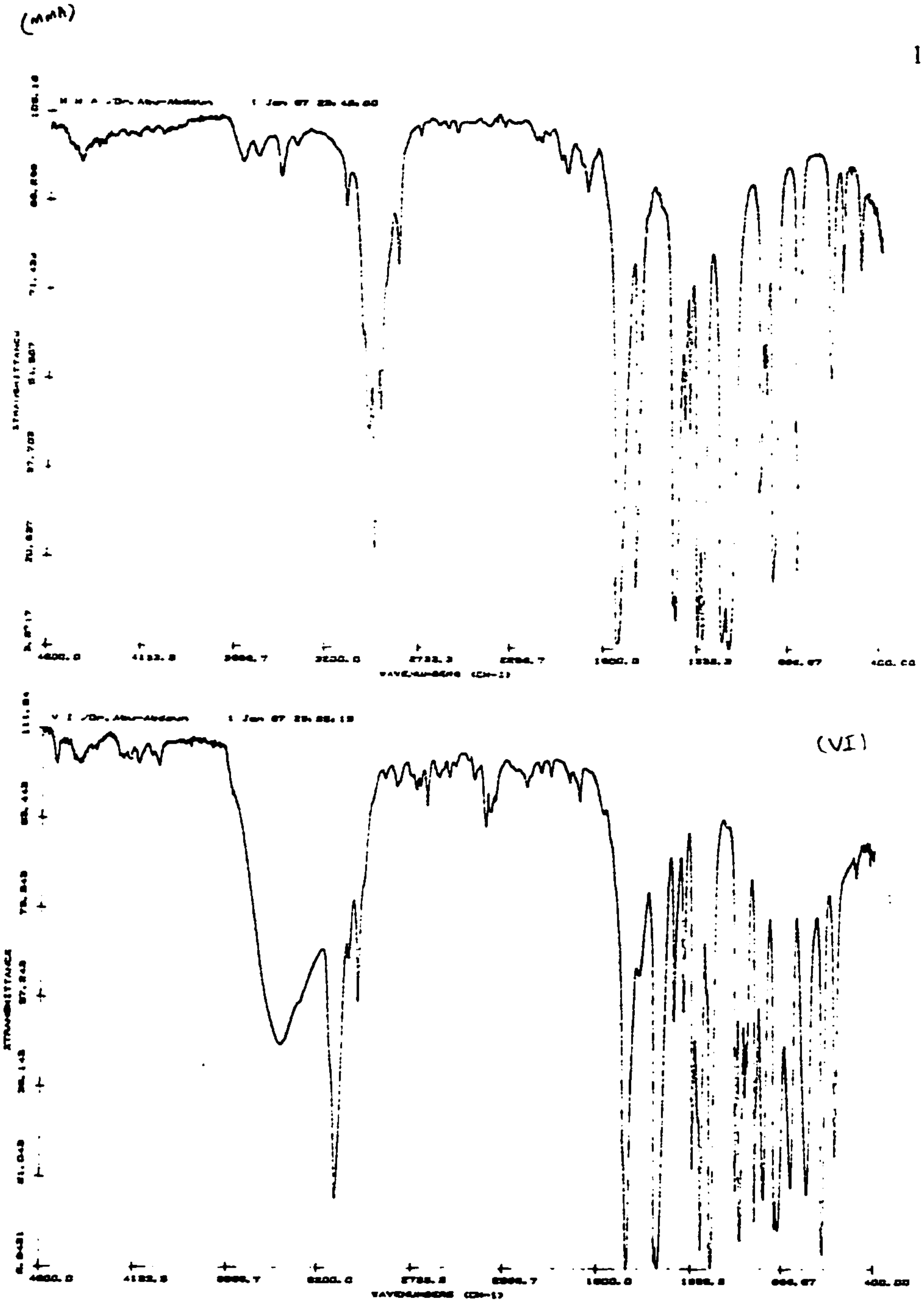


Figure 4-5b : Foruier Transition Infra-Red Spectroscopy of sample MMA and VI, or characterization of the monomers methylmethacrylate and vinylemadazole using Perkin-Elmer spectrometer in the range of 400 cm-1 to 4600 cm-1 as wavenumber.

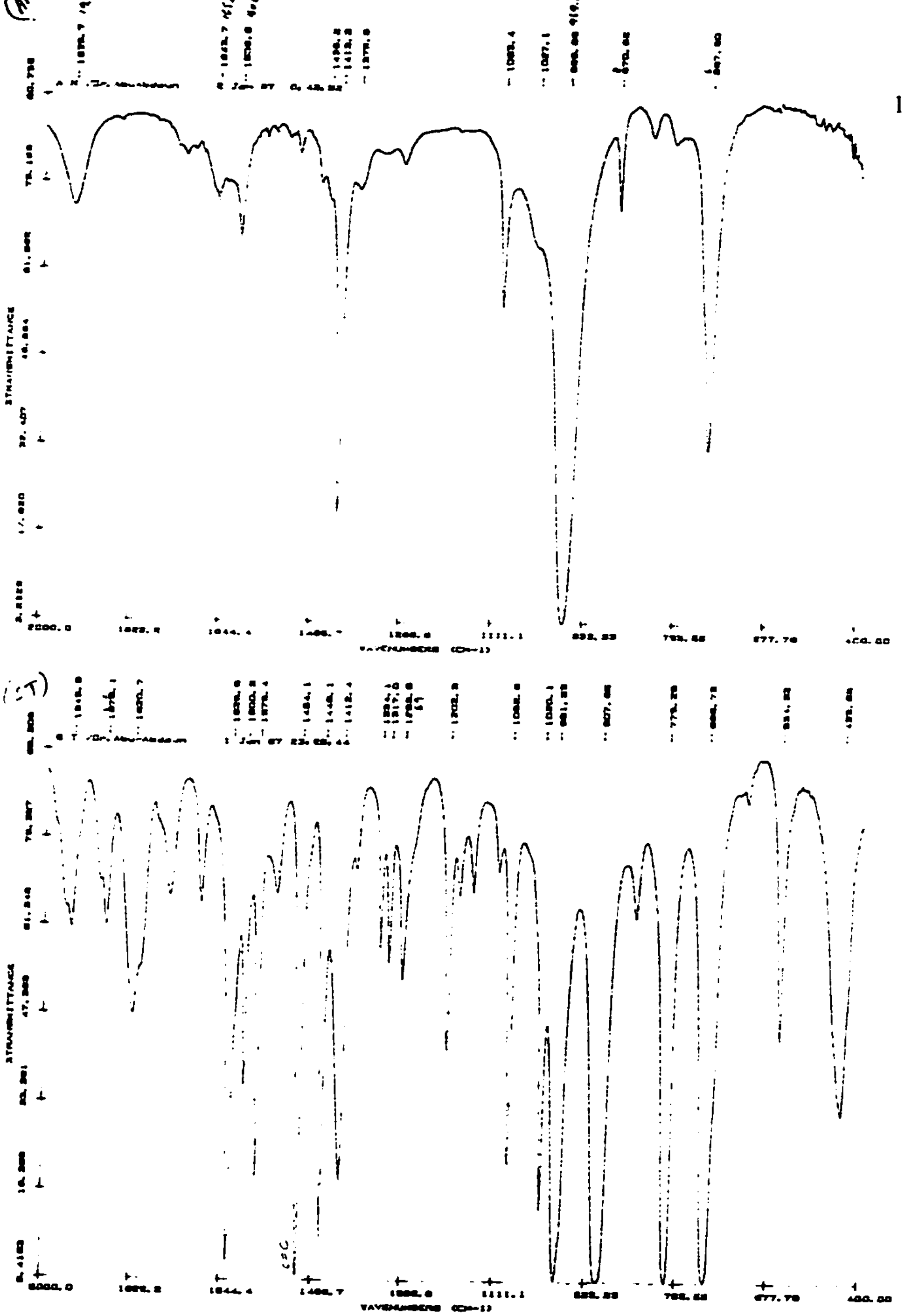


Figure 4-6a:Foruier Transition Infra-Red.Spectroscopy of sample AN and ST, or characterization of the monomers acrylonitrile and styrene using Perkin-Elmer spectrometer in the range of 400 cm-1 to 2000 cm-1 as wavenumber.

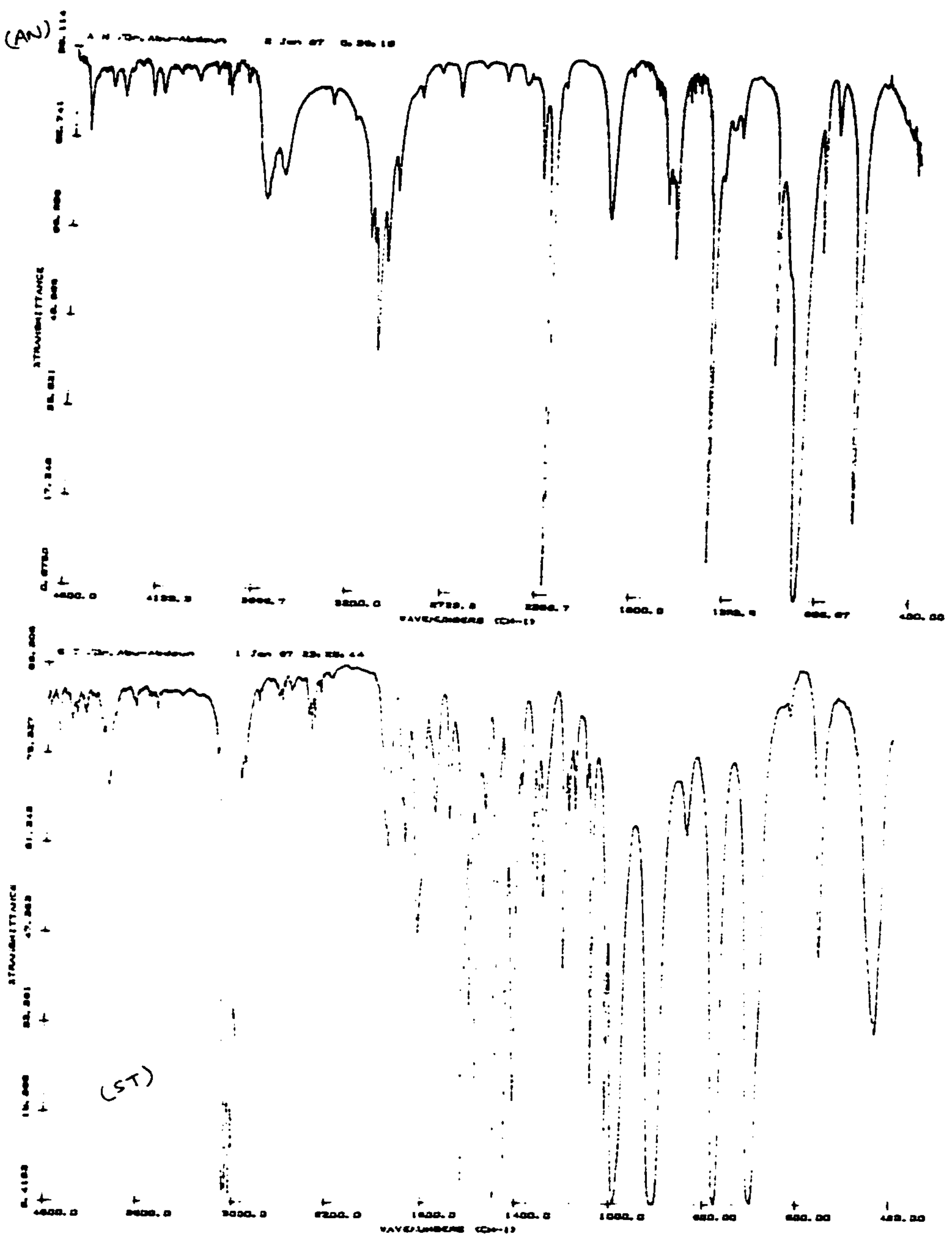


Figure 4-6b : Foruier Transition Infra-Red Spectroscopy of sample AN and ST, or characterization of the monomers acrylonitrile and styrene using Perkin-Elmer spectrometer in the range of 400 cm-1 to 4600 cm-1 as wavenumber.

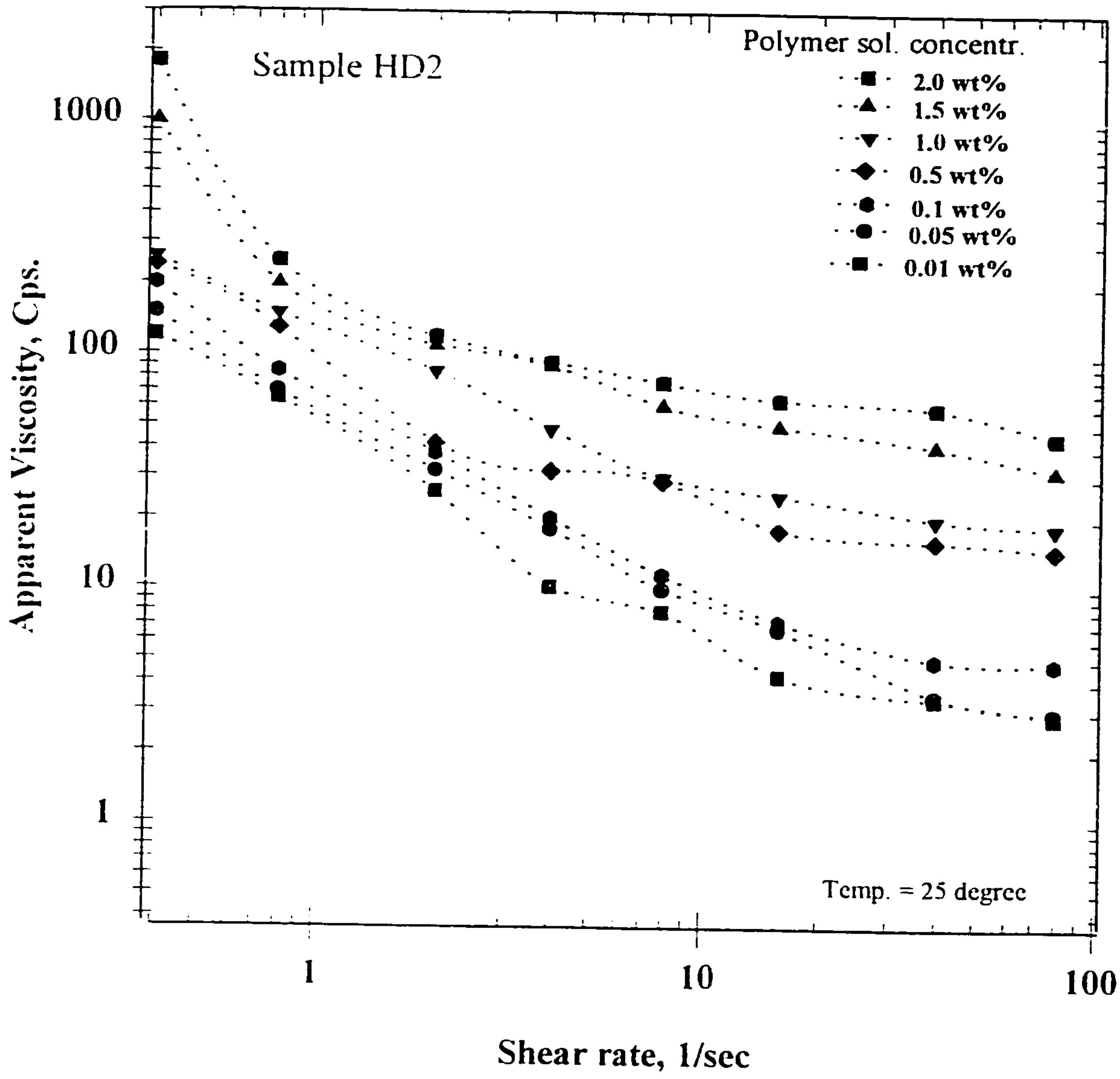


Figure 4-7; Effect of shear rate on the apparent viscosity of di-block copolymer or Na-poly(MA-b-AN), hydrolyized poly(MMA-b-AN) or HD2 in 0.225 mol NaOH. Hydrolizing solvent : isopropanol. Samples are prepared in deionized water.

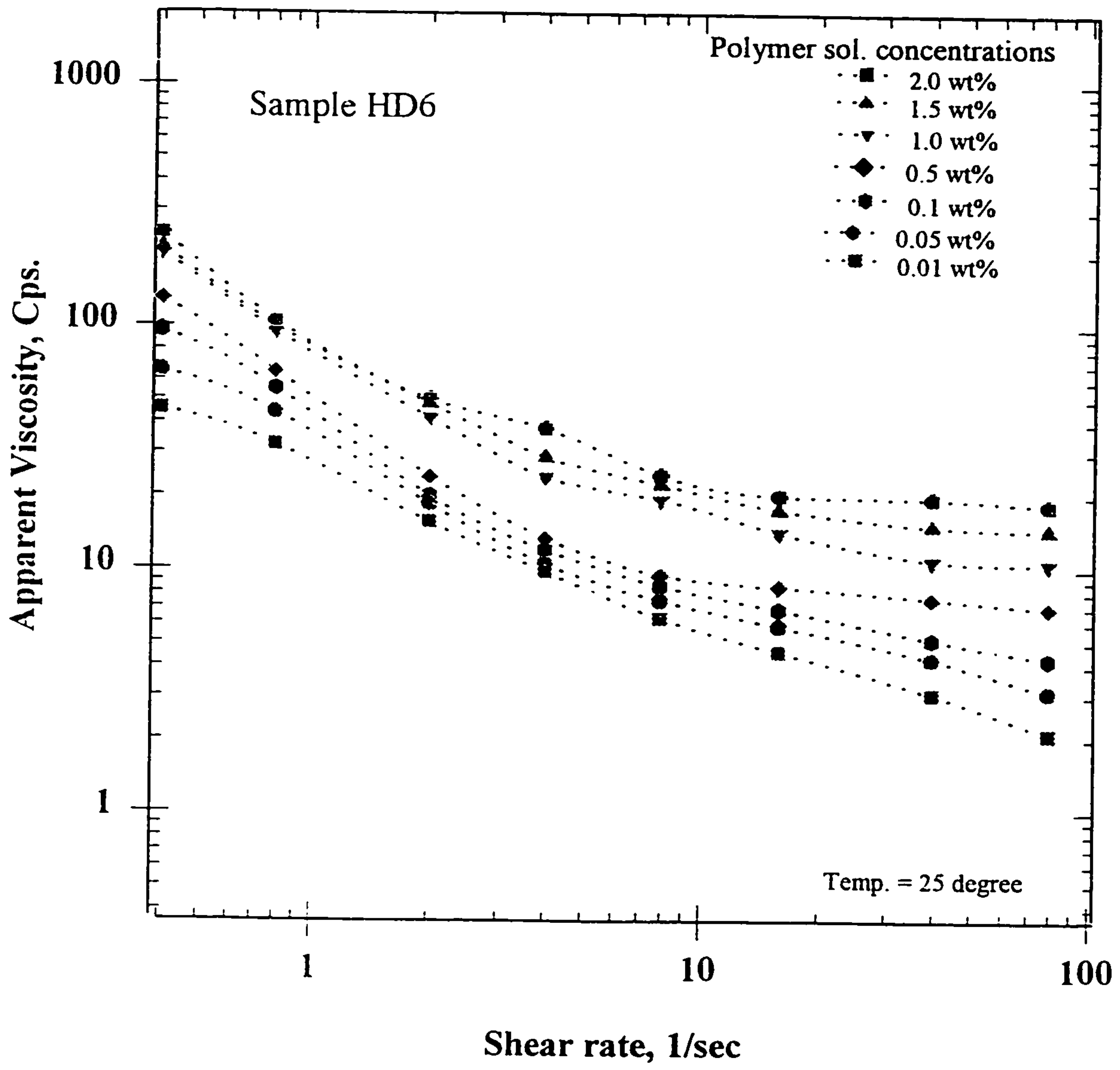


Figure 4-8; Effect of shear rate on the apparent viscosity of di-block copolymer or Na-poly(MA-b-AN), hydrolyized poly(MMA-b-AN) or HD6 in 0.225 mol NaOH. Hydrolizing solvent : isopropanol. Sample prepared in deionized water.

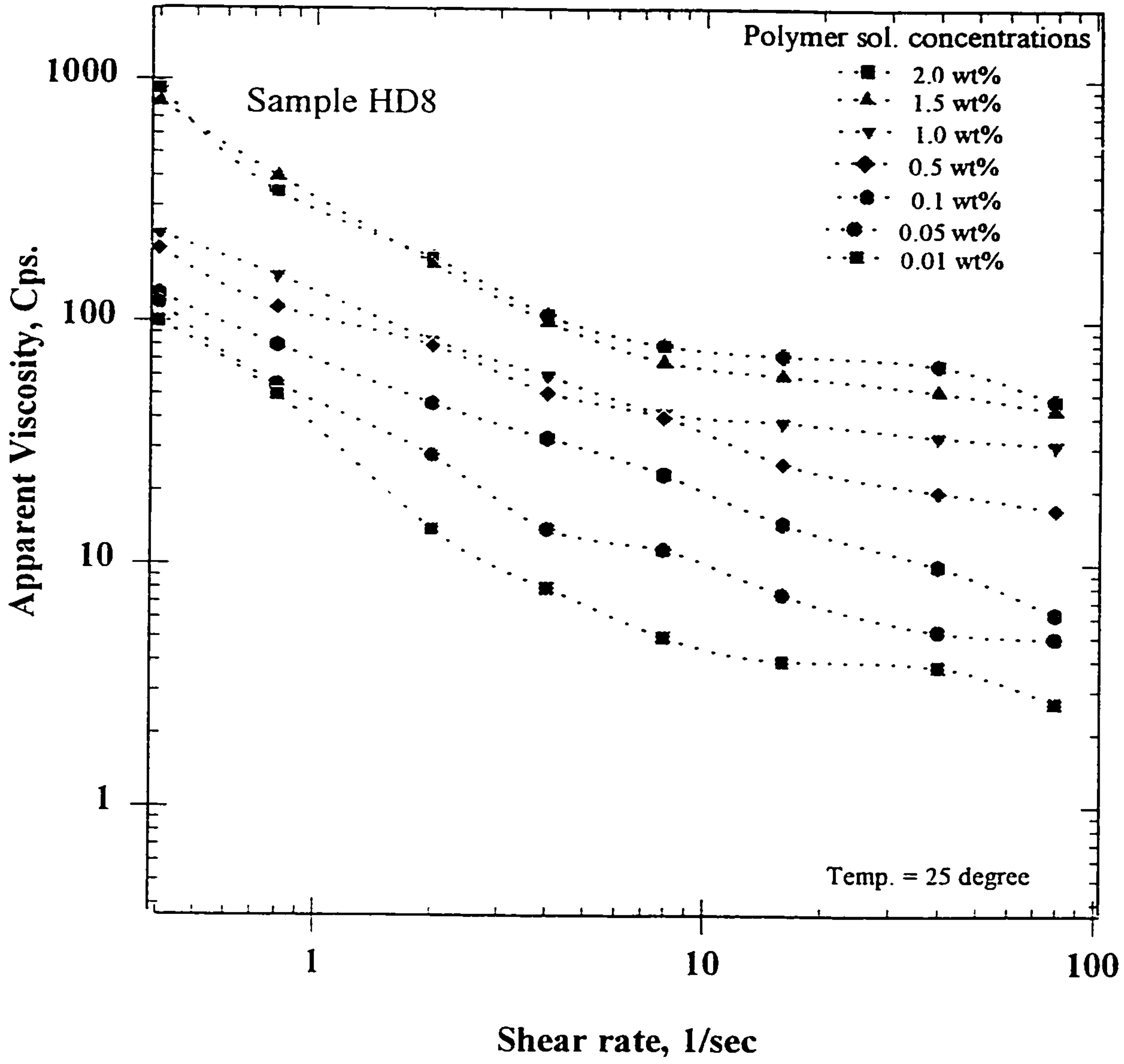


Figure 4-9; Effect of shear rate on the apparent viscosity of di-block copolymer or Na-poly(MA-b-AN), hydrolyized poly(MMA-b-AN) or HD8 in 0.305 mol NaOH. Hydrolizing solvent : isopropanol. Sample prepared in deionized water.

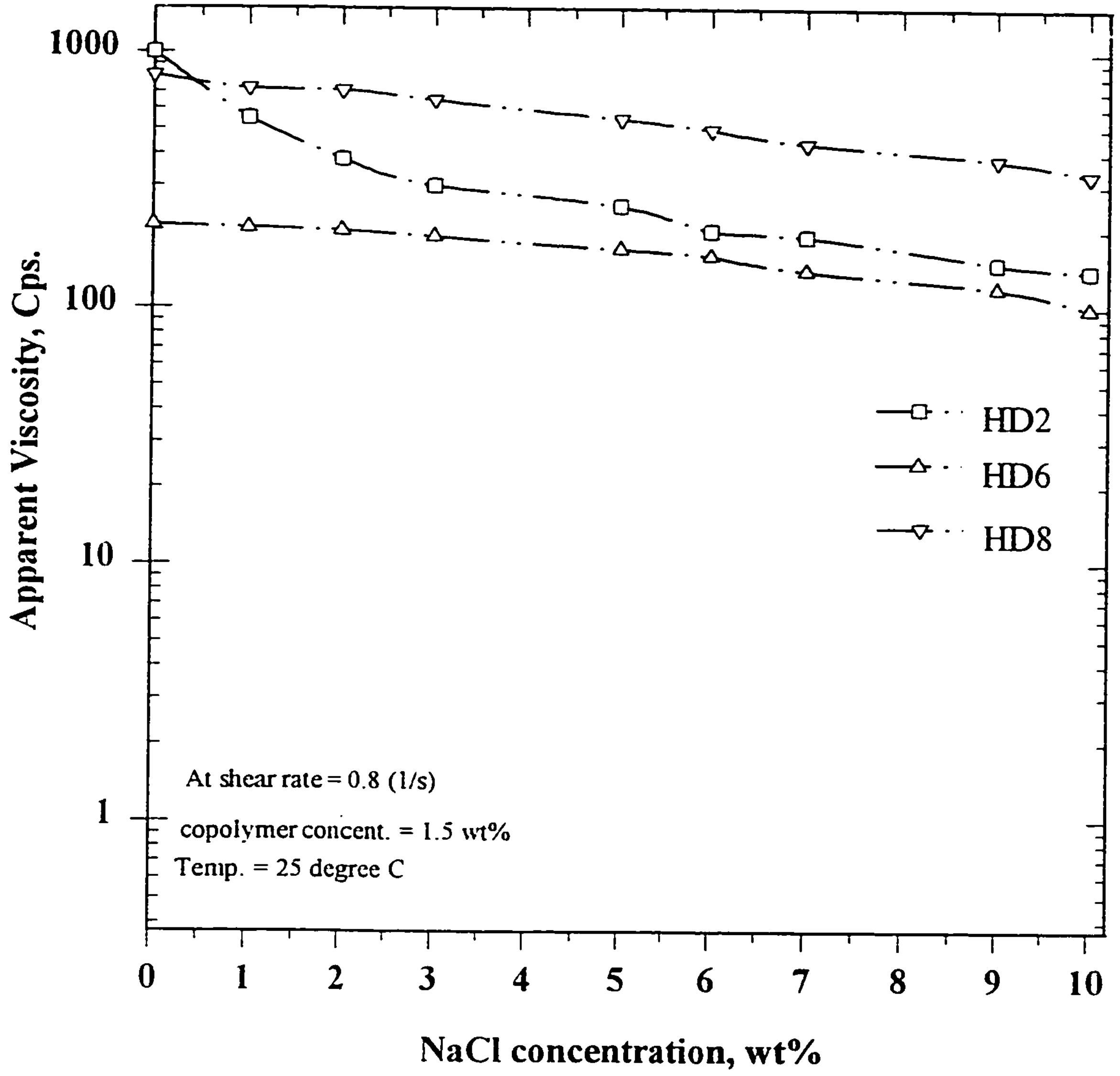


Figure **4-10**; Effect of NaCl concentration on the apparent viscosity of di-block copolymer of HD2 and HD6 (poly AN-b-poly MMA) with 38 mol% MMA. HD8 Na-poly (MA-b-VI), 34 mol% MMA in feed.

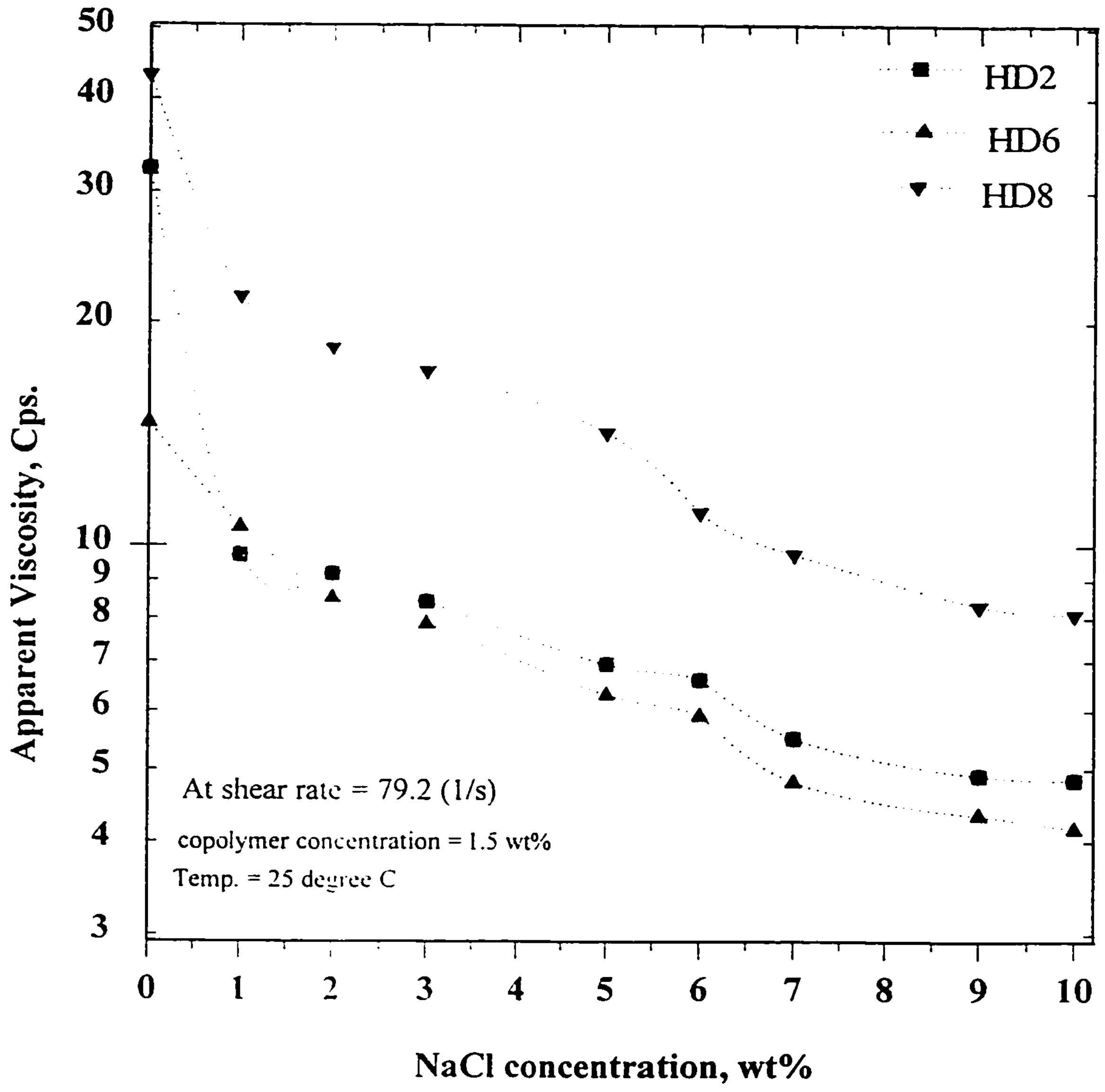


Figure 4-11; Effect of NaCl concentration on the apparent viscosity of di-block copolymer of HD2 and HD6 (poly AN-b-poly MMA) with 38 mol% MMA. Sample HD8, poly (MA-b-VI), 34 mol% MMA in feed.

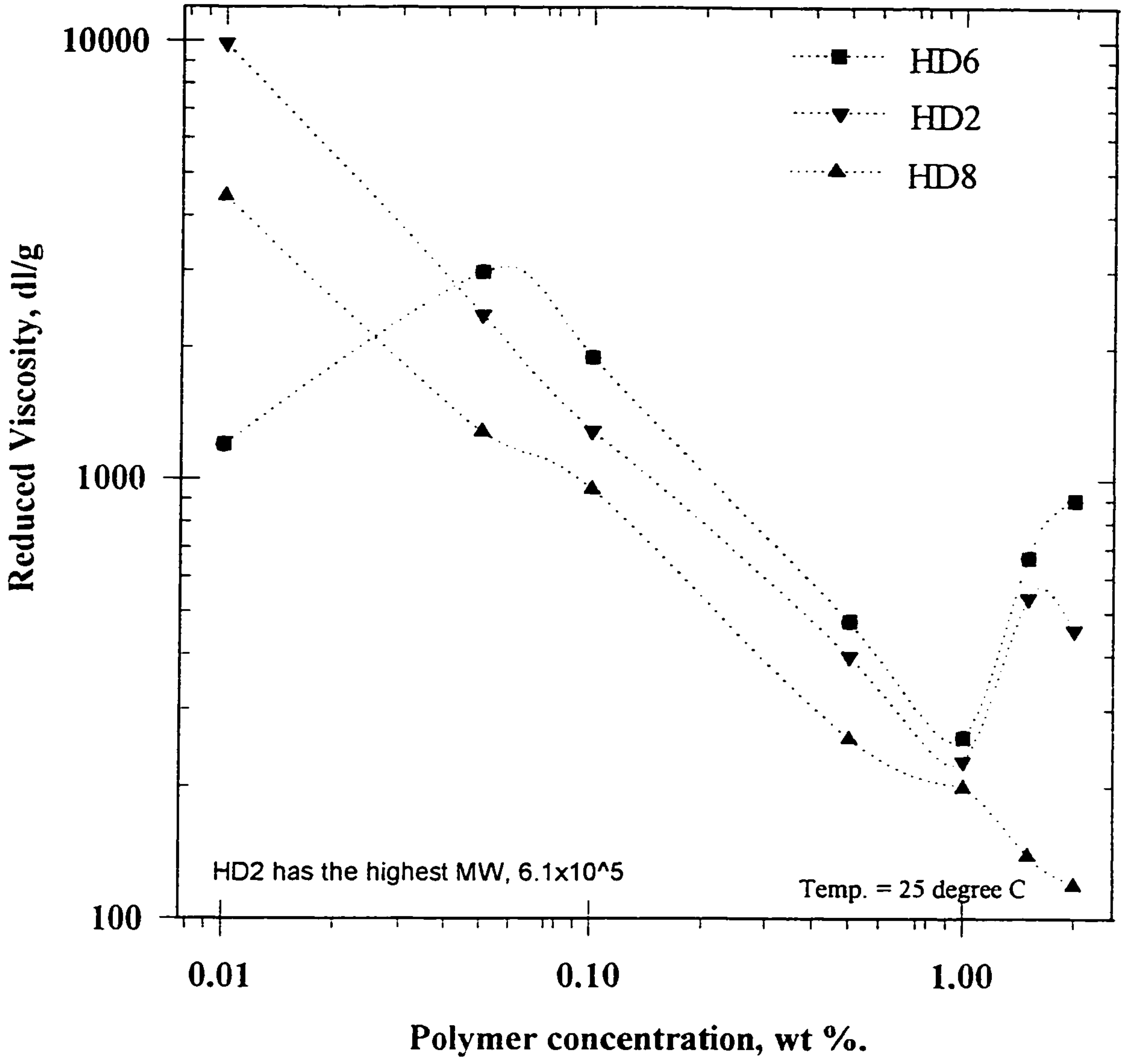


Figure **4-12**; Effect of polymer concentration on the apparent reduced viscosity of di-block copolymer of HD2 and HD6 (poly AN-b-poly MMA) and HD8 Na-poly (MA-b-VI), 34 mol% MMA in feed. Samples were hydrolized by NaOH in isopropanol. Then prepared in deionized water at a shear rate of 0.4^{-1}.

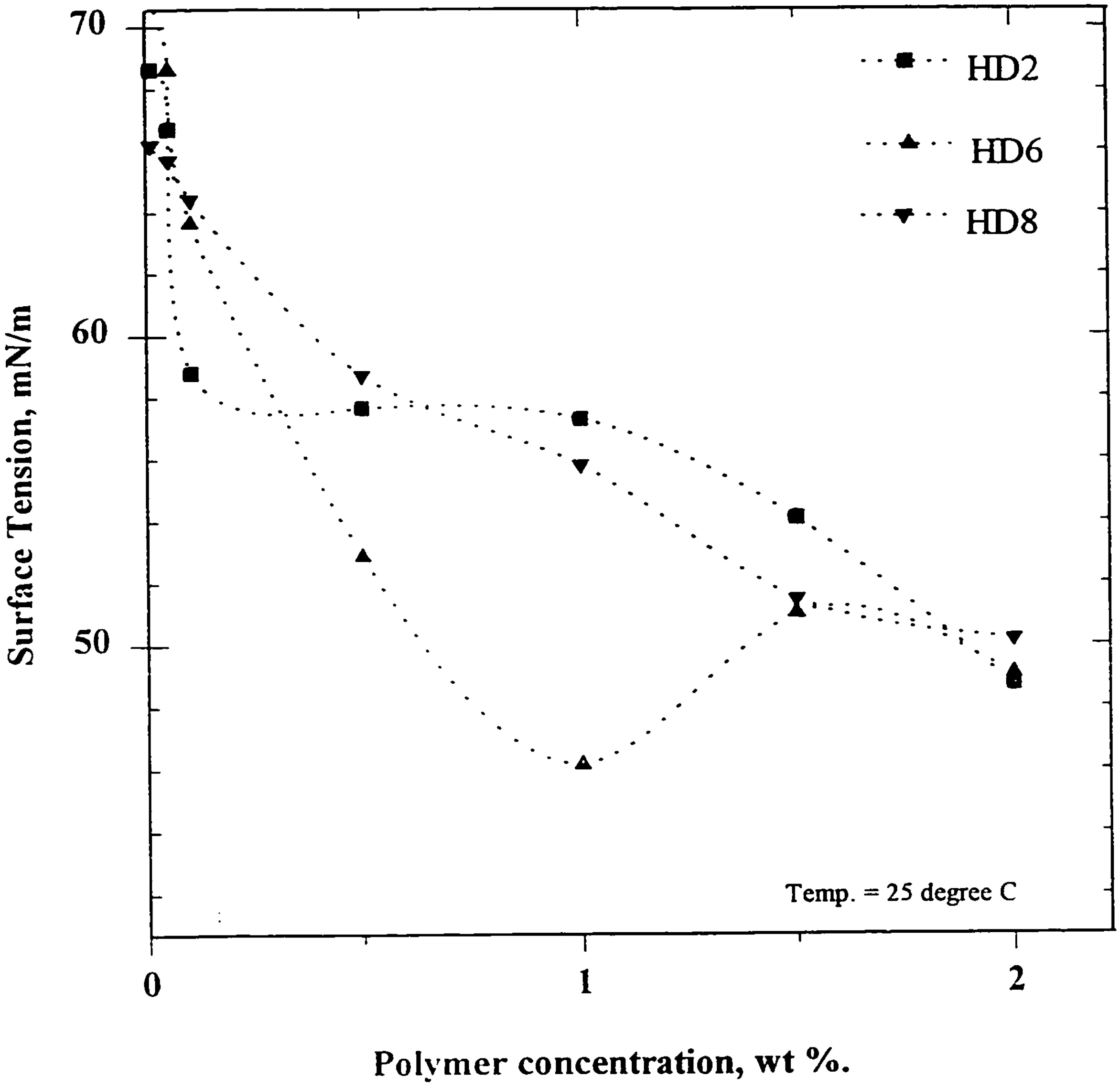


Figure 4-13; Effect of polymer concentration on the surface tension of di-block copolymers of HD2 and HD6 (poly AN-b-poly MMA) with 38mol% MMA each. HD8 (poly VI-b-poly MMA), 34 mol% MMA.

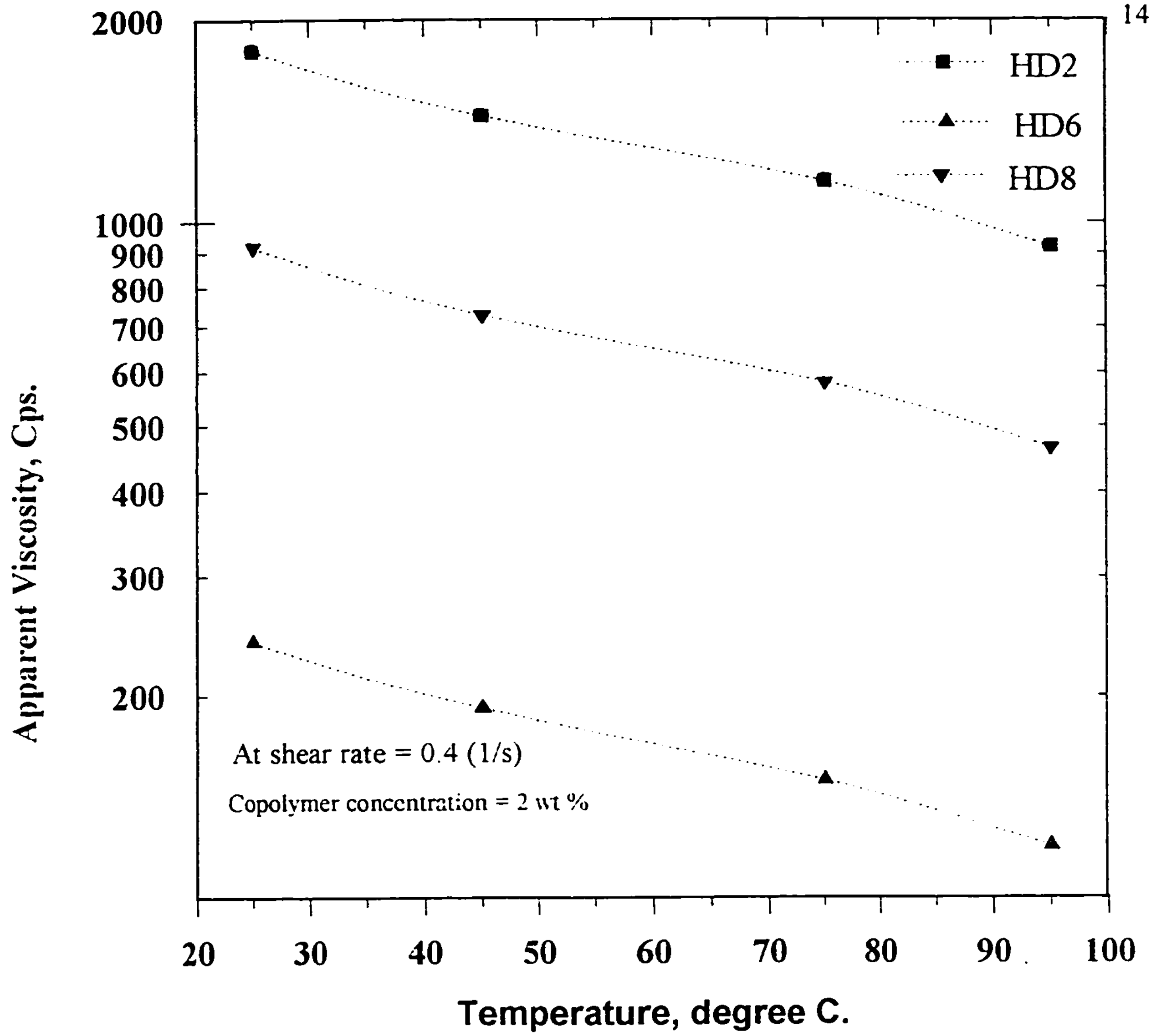


Figure 4-14; Effect of Temperature and shear rate on the viscosity of di-block copolymers of HD2 and HD6 (poly AN-b-poly MMA) with 38mol% MMA each. HD8 (poly VI-b-poly MMA), 34 mol% MMA. Polymer concentration is 2 wt % and shear rate is 0.4^{-1}.

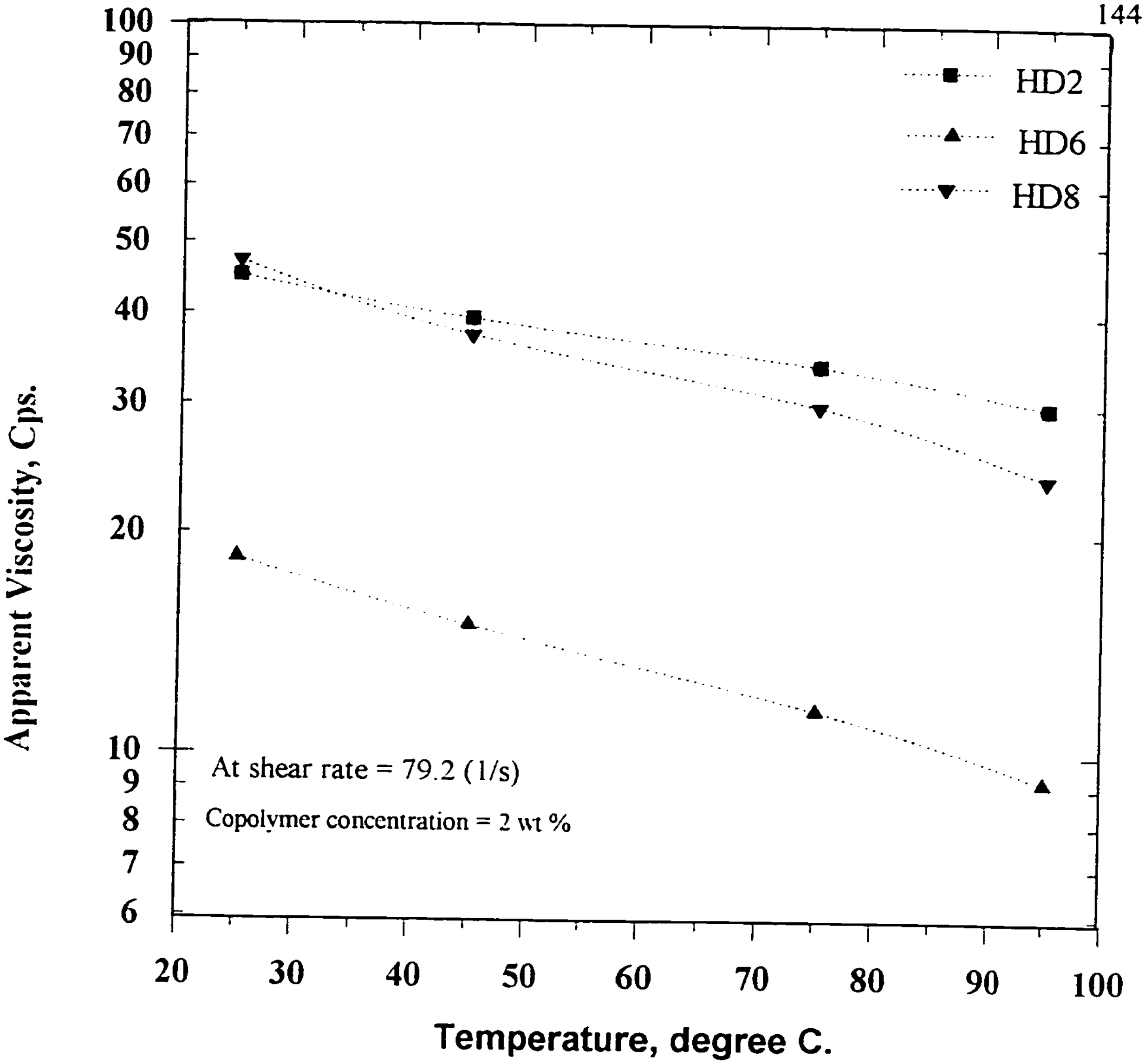


Figure 4-15; Effect of Temperature and shear rate on the viscosity of di-block copolymers of HD2 and HD6 (poly AN-b-poly MMA) with 38mol% MMA each. HD8 (poly VI-b-poly MMA), 34 mol% MMA. Polymer concentration is 2 wt % and shear rate is $0.79.2^{-1}$.

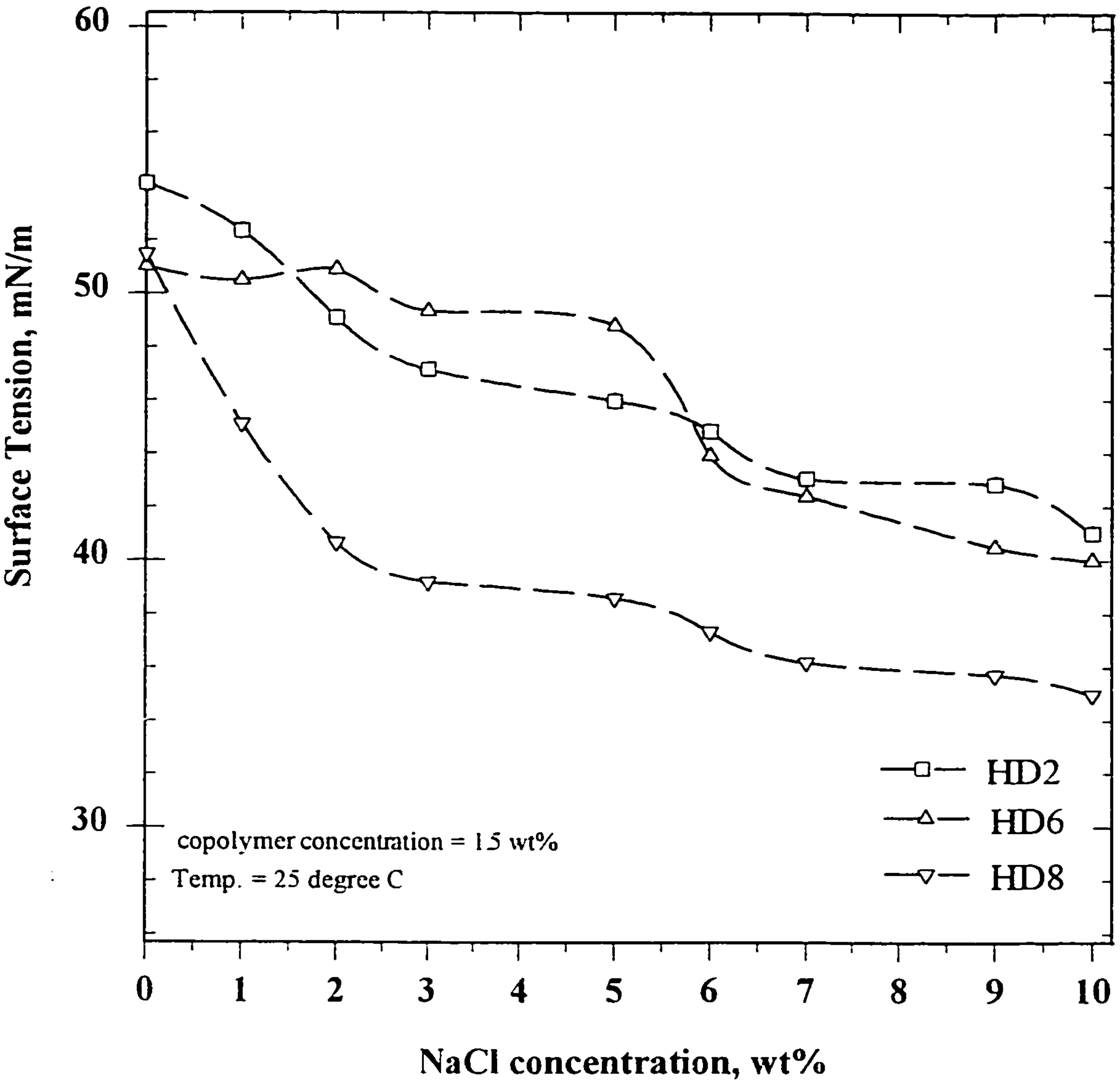


Figure 4-16; Effect of NaCl concentration on the surface tension of di-block copolymer of both HD2 and HD6 (poly AN-b-poly MMA) with 38mol% MMA. HD8 (poly VI-b-poly MMA), 34 mol% MMA.

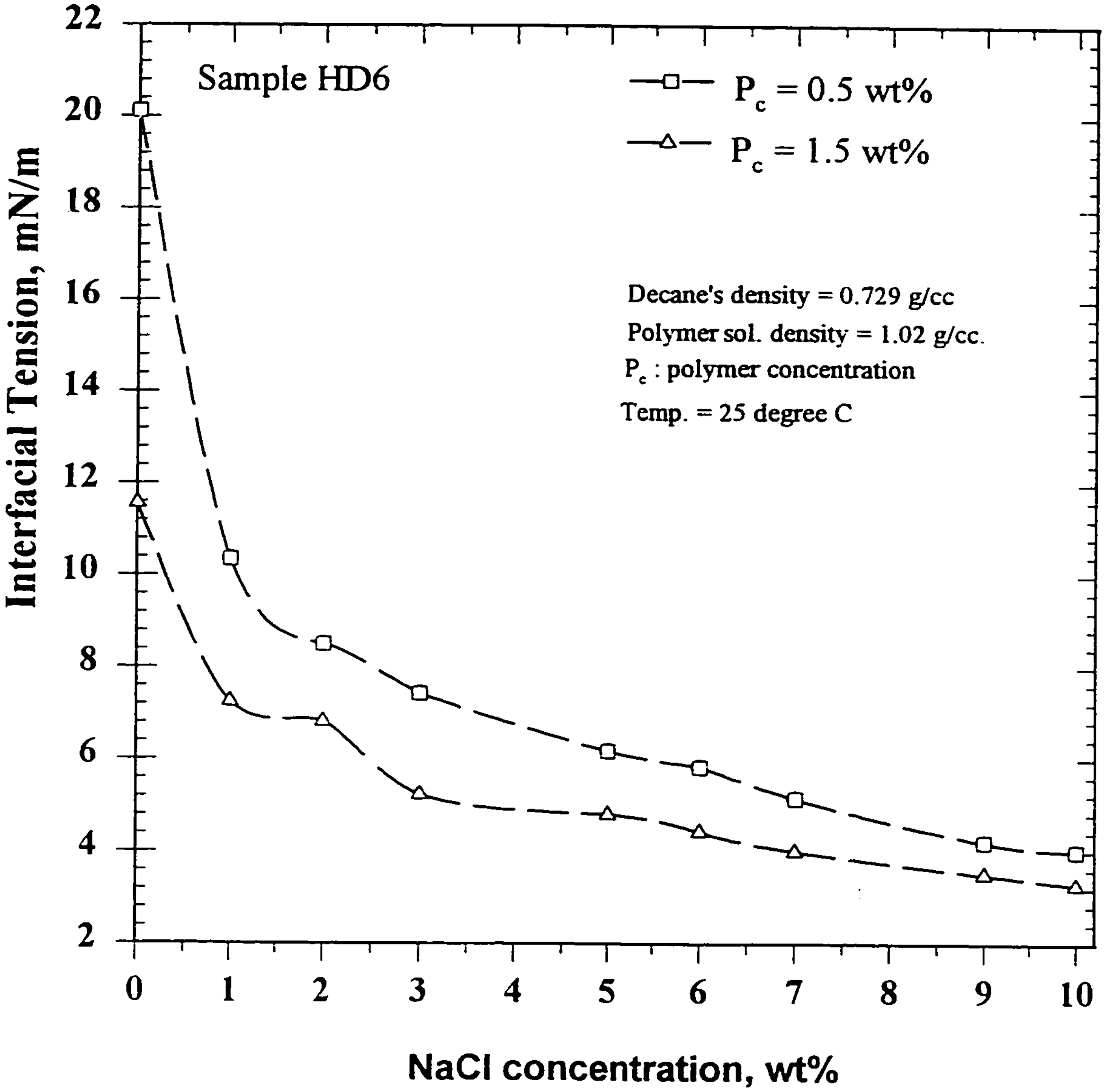


Figure 4-17; Effect of NaCl concentration on the interfacial tension of a hydrolized di-block copolymers of HD2 and HD6 (poly AN-b-poly MMA) with 38mol% MMA in feed.

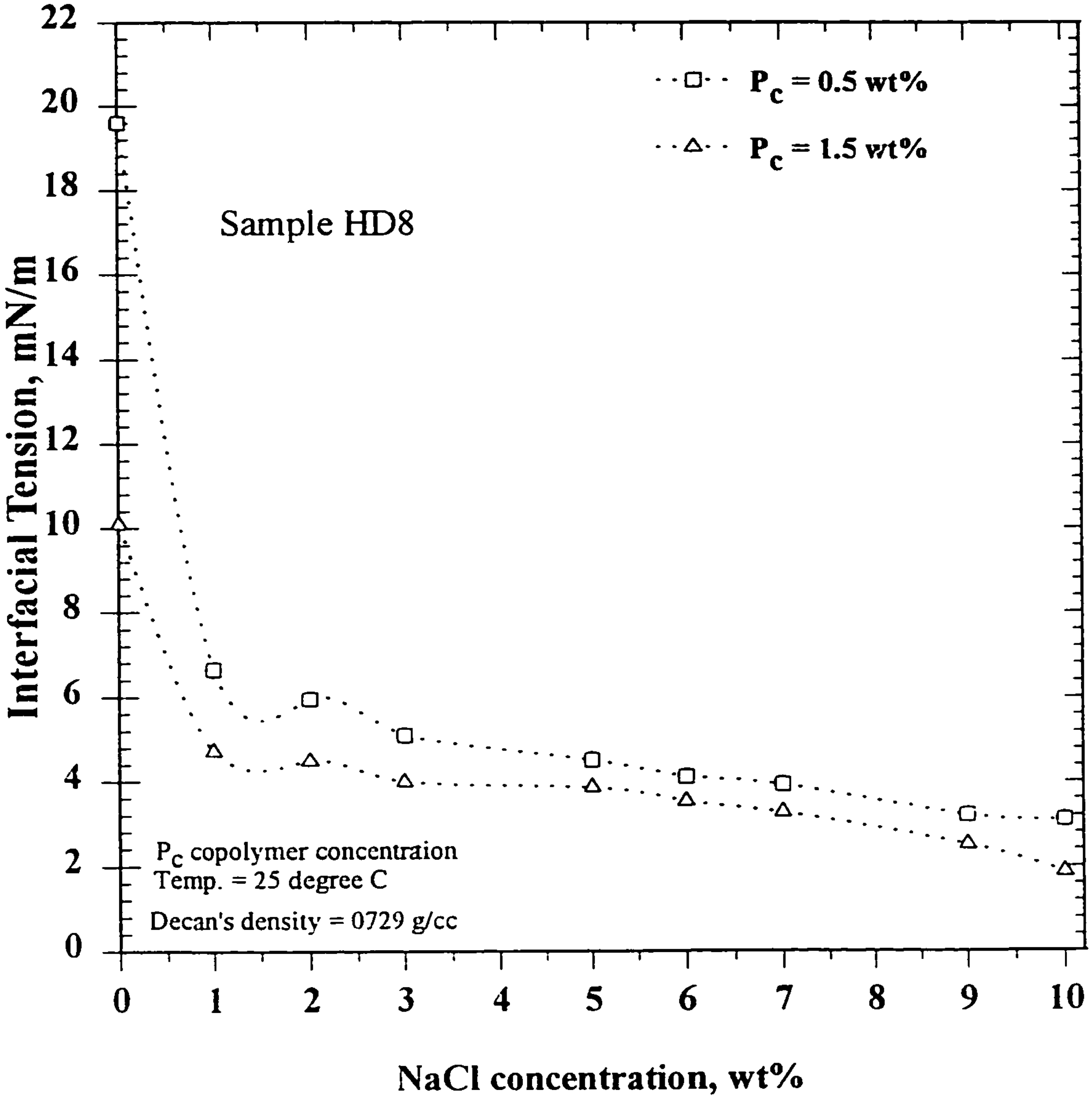


Figure 4-18; Effect of NaCl concentration on the interfacial tension of a hydrolized di-block copolymer of HD8 (poly VI-b-poly MMA) with 38mol% MMA. Polymer solution density 1.051 g/cc.

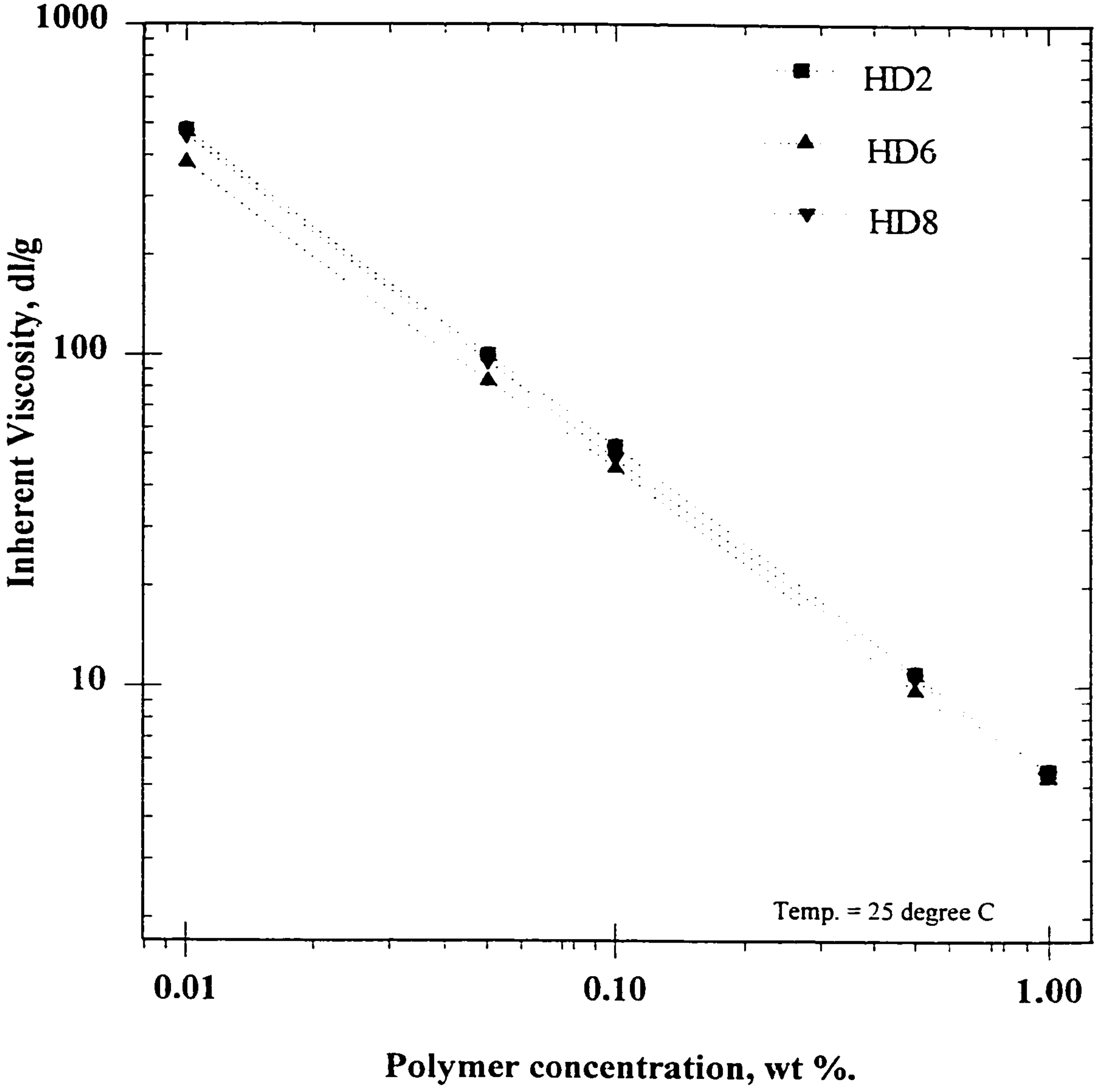


Figure 4-19; Effect of polymer concentration on the inherent viscosity of di-block copolymers; HD2 and HD6 (MMA-b-AN), and HD8 poly (MMA-b-VI) with 38 mol% MMA (in feed). Samples dydrolyized by NaOH in isopropanol. Samples are prepared in deionized water at a shear rate of 0.3 s^{-1} .

CHAPTER FIVE

AMPHIPHILIC MULTI-BLOCK COPOLYMERS OF ACRYLAMIDE WITH OTHER HYDROPHOBES:

SYNTHESIS AND AQUEOUS SOLUTION BEHAVIORS

5.1 Introduction

Water-soluble polymers such as polyacrylamides and hydrolized polyacrylamides have gained a great deal of interest in the petroleum industry, particularly in enhanced oil recovery (EOR) processes, because they can be polymerized to high molecular weights, 10^6. This type of polymers is mainly used as mobility control agents or thickeners to improve the performance of water flooding operations. However, due to deficiencies attached to such polymers, specialists switch to water-soluble hydrophobic associative polymers (associative thickeners) that are first used as model compounds in the study of protein conformations.

For the last several years, there has been a substantial interest in associative polymers. Research in this area (oil recovery) has concentrated on the synthesis and properties of water-soluble hydrophobically associating polymers which are based on copolymers of acrylamide and hydrocarbon derivatives of acrylates, methacrylates or acrylamides and hydrocarbon derivatives of cellulose-based polymers [4,8,9,15]. Such materials find applications in enhanced oil recovery (EOR) processes, because they can efficiently control the flow properties of

(EOR) processes, because they can efficiently control the flow properties of displacement fluids. Small concentrations of hydrophobically modified polymers substantially increase water viscosity. This has led to proposals for their use in various applications such as latex paints and water-based applications. However, these polymers are relatively expensive. So less expensive techniques ought to be initiated to reduce cost efficiency value.

Hydrophobic interactions in polymer aqueous solutions can be an important factor in molecular conformations and intermolecular associations and hence in rheology. In the same way, hydrophobic regions of proteins are key factors in determining protein conformation and enzymatic activity. However, the nature of hydrophobic interactions and the effects of structural parameters on the aqueous solution properties of such polymers have not been studied extensively and still unclear.

Substantial hydrophobic character in compounds (long hydrocarbon chains), that exhibit low surface energy, may be related to the low values of the cohesive energy density (CED). In polymer chemistry, a measure of strength in intermolecular forces is indicated by CED which itself is related to solubility parameters of compounds, polymers and solvents. Generally polymers with like solubility parameters are apt to dissolve the same solutes and to be mutually compatible. It is expected that when the polymer and solvent have the same solubility parameter, the maximum coil expansion will occur and therefore the highest viscosity will be obtained regardless of the presence of small hydrophobic moieties in the polymer structure. It is expected that polymers with high polarity or high CED should have high transition temperatures than nonpolar materials.

The incorporation of small hydrophobic blocks with a predominantly hydrophilic polymer backbone result in *amphiphilic hydrophobically associating* *block copolymer* with interesting solution properties [31]. In an aqueous solution, these amphiphilic polymers usually associate to protect the hydrophobic moieties from contact with water, thus minimizing their overall free energy. The nature and the extent of association depend, among other things, on the type and length of the hydrophobic blocks, the polymer molecular weight and concentration. At very low polymer concentrations, the chains have little chance of interacting with each other and, as a result, each chain forms a compact micellar structure where the hydrophobic blocks occupy the core region of the micelle while hydrophilic blocks constitute the outer shell extending toward the continues aqueous medium. As the concentration increases, association takes place and large aggregates are formed causing an increase in the hydrodynamic volume (solvation) and hence in the solution viscosity.

Hydrophobically associating polymers fall into two categories: (1) those that form *intra-molecular associations* (within molecules), and (2) those that form *inter-molecular associations* (between molecules). Each type possesses unique solution characteristics based on hydrophobic interactions and associated water ordering. The parameters determining inter- or intra-molecular aggregation include the molar volume of the copolymer, chemical composition, hydrophilic segmental length and hydration, type of hydrophile as ionic or nonionic, total molecular weight, and relative placement of the hydrophobe as a core or corona of the micelle [18].

These parameters may be varied to optimize or in fact *design* a copolymer for a particular end use application, an objective of the present work. In general, intra-molecular micellelike associations occur for high concentrations, i.e., melts, of long pendent hydrophobic groups on flexible hydrophilic chains. The micellization theory of this particular type has been recently studied thoroughly [48,97,98,60-64]. Inter-molecular interactions require a critical concentration of polymer molecules with relatively small minor concentration (0.1-7 mol %) of nonpolar groups to form these interactions.

Hydrophobically associating polymers (HAP) are used mainly in applications that require control, i.e., viscosity control, of rheological properties of water-based fluids, e.g., improving waterflood process in oil reservoirs, the present objective. These properties depend on the solubility characteristics of the polymers. Intermolecular hydrophobic interactions in these polymers lead to the formation of polymolecular associations, such as micelles. As a consequence, small amount of these polymers exhibit thickening properties in water equivalent to those observed for higher molecular weight (MW) homopolymers. Under increasing shear, the physical links between chains are disrupted but reform with decreasing shear, shear thinning behavior. By this way, it is possible to avoid the irreversible mechanical degradation that occurs for high MW samples when subjected to high shear stresses. Such properties give rise to particular rheological behaviors of great technological importance as a function of shear rate or shear time. The aggregation pattern of HAP is shown in Figure (5-1) at the end of this chapter along with other Figures of Chapter 5.

Polymer solutions of HAPs are actually microheterogenous in nature with specific polymer-polymer and polymer-solvent interactions. The nature of hydrophobic associations and their effect on the structure and properties of water have been extensively studied for small molecules (surfactants). However, hydrophobic associations of synthetic water-soluble polymers have received limited study. Polymer solubility depends on the chain length and concentration of hydrophobic functionality as well as the nature of the water-soluble portion of the polymer molecule. Therefore, hydrophobes should be used in a small weight/mole percent in the copolymerization process. The introduction of hydrophobic groups into a water-soluble polymer has a different effect on the solution viscometric behavior than on rheological properties above a critical concentration C* (the overlap concentration). Below C*, hydrophobic associations tend to create hypercoiling of the polymer molecules. This results in a decrease in the intrinsic viscosity [η] and an increase in the Huggins' coefficient, k', owing to intra-molecular associations. This usually occurs at low polymer concentration where only single molecules are present [18].

Because of the importance of micellization process in a wide range of industries, a lot of attention has been devoted not only to experimental studies of micelles but also to thermodynamic and theoretical investigations. Micelle formation requires the presence of two opposing forces: an attractive force between the amphiphiles leading to aggregation and a repulsive force that prevents unlimited growth of the micelles into a distinct macroscopic phase. Regular micelle formation by amphiphiles is mainly due to a positive standard entropy of micellization ($\Delta S°$). In this case, an attractive force arises from the hydrophobic interactions which are a result of reorganization of the structure of water which takes place when the hydrocarbon units are removed from it. From thermodynamic approaches, it was found that the micellization process of block copolymers as well as some low molecular weight amphiphiles is sufficiently cooperative to yield colloidal particles with a narrow size distribution and a high aggregation number. The change in cmc with temperature provides an indication of the enthalpy of micellization. The hydrophobic effect represents the main driving force for micellization that obeys the scheme of closed association mechanism.

The micellization of amphiphilic block copolymers is a process in which critical phenomena are important. Micelles only exist above a critical minimum concentration, i.e., the critical micelle concentration (CMC). The CMC can, most conveniently, be defined as that concentration below which only single chains are present but above which both single chains and micellar aggregates can be found. It should be noted that the phenomena of CMC in block copolymer systems occur at very much lower concentrations than in low molar mass amphiphiles [61].

The most interesting feature of the rheology of HAPs is the unique response to shear rate and solvent quality (e.g., salt content). The viscosity can be shear-independent (Newtonian), decrease (pseudoplastic), or even increase (dilatent) with shear rate depending on the amount and type of hydrophobe, polymer concentration, and solvent quality. Therefore, shear thickening and shear thinning behaviors can be exhibited by the solutions of hydrophobically associating polymers depending on synthesis conditions. The former behavior involves a change in the relative amount of intra- or inter-molecular associations with shear in hydrocarbon solvents. As the polymer molecules are extended under a shear field, the number of inter-molecular associations increase, resulting in enhanced viscosity. A similar phenomenon of enhanced viscosification imparted by HAPs when dissolved in water is observed and attributed to inter-molecular hydrophobic associations [8].

Experimental studies have shown that amphiphilic block copolymers can form different structures of micelles in a closed association mechanism upon dissolution into a selective solvent that acts thermodynamically as good solvent for one block and a precipitant for the other block. These materials have important properties that are very important from both technological and experimental points of view. They can be used in a variety of applications such as in the formulation of stabilizers, pharmaceuticals, cosmetic, agricultural chemicals, coatings, drug carrier systems, catalysis, drag reducers in turbulent flow, water treatment, and mobility control agents in oil recovery industry. However, less is known about block copolymer behaviors involving water-soluble blocks and forming regular micelles upon micellization process.

The *main aim* of this work is to focus on the possibility of combining both the mobility control and the IFT reduction properties in a single chemical compound, for oil reservoir flooding operations, which is here an amphiphilic non-ionic multi-block copolymer. The hydrophilic monomer (water-soluble) will be exclusively acrylamide. Styrene (ST) and 1-dedecene (C12) (water-insoluble) will be chosen as uncharged hydrophobic comonomers in this study to produce non-ionic block copolymers with polyacrylamide (PAM) block. Only micellar/solution copolymerization technique will be used since it is proven to yield polymers with high thickening ability and provide good synthesis control [6].

Because mixing polymeric molecules with surface active molecules has proven to create many problems to oil-field operations as encountered in surfactant-polymer flooding technique, polymer systems are meant, in this work, to be exclusively used in flooding operations if they hold desired properties. Interactions between surfactant molecules and the polymer macromolecules, in such a complex combination upon mixing, believed to result in unfavorable changes in porous aqueous media such as alteration of the phase composition from the original design and phase separation, which would result in pore clogging and high chemical loss by entrapment. Therefore different new mechanisms should be introduced to the oil industry to lower the cost of the chemicals used and the tedious operations.

In the literature, there has been an extensive information on the micellization of low molecular weight amphiphiles but much less work dealing with multi-block copolymers, or even block copolymers in general, of acrylamides with hydrophobes has been performed. Volpert, Selb, and Candau [26], investigated the influence of hydrophobic structure on the rheology of Amphiphilic associating block copolymer of polyacrylamide modified with small amount of alkylacrylamides prepared by micellar copolymerization process. They concluded that at similar hydrophobe levels, double-chain hydrophobes considerably enhances the thickening efficiency with respect to single chain-hydrophobes [26]. They observed that the high density of hydrophobic molecules, condensed core, in the micelles should favor their incorporation as block in the copolymer backbone. But actually Peer first suggested the formation of a blocky structure to such type of polymeric amphiphiles (in 1987). Also direct experimental evidence was reported by Thomas et al. [7] and McCormick et al. from photophysical studies of PAM derivatives with hydrophobes.

Branham, Shafer, Hoyle and McCormick studied the synthesis and the microstructure behavior of block terpolymers of acrylamide, acrylic acid and n-[(1-pyrenyl-sulfonamido)ethyl]acrylamide by micellar process. Their results by viscometry and dynamic light scattering indicated that no intermolecular hydrophobic aggregation in a brine solution is evident. However, steady state fluorescence studies explained that the degree of associative thickening behavior (intermolecular association) to be a function of the surfactant to hydrophobe ratio in the polymerization of AM/NaA copolymers [12]. McCormick et al. also investigated the synthesis and solution properties of copolymers of acrylamide/N-alkylacrylamide using micellar process. They concluded that a remarkable increase in viscosity observed at low hydrophobe due to the formation of interchain hydrophobic associations in aqueous solutions [67,92,94,95]. McCormick et al. also studied the behavior of random and graft copolymers of polyacrylamide and polyacrylamide derivatives using potassium persulfate initiator in a heterogeneous media and found these polymers only slightly salt tolerant, and the hydrophobic interaction do not occur significantly, hence there were no improvements in thickening ability [20, 24,68].

Copolymerization of acrylamide with acrylamide derivatives, i.e., N-(4-ethyl-phenyl)acrylamide, synthesized by micellar process, reported by Hill A., Candau F., and Selb J. [6,8,96], was proven to be a very appropriate way of synthesizing and studying amphiphilic multiblock copolymers with improved thickening properties.

They concluded that polymer aqueous solutions strongly depend on the conditions of the synthesis. Moreover, copolymers prepared by the homogenous and heterogeneous processes behave like polyacrylamide, hydrophobic groups are distributed as discrete units. They do not exhibit their hydrophobicity and the conformation of the water-soluble macromolecule is not affected.

Below are outlined the major differences between the *micellar process* and the more conventional polymerizations carried out in the presence of a surfactant, i.e., *emulsion* or *microemulsion* process.

- In an aqueous emulsion polymerization, the amount of surfactant is low with respect to that of the hydrophobic monomer. On the contrary, in the present micellar process, the surfactant over hydrophobe ratio ([SDS]/[ST]) is quite high (typically in the range 15/1 to 17/1 by weight).

- Direct emulsion copolymerization implies a low water solubility of the monomers; i.e., the monomers are essentially located in the dispersed phase (large monomer droplets and small micelles). The situation is quite different in the micellar copolymerization, since the major part of the monomeric species. i.e., acrylamide, is soluble in the aqueous continuos phase; the hydrophobic monomer located within the micelles represents only a very small fraction of the total monomer feed, hydrophobically associating polymerization ($\cong$ 2-7 wt %).

- In the micellar process, the two monomers are segregated at the beginning of the polymerization into two distinct phases due to their very different solubilities, styrene hydrophobicity is very high. Such a situation affects the mechanism of the copolymerization.

- In the micellar process, the copolymerization reaction occurs in both the continuos and phase and dispersed phase. Therefore, although this process was called "*micellar copolymerization*", it involves in fact a combination of a micellar polymerization and a solution polymerization.

- In the micellar process, a macromolecular chain never penetrates completely inside a micelle as opposed to the emulsion polymerization. Also the interfacial micellar layer is a region where both monomer species are in close proximity.

- The final reaction mixture in micellar process is not a latex but a homogenous, clear, and strongly viscous polymer solution. A *latex*, which is the basis for natural rubber, is a fluid dispersion of insoluble polymer particles in water. Besides, the copolymerization of a hydrophilic and a hydrophobic monomer by an emulsion process, 100 of microns particle size, gives a latex functionalized with hydrophilic groups because of the reverse proportion of the two monomers. In the microemulsion and the micellar processes the particle size is much smaller; only tens of nanometers, 1.0 nm is eqivalent to 10 A° or Angstrom, making the solution transparent and homogenous. In the other hand the smallest commercially available latex particles are on the order of 300 A° in diameter.

- In the micellar process, the role of surfactant is twofold: not only does it ensure the solubilization of the hydrophobic monomer in the aqueous medium but also induces the formation of hydrophobic sequences whose length depends on the micellar concentration, i.e., the number of hydrophobes in a micelle. This mechanism allows the formation of polymers with high thickening abilities.

Series of non-ionic *multi-block copolymers* $-[A\text{-}B]_n-$ are synthesized via a novel micellar co-polymerization technique, which itself differs significantly form microemulsion polymerization technique as stated earlier where different mechanism of polymerization is followed, in an attempt to produce suitable polymers for EOR application. Sodium dodecylsulfate (SDS) and hexadecyltri-ethylammoniumbromide (CTAB) are used in this research as supporting surfactants to solubilize the hydrophobes (ST or C12) in the inter/intra micellar polymerization reaction to produce a homogenous aqueous micellar medium. Water-soluble free-radical initiator, potassium persulfate ($K_2S_2O_8$) is going to be utilized in the micellization process in different quantities to produce polymers with various molecular weights. Polymerization conditions will be varied to study the various effects on the finished polymers and eventually to design polymers with high thickening ability and surface activity.

Copolymerization of a hydrophobic monomer with a hydrophilic monomer can result in an amphiphilic polymer, the specific nature of which can be controlled via polymerization parameters, temperature, type and level of hydrophobe, type and level of surfactant and level of initiator as well as polymer recovery technique. The dual hydrophilic/hydrophobic nature provides unique solubilization characteristics and modifies physical properties of the bulk polymer. A combination of polymers and surfactants can be utilized to even increase the solubilization of sub-surface oil spills through the use of EOR technology [186]. Acrylamide copolymers provide a mean to achieve diverse fundamental properties to be used in many industrial water-based applications. Acrylamide is mainly used extensively in petroleum processes because it can be polymerized to high molecular weights, $5.0\text{x}10^6$.

In the present study, a detailed investigation on the synthesis-structure-property relationships for acrylamide-based copolymers is presented. The objective is to synthesize multi-block copolymers of valuable properties highly interested in the oil recover industry. By varying the formulation of the initial reaction mixture, it is hoped to induce new reaction routes that in turn should alter the aqueous solution properties. After the synthesis part, it is planned to study (1) the viscometric behavior in dilute solution, (2) the rheological behavior as a function of shear rate, polymer concentration and salinity in the semi-dilute range, and (3) the surface activity of air-solution interface and interfacial activity of oil-solution interface of the aqueous polymer solutions of different concentrations and salinities.

5.2 The Synthesis of Hydrophobically-modified PAM Copolymers

Series of non-ionic multi-block copolymers $-[A\text{-}B]_n-$ were synthesized via a novel micellar co-polymerization technique which itself differs significantly form microemulsion polymerization technique. Sodium dodecylsulfate (SDS; $C_{12}H_{25}SO^{-}{}_{3}Na^{+}$) and n-hexa-decyl-triethyl-ammonium-bromide (CTAB; $C_{16}H_{33}N(CH_3)^{+}{}_{3}Br^{-}$) was used separately as surfactants to solubilize the hydrophobes (ST and C12) in the inter/intra micellar polymerization reaction to produce an aqueous micellar mixture. Water-soluble free-radical initiator, potassium persulfate ($K_2S_2O_8$) was utilized in the micellization process in different quantities to produce polymers with various molecular weights (MW). Polymerization conditions were varied to study the various effects on the finished polymers and eventually to design polymers with high thickening ability and surface activity.

Copolymerization of a hydrophobic monomer with a hydrophilic monomer result in an amphiphilic polymer, the specific nature of which can be controlled via polymerization parameters, temperature, type and level of hydrophobe, type and level of surfactant and level of initiator as well as polymer recovery technique. The dual hydrophilic/hydrophobic nature provides unique solubilization characteristics and modifies physical properties of the bulk polymer. Acrylamide copolymers provide a means to achieve diverse fundamental properties to be used in many industrial applications. Acrylamide is mainly used extensively in petroleum processes because it can be polymerized to high molecular weights, $5.0\text{x}10^6$, which is due to its high propagation to termination rate constants.

The objective of the investigation is to study how the conditions of the synthesis by micellar process, i.e., initial monomer segregation by SDS or CTAB, could affect the hydrophobe distribution within the copolymer and in turn the rheological properties of the polymer solutions. Variable hydrophobe contents in one hand and variable surfactant/initiator contents in the other hand are going to be followed, since high MW is dependent on surfactant and hydrophobe concentrations besides the initiator content. To achieve the desired properties, various series of multi-blocks copolymers of acrylamide with a hydrophobe of high hydrophobicity, i.e., styrene (ST), have been synthesized in an aqueous media by radical copolymerization using sodium dodecyl sulfate (SDS) or (CTAB) as a surfactant to solubilize the hydrophobe. High hydrophobicity is believed to induce high degree of association. A water-soluble free-radical initiator, potassium persulfate ($K_2S_2O_8$), has been used to induce the initiation. Another different hydrophobe, i.e., 1-dodecene (C12), has been utilized with an attempt to synthesize second series of multi-block copolymers with predominantly polyacrylamide content using SDS to solubilize the hydrophobe. Both surfactants, SDS and CTAB (hexa-decyle-tri-ethyle-ammonium-bromide), were used separately in two groups in synthesizing the first series of multiblocks using the same water-soluble initiator ($K_2S_2O_8$) for comparison purposes as indicated in Table 5-1. *Micellar process* was also used to produce PAM homopolymer with the same composition and MW. AM/C12 and AM/ST multiblock copolymers were synthesized by varying the formulation of the initial reaction mixture. Also AM/ST random copolymer was synthesized, by *homogenous process* using a miscible cosolvent (formamide), with an attempt to establish a valid comparison with other copolymers prepared by the micellar technique.

5.2.1 Polymer Synthesis of AM/ST Multi-block Copolymers

Monomers, i.e., styrene (ST) and 1-dodecene (C12), were first distilled at reduced pressure at 30 °C prior to use to remove the inhibitors. Acrylamide monomer was used as received from Fluka Chemical Co. Sodium dodecyl sulfate (SDS), and potassium persulfate initiator ($K_2S_2O_8$) were purchased from BDH Limited Pool, England. Hexadecyle-triethyle-ammoniumbromide (CTAB) was obtained from Sigma Chemical Co. Formamide was purchased from Flucka chemical co. and used as received.

Solvents and other reagents were used as received without any further purification. Methanol, dichloromethane, diethylether, and acetone were used extensively through out the preparation of polymers. Deionized and distilled water were used extensively for all aqueous solutions.

5.2.1.1 Series Preparations of polyAM-b-polyST Copolymers

a. Preparations in a micellar media using SDS surfactant:

Micellar process first described by Evani and Valint et al.[147]. The general experimental procedure used for synthesizing series of multi-block copolymers by the micellar process was extracted from the work of Hill. et al. [8] with slight modifications to study how the conditions of the synthesis affects the hydrophobe distribution within the copolymer and polymer's rheological properties. Reaction conditions are provided in Table 5-1.

As a typical example: The experimental procedure was as follows. First, aqueous solutions of acrylamide (AM) were charged into a 500-ml three-necked Erlenmeyer flask (reactor) equipped with a reflux condenser, nitrogen inlet/outlet and rubber septum cap. The solution was constantly purged by gentle bubbling with nitrogen gas (to stop oxygen radicals degradation) for 20 minutes while stirring. After complete dissolution, the surfactant, sodium dodecyl sulfate (SDS) or CTAB, was added with gentle stirring for 10 minutes to avoid forming bubbles. The reagents should be added carefully and quickly along with slowly keeping the nitrogen to deaerate the flask to avoid forming bubbles or air to enter. After 10 minutes of dissolution, the flask inlet and outlet were covered with septum caps. After 15 minutes (or more depending on the amounts) of gentle stirring, the second comonomer, either styrene (ST) or 1-dodecene (C12), was added by injection with a syringe into the reaction mixture and stirring was continued for 1/2 - 1.0 hr. depending on the amounts of hydrophobes until a micellized homogenous clear transparent solution was obtained, otherwise expectation of copolymeriztion is less. The micellization should be closely checked and eye-inspected before the comonomer is added. Then the whole setup with an oil bath underneath was placed on top of heater/stirrer plate and the temperature was controlled at 50 °C not more or less. Then the polymerization was initiated by charging with a syringe an appropriate amount of a water-soluble initiator solution, potassium persulfate ($K_2S_2O_8$). The reaction mixture was left under moderate stirring for 48 hours to get a high yield. The conversion was about 90 %. The reaction conditions for each experiment conducted is given in Table (5-1).

The polymers were then recovered, after enough cooling, through several precipitation/dissolution cycles to the final reaction mixture. Usually the finished polymer solution is slowly poured drop wise into a constantly stirred five-times excess of methanol. The solid polymer recovered by filtration was repeatedly washed several times in methanol under stirring to remove all traces of water, surfactant and residual unreacted monomers. Then the polymer is vacuum-dried in an oven at 50 °C for 24 hr. Finally the polymer was crushed into a fine powder and then dried again for 6 hr and then stored for characterization.

Because the mode of preparation and the way the samples are recovered have a marked effect on polymer properties; i.e., viscosity, it was crucial to remove all traces of foreign materials, i.e., SDS and CTAB, by several washing and purification for future investigation on solution properties.

b. Preparations in a micellar media using CTAB surfactant:

The procedure taken was as previously mentioned with the exception of using variable amounts of CTAB (n-hexa-decyl-triethyl-ammonium-bromide (CTAB; $C_{16}H_{33}N(CH_3)^+{}_3Br^-$)) as the supporting surfactant instead of SDS and the samples synthesized are: P15, P10', P11, P12, P13, and P8. Feed or polymerization parameters are shown in Table (5-1). Since CTAB is a cationic surfactant and can hold more hydrophobes in its micelles than SDS, it is believed that the micellization will induce new routes and hence good results, i.e., CTAB aggregation number may increase with adding styrene comonomer. CTAB aggregation number in aqueous solution is 60 and its cmc is 9.2×10^{-4} M. In a different experimental condition, attempts have been made to prepare block copolymer (trial P8) using an oil-soluble initiator (AIBN) to initiate the reactions to produce AM/ST copolymer but the polymerization did not take place at all, even after doubling the initiator's dose. Reaction mixtures are provided in Table (5-1).

5.2.2 Polymer Synthesis of AM/C12 Multi-block Copolymers

5.2.2.1 Series Preparations of polyAM-b-polyC12 Copolymers

Preparation of AM/C12 Copolymers with SDS surfactant:

The typical procedure was followed as mentioned earlier with the exception of using variable amounts of 1-dodecene (C12) comonomer instead of ST. Series of AM/C12 copolymers were synthesized at 50 °C. Reaction mixtures are provided in Table 5-1 where the total monomer concentration was kept constant (3.0 wt %). The persufate initiator ($K_2S_2O_8$) concentration was 0.3 wt % relative to the monomer feed. The surfactant (SDKs) used in the series at constant amount (3 wt %). The precipitation and redissolution cycles were performed several times to purify/wash the polymers. Then the recovered polymer was vacuum-dried in an oven at 50 °C for two days.

5.2.3 Synthesis of AM/ST Random Copolymer

The synthesis of AM/ST copolymer has been done in a homogenous process where the hydrophobe is solubilized by a cosolvent. Formamide was found to be the most suitable cosolvent to produce copolymers of comparable molecular weights, since alcohols, if used, are found to be superior chain transfer agents lowering the molecular weight of polymer.

Preparation of polyAM-r-polyST Copolymer by homogenous process:

The experimental procedure followed in this method was almost analogous to that described in the previous section. However, it was of primordial importance to dissolve first styrene monomer (3 mol %) *in formamide* before adding the aqueous acrylamide solution. The experimental parameters are shown in Table (5-1) and the copolymer (sample P) prepared was then washed and filtered several times before being dried as discussed earlier. The polymerization in the solvent mixture (formamide and water) was found to give rise to lower molecular weight.

5.3 Copolymer Characterization and Identification

5.3.1 Elemental Analysis

Testing a sample is as important as making it. So elemental analysis has been performed to know the composition of the copolymers synthesized. The presence of elements, e.g., carbon, hydrogen, nitrogen, oxygen, and sulfur, were checked in the copolymers. Particularly, sulfur content was checked so as to know any surfactant impurities in the copolymers. Table 5-2 shows the results of elemental analysis carried out in the Central laboratory of the Research Institute in K.F.U.P.M.

Carlo Euba model 1106 elemental analyzer was used for the determining the concentration of the relevant elements. Routinely, for solid samples, the elemental analyzer accuracy is within ± 0.3%.

Table 5-1; Copolymerization Conditions in the Synthesis of Multi-block Co-polymers of Poly(AM^a-b-ST) and Poly(AM-b-C12) by Micellar technique with Variable amounts of Hydrophobe, Surfactant and Initiator at 50 °C.

Sample code	Structure	[ST]^b or {[C_{12}]}; mol %	^{d}[SDS] or{[CTAB]}; wt %	[$K_2S_2O_8$]; M
P5, 2ST-2SDS	Poly(AM-b-ST)	2	2	$2.76X10^{-3}$
P4, 3ST-2SDS	Poly(AM-b-ST)	3	2	$2.76X10^{-3}$
P7, 6ST-2SDS	Poly(AM-b-ST)	6	2	$2.76X10^{-3}$
P6, 7ST-3.15SDS	Poly(AM-b-ST)	7	3.15	$2.76X10^{-3}$
P15, 1ST-1CTAB	Poly(AM-b-ST)	1	{0.99}	$3.69X10^{-3}$
P10' 3ST-1.36CTAB	Poly(AM-b-ST)	3	{1.36}	$2.76X10^{-3}$
P8 3ST-1.36CTAB	Poly(AM-b-ST)	3	{1.36}	f
P11, 6ST-2.68CTAB	Poly(AM-b-ST)	6	{2.68}	$2.76X10^{-3}$
P12, 7ST-3.97CTAB3	Poly(AM-b-ST)	7	{3.97}	$2.76X10^{-3}$
P13, 7ST-3.97CTAB4	Poly(AM-b-ST)	7	{3.97}	$4.58X10^{-3}$
^{e}E1, 0C12-3SDS	*HomoPoly(AM)*	{0}	3	$3.36X10^{-4}$
E2, 1C12-3SDS	Poly(AM-b-C12)	{1}	3	$3.36X10^{-4}$
E3, 2C12-3SDS	Poly(AM-b-C12)	{2}	3	$3.36X10^{-4}$
E4, 3C12-3SDS	Poly(AM-b-C12)	{3}	3	$3.36X10^{-4}$
P,^{c} 3ST-200FRM	*Poly(AM-R-ST)*	3	-	$2.05X10^{-3}$

a AM: Acrylamide, FW = 71.08; ST: Styrene, FW = 104.15; C_{12}: 1-dodecene, FW = 168.32.

b Mole percent in feed = [ST]/{[ST] + [AM]}, or = [C12]/{[C12] + [AM]}.

c A Random co-polymer by Homogenous process (in 50 wt % formamide by vol. of water).

d SDS concentration in feed is based on volume of distilled water. Aggregation No. for SDS in an aqueous solution, Nagg = 60 at 50 °C. and its cmc = $9.2x10^{-3}$ M.

e For E1 to E4, $K_2S_2O_8$ at 0.3 wt % of the monomer feed is used, total monomer conc. = 3 wt %.

f Oil-soluble initiator (AIBN) is used instead ($4.39X10^3$ M).

CTAB n-hexa-decyl-triethyl-ammonium-bromide $C_{16}H_{33}N(CH_3)^+_3Br^-$

As an example for the analyzer: A standard compound, di-nitro-phnylhydrazone ($C_{12}H_{14}N_4O_4$), contained 51.79%C, 5.07%H and 20.14%N gave 51.81, 5.08 and 20.22 for the respective elements.

It is clearly observed that there were no surfactant present in the samples as depicted in Table (5-2). It is inferred from Table 5-3 that the composition in copolymers is almost equivalent to feed composition.

Table 5-2; Elemental Analysis for the Copolymers of Acrylamide.

Sample ID	% C	% H	% N	% S	% O
P, Poly(AM-r-ST)	48.9	7.8	18.0	ND*	26.1
P4, Poly(AM-b-ST)	47.4	7.9	16.7	ND	28.1
P6, Poly(AM-b-ST)	49.4	7.8	16.3	ND	26.1
P12, Poly(AM-b-ST)	51.1	7.7	15.6	ND	25.1
E1, Poly(AM)	43.6	7.3	16.4	ND	28.5
E4, Poly(AM-b-C12)	44.2	7.4	15.3	ND	26.5

* ND: not detected

Table 5-3; Co-polymer Compositions (mol %) from Elemental Analysis for Multi-block (Co)polymers and A Random Copolymer

Sample code	Structure	Y/X %	X %
P4	Poly(AM-b-ST)	12.24	89.09
P6	Poly(AM-b-ST)	14.22	87.55
P12	Poly(AM-b-ST)	17.92	84.80
E1	Homo-Poly(AM)	8.487	92.17
E4	Poly(AM-b-C12)	12.13	89.18
P	Poly(AM-R-ST)	6.43	93.96

X % ; represents PAM
Y % ; stands for either PST or PC12
From Y/X %; $X\ \% = (1 + Y/X)^{-1}$

Table 5-4; Reduced Viscosity* (dl/gm) for Nonionic Multi-block copolymer Solutions in Deionized Water and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt % at 25°C and $\gamma' = 0.3\ s^{-1}$

Sample code	Polymer Structure	η_{red}, (dl/g) at 0.01 wt %	η_{red}, (dl/g) at 0.05 wt %	η_{red}, (dl/g) at 0.1 wt %	η_{red}, (dl/g) at 0.5 wt %	η_{red}, (dl/g) at 1.0 wt %	η_{red}, (dl/g) at 1.5 wt %	η_{red}, (dl/g) at 2.0 wt %
P10'	Poly(AM- b -ST)	11900	2580	1390	342	190	153	269
P11	Poly(AM- b -ST)	3950	1180	791	198	209	221	144
P12	Poly(AM- b -ST)	6920	2190	1980	820	720	1066	4574
P13	Poly(AM- b -ST)	2910	886	595	178	199	1333	4509
P15	Poly(AM- b -ST)	4950	1580	1490	338	179	133	134
P4	Poly(AM- b -ST)	4950	1590	1190	378	209	173	149
P5	Poly(AM- b -ST)	12900	3780	1990	458	250	336	1004
P6	Poly(AM- b -ST)	2750	1196	990	298	189	153	139
P7	Poly(AM- b -ST)	12900	2980	1690	358	189	166	177
E1	Poly(AM)	1410	584	491	119	89.1	79.3	74.5
E2	Poly(AM- b -C12)	9900	2180	1190	278	420	333	309
E3	Poly(AM- b -C12)	44900	9780	5490	1160	650	520	430
E4	Poly(AM- b -C12)	5910	1764	953	218	159	139	199

* η_{red} = reduced viscosity = $(\eta-\eta_s) / (\eta_s \times C)$
η_s = solvent viscosity (water) = 1.0 cps. at 20°C.

5.3.2 Molecular Weight Determination

The polymer solution viscosity of the copolymers were determined in an aqueous solution using Brookfield viscometer at 25°C. The measurements were discussed in detail in Chapter (3). Direct viscosity measurements can not be used to determine molecular weights in samples exhibiting composition and structure polydispersity. However, for block copolymers of definite structure and homogenous composition, the Mark-Houwink-Sakurada (MHS) relationship between intrinsic viscosity [η] and molecular weight is applicable. The intrinsic viscosity was derived from the reduced viscosity of Figure 5-10 and 5-11 and the results are shown in Table (5-4). From the intrinsic viscosity, the molecular weight of the block copolymers can be calculated assuming that the hydrophoically-modified polymers behave according to MHS equation with the exponent, a, and coefficient, K, that is used for homopolymer, polyacrylamide, and would exhibit close behavior, since the hydrophobes are small. Parameters, a and K, governing the relation between [η] and MW, i.e. $[\eta] = K \times (MW)^a$ are considered to be 0.75 and 9.33×10^{-3} respectively [119,7]. The estimated molecular weights of the copolymers are summarized in Table 5-21.

5.4 Copolymer Solution Behaviors in Aqueous Media

5.4.1 Rheological/Viscosity Behavior of the Copolymer Solutions

a. Effect of Shear Rate and Concentration:

Tables 5-5 to 5-18 in Appendix A and Figures 5.2 to 5.9 show the variation of viscosity as a function of shear rate at different polymer concentration. For the all polymers considered, an almost shear rate independent in viscosity is observed when the shear rate is high, i.e. 15.8 to 79.2 S^{-1}, as depicted in Figures (5-4, 5-.6, and 5-8). Samples P10' and P4 prepared using 3 mol % ST exhibit similar thickening ability. However, the random copolymer prepared using 3 mol % ST shows a decrease in viscosity. Samples P12 and P13 prepared using 7 mol % ST exhibit close thickening ability. But sample P6 behaves differently. Generally, the flow curves indicate that as shear rate increases, the solution viscosity slightly decreases which is a case of shear-thinning effect but the situation is different at low shear rates where there exist a strong shear-thinning behavior, since the physical interchain associations are disrupted upon shearing, an advantage to polymer flooding operations at the start where the shearing is high during injection but not afterwards. The solution shear viscosity of the polymers considered, however, is restored when the shearing force is removed. It should be noted that the viscosity falls rapidly under low shearing values but then it levels off indicating shear-thinning behavior for most of the samples.

Furthermore, all the copolymers (cf. Appendix A) show an increase in viscosity as the polymer concentration increases from 0.01 wt % to 0.1 wt % and 0.5 wt % to 2.0 wt %. Three polymers (cf. Table 5-6, 5-10, and 5-17) considered to exhibit good behavior (samples P12, P13, and E3) than others. At 2.0 wt % (20,000 PPM or 20,000 mg/l) polymer concentration, The polymer, P12, exhibits the highest response in solution viscosity, 9150 cps., at 0.4 (1/s) among the other polymers due to strong intermolecular hydrophobic association into multimolecular micelles that increases the HDV of the coil. PAM homopolymer, however, does not show enhancement in viscosity at high shear rate. It is readily observed that the degree of association were lower in the case of the random copolymer, sample P.

As expected the behavior of such polymers in deionized water (no other additives were added at this point) which is a solvent selective for one of the blocks is significantly worth investigating since these polymers when dissolved in water behave as high molecular weight species. At critical polymer concentration they start to rearrange their single chains in such away that they associate or aggregate hydrophobically (Figure 5-1) to minimize their exposure to water by forming regular micelles of nonpolar dense core and polar, diffuse outer shell (coronas) formed from the soluble blocks. Micelles can have different forms, spherical or rodlike shapes. The latter would be characteristics of high solution viscosity.

The low viscosity in E4 copolymer compared to others is mainly attributed to an increase in intra-molecular aggregation over inter-molecular aggregation keeping the hydrodynamic radius small. However, P11 polymer exhibits higher intra-molecular association due to the hydrophobic effect, i.e., high contents of insoluble groups preclude intermolecular association. It should be noted that generally high viscosities and pseudoplastic behaviors are observed for these nonionic multiblock copolymers in deionized water.

It should be noted here that the polymer solution viscosity falls rapidly under low shearing values but then it levels off indicating shear-thinning behavior for most of the samples. Also the complete breaking up of the hydrophobic interactions is a slow process. Actually, it takes several hours. Moreover, the psuedoplastic behavior increases with increasing polymer concentration. Therefore, these properties of hydrophobically associating polymers give rise to important technological applications.

Table 5-6: The Viscosity-Shear Rate Relationship for Multi-block Copolymers of PolyAM-block-PolyST, P13, for Specified Polymer Concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt %, in Cps	η_a of 1.5 wt %, in Cps	η_a of 1.0 wt %, in Cps	η_a of 0.5 wt %, in Cps
0.3	0.4	9020	2000	200	90.2
0.6	0.8	3200	485	110	30
1.5	2.0	910	86.2	50.2	10
3.0	4.0	183	67.1	21.0	6.0
6.0	7.9	150	60.8	15.5	4.51
12	15.8	138	53.2	11.5	2.76
30	39.6	96	44.4	8.32	2.40
60	79.2	50	43.0	5.31	2.35

Table 5-10: The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P12 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt %, in Cps	η_a of 1.5 wt %, in Cps	η_a of 1.0 wt %, in Cps	η_a of 0.5 wt %, in Cps
0.3	0.4	9150	1600	721	411
0.6	0.8	4830	782	361	195
1.5	2.0	1970	391	146	56.1
3.0	4.0	1280	151	58.1	27.0
6.0	7.9	515	91.0	36.1	19.0
12	15.8	237	57.0	22.0	15.3
30	39.6	96.5	38.0	11.1	10.5
60	79.2	48.4	20.0	9.01	8.32

Table 5-17: The viscosity-shear rate relationship for a multiblock copolymer of polyAM-block-polyST or (sample E3) for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	862	781	651	581	550	490	450
0.6	0.8	321	250	230	210	195	175	115
1.5	2.0	112	92.1	73.8	60.2	55.1	50.1	44.6
3.0	4.0	86.2	58.2	38.1	29.1	25.0	19.0	12.0
6.0	7.9	39.4	36.1	28.1	20.5	18.0	15.5	10.1
12	15.8	27.1	18.2	13.0	10.8	8.20	7.77	6.01
30	39.6	21.7	11.8	8.68	7.51	6.91	4.61	4.21
60	79.2	20.5	9.17	6.46	4.01	3.67	2.76	1.85

η_a, Apparent viscosity ; RPM, Revolution Per Minute.

b. Intrinsic Solution Viscosity of the Copolymers:

The results of intrinsic viscosity are summarized in Table 5-21. Intrinsic viscosity was determined by using Kraemer equation and the inherent viscosity of the samples in the dilute regime.

Table 5-4; Reduced Viscosity* (dl/gm) for Nonionic Multi-block copolymer Solutions in Deionized Water and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt % at 25°C and $\gamma' = 0.3\ s^{-1}$

Sample code	Polymer Structure	η_{red}, (dl/g) at 0.01 wt %	η_{red}, (dl/g) at 0.05 wt %	η_{red}, (dl/g) at 0.1 wt %	η_{red}, (dl/g) at 0.5 wt %	η_{red}, (dl/g) at 1.0 wt %	η_{red}, (dl/g) at 1.5 wt %	η_{red}, (dl/g) at 2.0 wt %
P10'	Poly(AM- b -ST)	11900	2580	1390	342	190	153	269
P11	Poly(AM- b -ST)	3950	1180	791	198	209	221	144
P12	Poly(AM- b -ST)	6920	2190	1980	820	720	1066	4574
P13	Poly(AM- b -ST)	2910	886	595	178	199	1333	4509
P15	Poly(AM- b -ST)	4950	1580	1490	338	179	133	134
P4	Poly(AM- b -ST)	4950	1590	1190	378	209	173	149
P5	Poly(AM- b -ST)	12900	3780	1990	458	250	336	1004
P6	Poly(AM- b -ST)	2750	1196	990	298	189	153	139
P7	Poly(AM- b -ST)	12900	2980	1690	358	189	166	177
E1	Poly(AM)	1410	584	491	119	89.1	79.3	74.5
E2	Poly(AM- b -C12)	9900	2180	1190	278	420	333	309
E3	Poly(AM- b -C12)	44900	9780	5490	1160	650	520	430
E4	Poly(AM- b -C12)	5910	1764	953	218	159	139	199

* η_{red} = reduced viscosity = $(\eta-\eta_s)/(\eta_s \times C)$

η_s = solvent viscosity (water) = 1.0 cps. at 20°C.

The results indicate that Kraemer's relation found to be more convenient to such data than Huggin's equation.

Table 5-20; Inherent Viscosity$^{\$}$ (dl/gm) for Multiblock Copolymer Solutions as a Function of Concentration(0.01 to 0.5 wt %) in Deionized water at 25°C and $\gamma' = 0.3\ s^{-1}$.

Sample code	Polymer Structure	η_{inh}, (dl/g) at 0.01 wt %	η_{inh}, (dl/g) at 0.05 wt %	η_{inh}, (dl/g) at 0.1 wt %	η_{inh}, (dl/g) at 0.5 wt %	η_{inh}, (dl/g) at 1.0 wt %	η_{inh}, (dl/g) at 1.5 wt %	η_{inh}, (dl/g) at 2.0 wt %
P10'	Poly(AM- b -ST)	479	97.0	49	10.4	5.2	3.6	3.1
P11	Poly(AM- b -ST)	370	81.8	44	9.2	5.3	3.9	2.8
P12	Poly(AM- b -ST)	425	92.0	54	12.0	6.6	4.9	4.6
P13	Poly(AM- b -ST)	340	76.3	41	9.0	5.3	5.1	4.5
P15	Poly(AM- b -ST)	392	87.6	50	10.3	5.2	3.5	2.7
P4	Poly(AM- b -ST)	391	87.7	48	10.5	5.3	3.7	2.8
P5	Poly(AM- b -ST)	487	105	53	11.2	5.5	4.1	3.8
P6	Poly(AM- b -ST)	335	82.1	46	10.1	5.2	3.6	2.8
P7	Poly(AM- b -ST)	487	100	51	10.2	5.2	3.7	2.9
E1	Poly(AM)	271	68.1	39	8.2	4.5	3.2	2.5
E2	Poly(AM- b -C12)	460	94.0	48	9.8	6.0	4.1	3.2
E3	Poly(AM- b -C12)	610	124	63	12.7	6.5	4.4	3.4
E4	Poly(AM- b -C12)	409	89.8	46	9.4	5.1	3.6	2.9

\$ η_{inh} = inherent viscosity = $[\ln(\eta/\eta_s)]/C$, where C = polymer concentration.
η_s = solvent viscosity (water) = 1.0 cps. at 20°C.

Using Kraemer equation (eq. 5.1) and making linear regression analysis to the data$^{\&}$ in (Table 5-20), the following results are obtained (cf. Table 5-21).

Kraemer equation: $$\frac{\ln(\eta/\eta_s)}{C} = [\eta] - k'' * [\eta]^2 * C \qquad (5.1)$$

Where k", Kraemer coefficient and

$[\eta]$, the intercept, and

$-k'' * [\eta]^2$ the slope.

Then the molecular weight is estimated using MHS relation.

Table 5-21; Kraemer's and MHS's Parameters ([η], k", and Mw) for Copolymers in the Dilute Solution Regime.

Polymer Structure	Polymer code	[η]^&^, dl/g	k", x10^3	Mw^$^, x10^-5
Poly(AM- b -ST)	P10'	2.16	5.6	6.59
Poly(AM- b -ST)	P11	1.97	11.1	5.83
Poly(AM- b -ST)	P12	2.27	9.58	7.05
Poly(AM- b -ST)	P13	1.82	12.0	5.25
Poly(AM- b -ST)	P15	2.11	10.3	6.39
Poly(AM- b -ST)	P4	2.10	10.4	6.35
Poly(AM- b -ST)	P5	2.57	8.6	8.32
Poly(AM- b -ST)	P6	1.83	11.8	5.29
Poly(AM- b -ST)	P7	2.55	8.7	8.23
Poly(AM)	E1*	1.50	14.0	4.05
Poly(AM- b -C12)	E2	2.40	9.2	7.60
Poly(AM- b -C12)	E3	3.19	6.9	11.1
Poly(AM- b -C12)	E4	2.17	10.1	6.64

* Sample E1 is a homopolyacrylamide.
$ Estimated molecular weight.
& Only dilute regime is considered, 0.01 wt % to 0.5 wt %.

- **Calculation of the Molecular Weights from Intrinsic Viscosities:**

The apparent *Molecular Weight* (MW) of the copolymers are estimated from the following relationship for acrylamide since the hydrophobe content is generally low in all synthesis. The intrinsic viscosities in Table 5-21 and Figure 5-11 were used. So the MWs are calculated as follows,

$$[\eta]/\mathrm{dl/g} = 9.33\mathrm{x}10^{-3}\ \mathrm{MW}^{0.75} \qquad (5.2)$$

For (sample P10'); since $[\eta] = 9.33\mathrm{x}10^{-3}\ \mathrm{MW}^{0.75}$ and
$[\eta] = 2.16$ dl/g,
hence, MW = $6.59\mathrm{x}10^{5}$

Similarly, other copolymers were characterized. Table 5-21 summarized MW determinations.

c. Effect of Temperature:

Tables 5-22 and 5-.23 show the effect of temperature on the solution viscosity of the copolymers (Samples P12 and E3). As it is the case for many polymer solutions of this type, a decrease in viscosity with increasing temperature is observed. All the copolymers examined experience a decrease in hydrodynamic radius on heating and that is mainly due to chain dehydration. Lowest and highest shear rates, conducted by the viscometer, were chosen in studying the temperature-shear rate-viscosity relationship. It is evident from results that the block copolymers maintain some of their thickening ability at high temperatures, > 90 °C. Such temperatures are usually encountered during injection into oil reservoirs. It was readily observed that the polymers maintain their viscosity after some time of heating especially those samples that show high degree of intermolecular hydrophobic association. Figures 5-41 and 5-42 show the behavior of the polymers.

Table 5-22, The Viscosity-Temperature-Shear Rate Relationship for the Copolymer of Poly(AM-block-ST), P12, for Polymer Concentration of 2 wt % at Lowest and Highest Shearing Rates.

Shear rate, S^{-1}	η_a, in Cps, at 25 °C.	η_a, in Cps, at 45 °C.	η_a, in Cps, at 75 °C.	η_a, in Cps, at 95 °C.
0.4	9150	8750	8100	6200
79.2	48.2	45.1	40.0	34.3

η_a apparent viscosity.

Table 5-23: The Viscosity-Temperature-Shear Rate Relationship for the Copolymer of Poly(AM-block-C12), E3, for Polymer Concentration of 2 wt % at Lowest and Highest Shearing Rates.

Shear rate, S^{-1}	η_a, in Cps, at 25 °C.	η_a, in Cps, at 45 °C.	η_a, in Cps, at 75 °C.	η_a, in Cps, at 95 °C.
0.4	862	832	795	710
79.2	20.5	18.7	17.4	16.8

η_a apparent viscosity.

d. ***Effect of Sodium Chloride (NaCl):***

The effect of salt on the viscosity of the polymer solutions was investigated using P11, P7, P12, E2, E3, and E4 block copolymers and the homopolymer, E1, and the random copolymer, P, (cf. Table 5-24). The behavior was investigated in the range of salt content of 1.0 to 10.0 wt %. The viscosity of the block copolymer solutions increased with increasing salt concentration, supporting their nonionic nature. Therefore the copolymers exhibit salt tolerancy beyond 10 wt % salt (NaCl), a good behavior for EOR application. In contrast the viscosity of the homopolyacrylamide solution was essentially invariant with changing in the ionic strength (NaCl). While for the random copolymer synthesized by homogenous process (sample P), the increase was not significant (cf. Figure 5-16 and 5-17). Samples P12, E3, and P11 exhibit viscosity enhancement in the presence of salt (1.0 to 10 wt % NaCl) much better than other copolymers (cf. Table 5-24) and (Figures 5-12 to 5-20). The results suggest that intermolecular hydrophobic association is enhanced upon by the addition of salt, such interaction is responsible for the high thickening property.

From viscometeric results it is clear that the thickening ability of amphiphilic block copolymers prepared by the micellar process is directly related to the initial micelle concentration used during the synthesis, i.e., feed ratio of surfactant to hydrophobe. Thus, the viscosity increases upon decreasing the initial surfactant concentration and that is attributed to higher number of hydrophobes solubilized in a micelle.

Furthermore, the viscosifing properties strongly depend on the amount of added salt to the solution mixture which causes an increase in the aggregation number of micelles. So, as expected, the addition of salt gives rise to copolymers with higher thickening properties as depicted from Table (5-24) where the copolymers considered are all of nonionic nature. The results summarized in Table 5-24 show that sample P12 exhibits a higher degree of intermolecular hydrophobic interactions attributed to an increase in the aggregation number by addition of salt. It is explained by maintaining high hydrodynamic volume upon increasing the number of micelles. Such behavior is a consequence of longer hydrophobic blocks attained by varying the hydrophobic content in the synthesis. A similar effect observed by; Hill, Candau, and Selb [8], and Srauss et al. for polysoaps in 1956. Other investigators reported the same behavior for different amphiphilic copolymers [4,92,96].

e. *Effect of Adding Surfactant (SDS):*

It was observed that the redissolution in water of the copolymers synthesized by the micellar process and recovered by precipitation in methanol was greatly facilitated by the addition of surfactant (SDS) which clearly demonstrates the existence of surfactant-polymer interactions. Adding surfactant to the polymer solutions, as expected, increases water solubility of the samples; particularly for those sample that show turbidity, which explains the polymer-surfactant interactions.

But the polymers lost a considerable degree of their viscosification efficiency. In such a case, more polymer hydrophobic moieties would be soluibilized inside the surfactant micelles which result in high soluibilization capacity. Generally, the addition of surfactants gives rise of dramatic reduction in polymer solution viscosity which makes the polymers less effective as thickeners. Therefore, mixing polymers with surfactants is not an appropriate way in applications that require enhancements in solution viscosity by polymers. All the polymers synthesized in this study show, with various degrees, negative results with respect to their properties when SDS is added to their polymer solutions making them less viscous and highly water-soluble. Increased water solubility results from increased segmental dehydration and increased free energy of mixing. So for enhanced oil recovery applications, such polymers should not be mixed with surfactants during operations.

f. Effect of Storage Time on Samples:

Storage instability (aging) is an important consideration for the quality of polymer solutions. Polymer solutions were kept in an ambient temperature for long time from the initial time of mixing to investigate any changes to the solution viscosity as time goes on. The results in Table 5-19 shows the behavior of the block copolymer solution as a function of shear rate after *10 months* of the initial mixing. The behavior of block copolymer solution (sample P15) does not change very much, only small percentage of loss in viscosity is experienced due to storage time. It is much more likely that the drop in solution viscosity with time storage is related to the disruption of some supermolecular aggregates that exists as a result of chin entanglements. Freezing the samples, however, could prevent aging.

5.5 Surface/Interfacial Activity of Amphiphilic Block Copolymer Solutions

Copolymer solution properties have also been examined by conducting measurements of the surface (air/liquid) tensions and interfacial (polymer solution/n-decane) tensions at different polymer concentrations; 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 wt %. The measurements were carried out at room temperature regulated at 25 °C. The surface tension was measured using a platinum plate method of plate-ring tensiometer where the plate was suspended from an electrobalance into the sample solution in a glass container with known geometry. While the IFT measurements were conducted using the ring method. The detailed description of the procedures is given in chapter 3. Furthermore, different NaCl concentrations ranging from 1.0 to 10 wt % were taken and then mixed with polymer solutions making desired concentrations where the surface tension of the brine solutions was then determined at 25 °C.

5.5.1 Surface Activity of the Copolymer Solutions

The results of the surface tension measurements as a function of salt concentration are summarized in Table 5-25 and demonstrated in Figures (5-21 to 5-23) which show the effects of salt concentration on the surface tension of copolymers; P7, P11, E3, and E4. As depicted in Table 5-25 for all copolymers, a decrease in surface tension is observed with increasing salt concentration over the whole range and that is due to more micellization. E3 copolymer shows more surface activity than the others. As the polymer concentration increases, the surface tension decreases because of the extent of adsorption of more molecules at the air-aqueous polymer solution interface as observed by other authors [116]. The results of the surface tension measurements as a function of polymer concentration are summarized in Table 5-24 and demonstrated in Figures (5-26 to 5-30). The increase in adsorption is attributed to the reorientation of the amphiphilic structure of the polymer and consequently that causes reduction in the surface tension [117]. The samples, P, P10', and P4 prepared using 3 mol % ST exhibit close surface activity. Generally the polymers reduce the surface tension of water to an extent. The more concentrated the solution, the stronger the effect.

The effect of adding salt to the polymer solution also affects the surface tension of the polymer solution. As depicted from Table 5-25 and demonstrated in Figures 5-21 to 5-23, the surface activity is more pronounced in sample P12 than others. The block copolymer P12 at 1.5 wt % exhibits the highest activity at 10 wt % salt (NaCl). Samples P7, P11 and P did not show close activity that is not strong. Homopolyacrylamide exhibits higher activity than the random copolymer at different salt content as depicted from Figure (5-23).

Comparisons are established as shown in Figures 5-21 and 5-22 to distinguish the effect of salt on the copolymer solutions. Samples E3 and E4 were considered to be the best candidates for lowering the surface tension of the brine solution. The reduction in surface tension is attributed to the surface equilibrium in reorientation process of hydrophobic moieties and additional adsorption from the bulk phase to the interface. As the adsorption increases, the surface tension decreases. With respect to enhanced oil recovery operations (EOR), the interfacial tension would be much more less than the surfaces tension.

Table 5-24; Surface Tensions (in mN/m) of Nonionic Multi-block Copolymers at 25°C and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt %.

Sample code	Structure	at 0.01 (wt %)	at 0.05 (wt %)	at 0.1 (wt %)	at 0.5 (wt %)	at 1.0 (wt %)	at 1.5 (wt %)	at 2.0 (wt %)
P10'*	Poly(AM-b--ST)	67.69	60.86	57.09	56.05	54.39	53.71	53.57
P11	Poly(AM- b--ST)	70.88	66.38	65.59	44.82	48.30	47.93	47.59
P12	Poly(AM- b--ST)	69.58	66.87	55.33	49.20	44.10	48.52	37.44
P13	Poly(AM- b--ST)	71.47	69.80	65.37	56.70	55.06	65.93	52.61
P15	Poly(AM- b--ST)	71.85	68.31	63.93	51.04	53.25	52.96	57.88
P4*	Poly(AM- b--ST)	65.72	59.85	59.50	85.20	57.58	57.12	56.89
P5*	Poly(AM- b--ST)	72.20	71.76	71.60	49.82	50.83	56.02	61.30
P6	Poly(AM- b--ST)	65.43	55.66	5020	54.01	55.17	55.53	57.91
P7*	Poly(AM- b--ST)	60.16	58.23	56.99	55.58	53.57	50.39	45.29
E1*	Poly(AM)	61.20	61.02	55.05	43.80	42.76	42.10	40.10
E2*	Poly(AM- b--C12)	60.32	53.24	51.69	40.04	39.54	35.60	32.33
E3	Poly(AM- b--C12)	50.68	52.95	48.18	47.41	39.02	37.21	34.67
E4*	Poly(AM- b--C12)	60.82	55.05	49.96	45.39	40.25	36.38	32.11
P*	Poly(AM-R-ST)	70.25	68.19	64.60	61.45	61.43	59.83	52.36

* A stock solution of 2 wt % of each sample was used to make the solutions by dilution, other solutions were prepared individually.

5.5.2 Interfacial Activity of the Copolymer Solutions

The interfacial tension (IFT) measurements between the polymer aqueous solution and n-decane (oil phase) are conducted using the ring method of the KRUSS tensiometer at 25°C.

Interfacial tension (IFT) measurements have been performed for those polymer solutions that exhibit high surface activity and at the same time maintain high viscosity at high salt tolerancy, samples P12 and E3. The multiblock copolymer, E3, exhibits the highest interfacial activity among the other polymers. At 10 wt % salt (NaCl) content, the IFT of the polymer solution at 1.5 wt % reduced up to 0.53 mN/m. While the multiblock copolymer, P12, show IFT activity less than E3 copolymer. At 10 wt % salt (NaCl), the IFT of the polymer solution reaches 1.87 mN/m where the polymer concentration is only 1.5 wt % (15,000 PPM.). The results are summarized in Table 5-26 and demonstrated in Figures (5-24 and 5-25) at different salt content and two polymer concentrations (0.5 wt % and 1.5 wt %).

The reduction in Interfacial tension (IFT) is ascribed to the extent of adsorption of the amphiphilic molecules at the interface. The IFT activity depends on the temperature, pressure drop, and concentration among many things as explained earlier in chapter 1. It is also known that in the case of ionic surfactants an increase in the ionic strength by addition of salt causes an increase in the aggregation number of micelles and that leads to an increase in the surface and/or interfacial activity. As a result to such behavior, a concomitant increase in the length of the hydrophobic blocks is expected. Indeed it was found that nonionic copolymers exhibit an increase in the viscosification efficiency (ratio of solution viscosity to polymer concentration) in these cases [131-137]. These results are illustrated by the curves of Figures 5-21 to 5-25.

Table 5-26: The Effect of NaCl Concentration on the IFT of Aqueous Solutions of Nonionic Multi-block Copolymers (P12 and E3) at 25°C.

NaCl conc., wt %	IFT, (mN/m) of Copolymer Sample P12, at Poly. Conc. of 0.5 wt %	IFT, (mN/m) of Copolymer Sample P12, at Poly. Conc. of 1.5 wt %	IFT, (mN/m) of Copolymer Sample E3, at Poly. Conc. of 0.5 wt %	IFT, (mN/m) of Copolymer Sample E3, at Poly. Conc. of 1.5 wt %
0.0	20.93	16.29	19.31	11.26
1.0	8.29	8.14	5.11	3.27
2.0	8.01	7.50	2.48	1.83
3.0	7.62	7.10	1.63	0.75
5.0	6.37	5.53	1.51	0.70
6.0	5.98	4.32	1.37	0.68
7.0	5.46	3.88	1.20	0.60
9.0	3.75	1.14	0.95	0.56
10.0	3.21	1.01	0.86	0.53

P12 ; poly(AM-b-ST)
E3 ; poly(AM-b-C12)

5.6 Discussions and Conclusions

An attempt has been made to synthesis series of multiblock copolymers exclusively using micellar copolymerization technique. Homogenous copolymerization using a cosolvent produced random copolymer characterized by exhibiting lower thickening ability in solution. In the micellar process, hydrophobes (ST and C12) were used to induce aggregation and they were incorporated into the main chain of the acrylamide in the form of blocks as poly(AM-b-ST) and poly(AM-b-C12) respectively. Block copolymers showed high foaming characteristics when dissolved in water which supports the blocky structure and amphiphilic nature of the copolymers.

Micellization differences were studied by varying the amount of SDS or CTAB in the synthesis. In general, the cmc of amphiphiles decreases as the number of carbon atoms (C) in the hydrophobic group increases, up to about 16 C atoms. It has also been observed that cmc of amphiphilic block copolymers is much lower than cmc of small amphiphiles. Furthermore, it has been observed that ionic surfactants (SDS or CTAB) have much higher cmc's than nonionic surfactants containing equivalent hydrophobic groups. Therefore, it is expected in this synthesis that an interaction in persulfate anion and ionic groups in surfactants would induce favorable results. Also, surfactants containing more than one hydrophilic group in the molecule show higher cmc's than those with only one hydrophilic group and the same hydrophobic group. Values of cmc in aqueous solutions also reflect the degree of binding of the counterion (geginion) causes a decrease in the cmc of the surfactant [131-137].

The structure of the hydrophilic blocks (ionic vs nonionic) affect the conformation of the chains and thereby the surface activity, which depends on how densely the amphiphilic polymer molecules are packed and aligned at the air/water surface. A similar behavior for a polymer/oil interface. Strong foaming ability was realized in all the polymers.

The viscosity and surface activity behavior summarized in Table 5-24 suggest that it is possible to substantially lower the concentration-cost ratio of the amphiphilic block copolymer, injected in the polymer flooding process of enhanced oil recovery, and yet maintain a reasonable solution viscosity of the displacing fluid and mobility ratio with the oil. The displacement efficiency during flooding is enhanced when the displacing fluid (aqueous polymer solution) exhibits lower interfacial tension between the polymer solution and the oil.

From the study, it is concluded that sample P12 exhibits the highest surface activity among the other copolymers. While the IFT activity was most demonstrated by the copolymer E3. Homopolyacrylamide, E1, prepared by the same conditions of poly(AM-b-C12) copolymers, shows surface activity greater than the random copolymer prepared by homogenous copolymerization. It was found from this study that the multi-block copolymer poly(AM-b-ST), sample P12, exhibits the best solution behavior in favor of EOR operations. It shows the highest viscosity (10110 cps.) at the highest salt content (10 wt %) and at concentration of 1.5 wt %. In addition the IFT of the copolymer, sample P12, is 1.01 mN/m at 1.5 wt %. The results are summarized in (Table 5-25 and 5-26) and Table 5-27 in Appindix B. Many other sample have synthesized but because of their insuitability to the objectives, they were discarded. Polymers that produced gels are discarded, since gels would affect the quality of the polymer solution and adsorb on rock surfaces bringing down the displacement efficiency of the flooding operations in oil fields. Nevertheless, gels are used to lower down the permeability of reservoir rocks in different areas of research.

Table 5-1; Copolymerization Conditions in the Synthesis of Multi-block Co-polymers of Poly(AM[a]-b-ST) and Poly(AM-b-C12) by Micellar technique with Variable amounts of Hydrophobe, Surfactant and Initiator at 50 °C.

Sample code	Structure	[ST][b] or {[C_{12}]}; mol %	[d][SDS] or{[CTAP]}; wt %	[$K_2S_2O_8$]; M
P5, 2ST-2SDS	Poly(AM-b-ST)	2	2	$2.76X10^{-3}$
P4, 3ST-2SDS	Poly(AM-b-ST)	3	2	$2.76X10^{-3}$
P7, 6ST-2SDS	Poly(AM-b-ST)	6	2	$2.76X10^{-3}$
P6, 7ST-3.15SDS	Poly(AM-b-ST)	7	3.15	$2.76X10^{-3}$
P15, 1ST-1CTAB	Poly(AM-b-ST)	1	{0.99}	$3.69X10^{-3}$
P10' 3ST-1.36CTAB	Poly(AM-b-ST)	3	{1.36}	$2.76X10^{-3}$
P8 3ST-1.36CTAB	Poly(AM-b-ST)	3	{1.36}	f
P11, 6ST-2.68CTAB	Poly(AM-b-ST)	6	{2.68}	$2.76X10^{-3}$
P12, 7ST-3.97CTAB3	Poly(AM-b-ST)	7	{3.97}	$2.76X10^{-3}$
P13, 7ST-3.97CTAB4	Poly(AM-b-ST)	7	{3.97}	$4.58X10^{-3}$
[e]E1, 0C12-3SDS	*HomoPoly(AM)*	{0}	3	$3.36X10^{-4}$
E2, 1C12-3SDS	Poly(AM-b-C12)	{1}	3	$3.36X10^{-4}$
E3, 2C12-3SDS	Poly(AM-b-C12)	{2}	3	$3.36X10^{-4}$
E4, 3C12-3SDS	Poly(AM-b-C12)	{3}	3	$3.36X10^{-4}$
P,[c] 3ST-200FRM	*Poly(AM-R-ST)*	3	-	$2.05X10^{-3}$

a AM: Acrylamide, FW = 71.08; ST: Styrene, FW = 104.15; C_{12}: 1-dodecene, FW = 168.32.

b Mole percent in feed = [ST]/{[ST] + [AM]}, or = [C12]/{[C12] + [AM]}.

c A Random co-polymer by Homogenous process (in 50 wt % formamide by vol. of water).

d SDS concentration in feed is based on volume of distilled water. Aggregation No. for SDS in an aqueous solution, Nagg = 60 at 50 °C. and its cmc = $9.2x10^{-3}$ M.

e For E1 to E4, $K_2S_2O_8$ at 0.3 wt % of the monomer feed is used, total monomer conc. = 3 wt %.

f Oil-soluble initiator (AIBN) is used instead ($4.39X10^3$ M).

Table 5-25 : Rheology (Viscosity vs Shear Rate) and Surface Activity of Amphiphilic Non-ionic Multi-block[a] Copolymer Solutions of 1.5 wt % in NaCl Concentrations Ranging from 1.0 wt % to 10 wt % at 25°C.

Sol. Poly. Conc., 1.5 wt %	Effects of NaCl Concentration on polymer solutions, in wt %								
NaCl Conc., wt %	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample Code: **P11** Surface Tension at 25°C vs. salt	47.93	47.51	47.22	46.98	46.51	46.34	46.21	46.01	45.89
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	332	501	811	1070	1220	1360	1470	1680	1820
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	10.8	12.0	12.7	14.1	16.0	16.7	19.2	23.4	27.2
Sample Code: **P7** Surface Tension at 25°C vs. salt	50.39	49.72	49.56	49.21	48.61	48.21	48.01	47.35	46.93
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	180	210	441	535	728	882	901	920	990
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	5.41	5.71	6.56	7.31	8.82	9.32	9.52	9.90	10.12
Sample Code: **P12** Surface Tension at 25°C vs. salt	48.52	46.40	41.21	45.81	43.10	45.01	38.81	40.11	34.18
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	1600	2510	3470	4270	6520	7430	8590	9010	10110
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	20.0	34.1	34.8	35.2	37.5	38.1	39.6	41.2	43.1
Sample Code: **E2** Surface Tension at 25°C vs. salt	35.60	28.43	27.70	27.26	26.90	25.67	25.55	23.78	23.00
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	501	550	600	642	720	780	810	890	952
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	10.6	10.7	11.1	11.5	11.7	11.9	12.2	12.5	13.2
Sample Code: **E3** Surface Tension at 25°C vs. salt	37.21	28.73	28.34	27.12	25.62	24.96	23.21	22.82	21.61
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	781	868	902	990	1062	1142	1220	1300	1380
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	9.17	10.3	11.0	11.4	12.1	12.4	13.2	14.1	14.8
Sample Code: **E4** Surface Tension at 25°C vs. salt	36.38	27.09	26.51	26.00	24.71	24.00	23.72	23.12	22.01
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	551	818	942	1010	1112	1150	1190	1210	1250
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	5.56	6.31	6.87	7.21	7.91	8.34	8.89	9.42	10.32

continued....

Ctd.Table 5-25: Rheology and Surface Activity of Amphiphilic Non-ionic Multi-block[b, c] Copolymer Solutions of 1.5 wt % in 1.0 wt % to 10 wt % NaCl at 25°C.

Sol. Poly. Conc., 1.5 wt %	Effects of NaCl Concentration on polymer solutions, in wt %								
NaCl Conc., wt %	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample: **P, Random** Surface Tension at 25°C vs. salt	59.83	50.76	50.80	52.72	51.73	53.89	50.11	45.45	47.74
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	65.1	68.2	70.5	65.5	71.0	68.5	66.2	63.2	63.9
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	7.50	7.77	8.02	8.32	9.4	8.5	8.3	7.82	7.72
Sample : **E1, PAM** Surface Tension at 25°C vs. salt	42.10	33.88	28.83	27.92	27.23	26.58	26.31	26.04	25.58
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	120	115	111	105.6	110	100.8	101	112	118
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	4.64	5.51	5.91	5.01	5.46	5.23	5.83	6.11	5.10

a : Sample codes of E2, E3, and E4 are block copolymers of AM/C12, others represent AM/ST block copolymers.

b E1 : homopolyacrylamide, PAM.

c P sample is a random copolymer, poly(AM-r-ST).

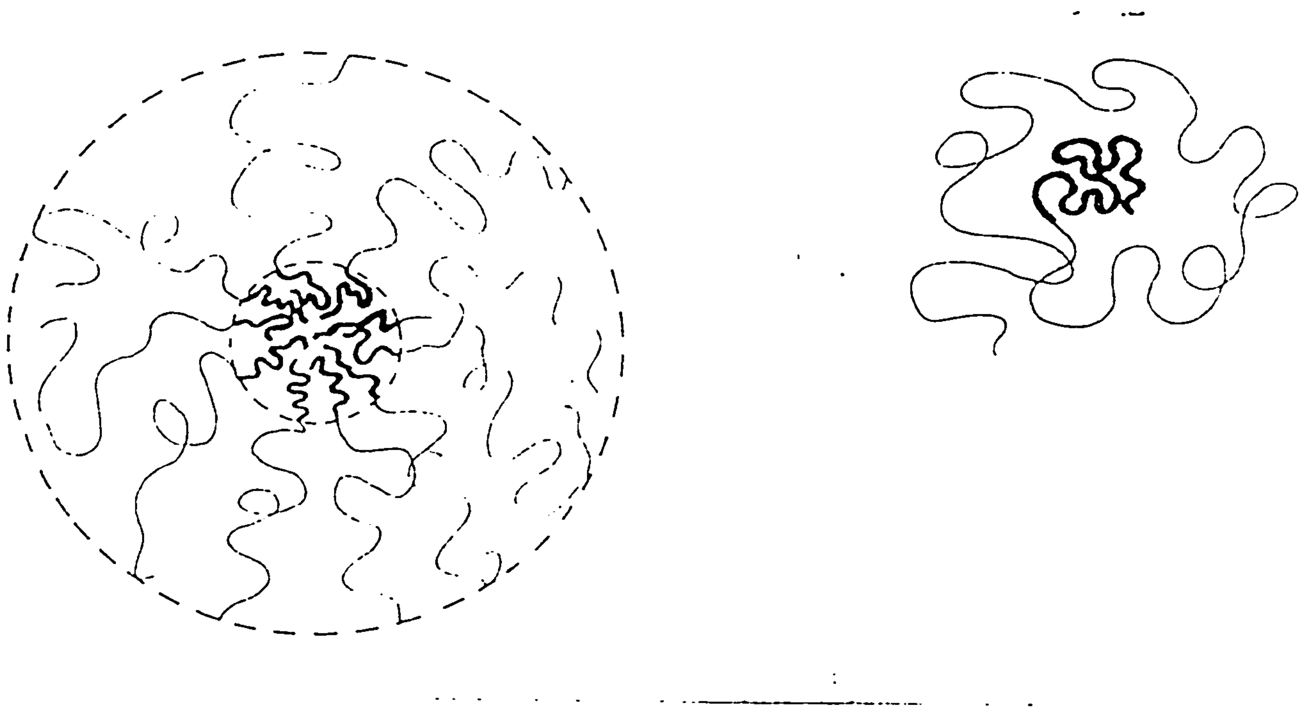


Figure 5-1; Aggregation of hydrophobically associating polymers. Micelle and rod- like micelle formation

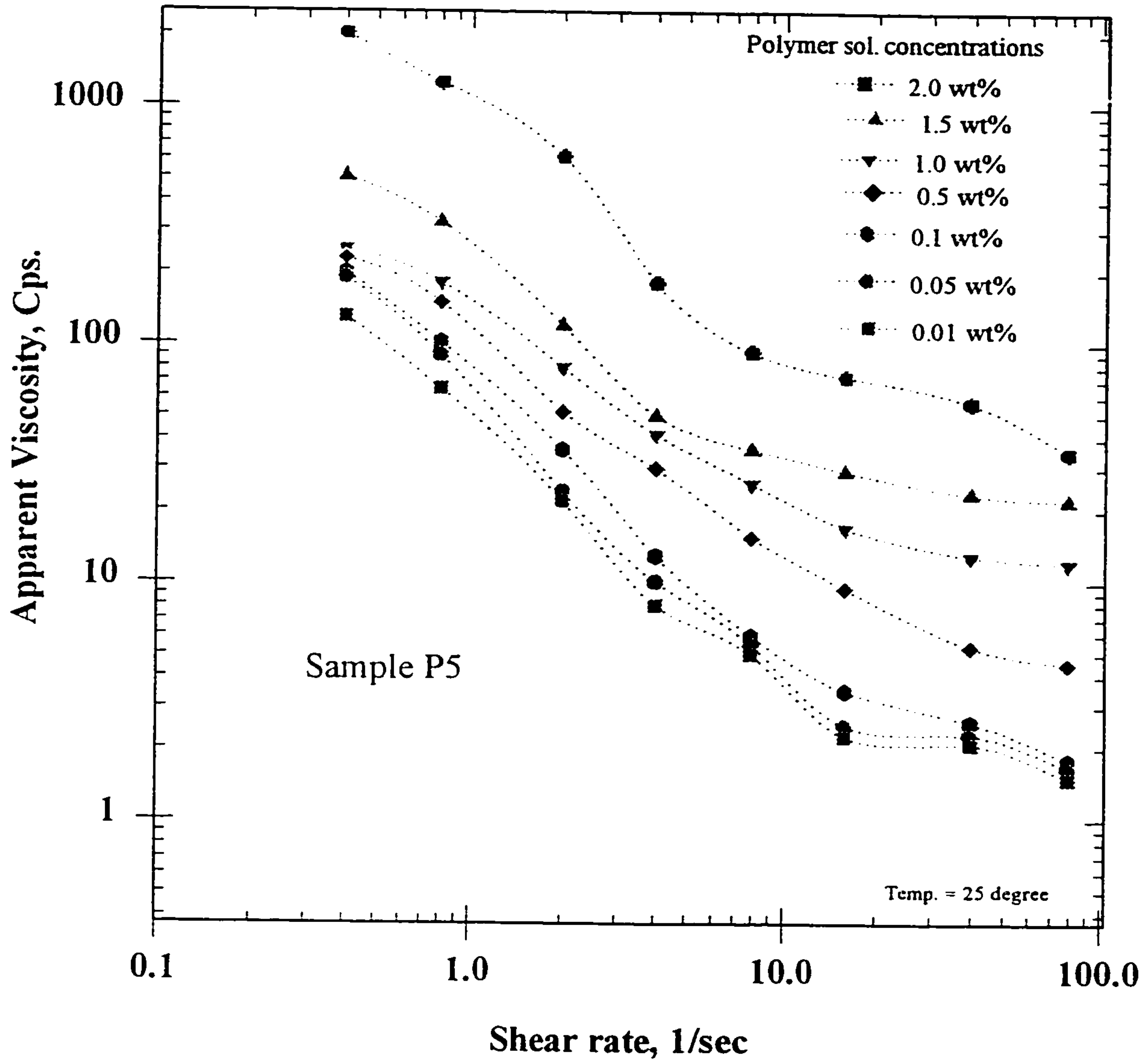


Figure 5-2; Effect of multi-block copolymer solution Poly (AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS,2 wt%), hydrophobe (ST,2 mol%) by micellar copolymerization.

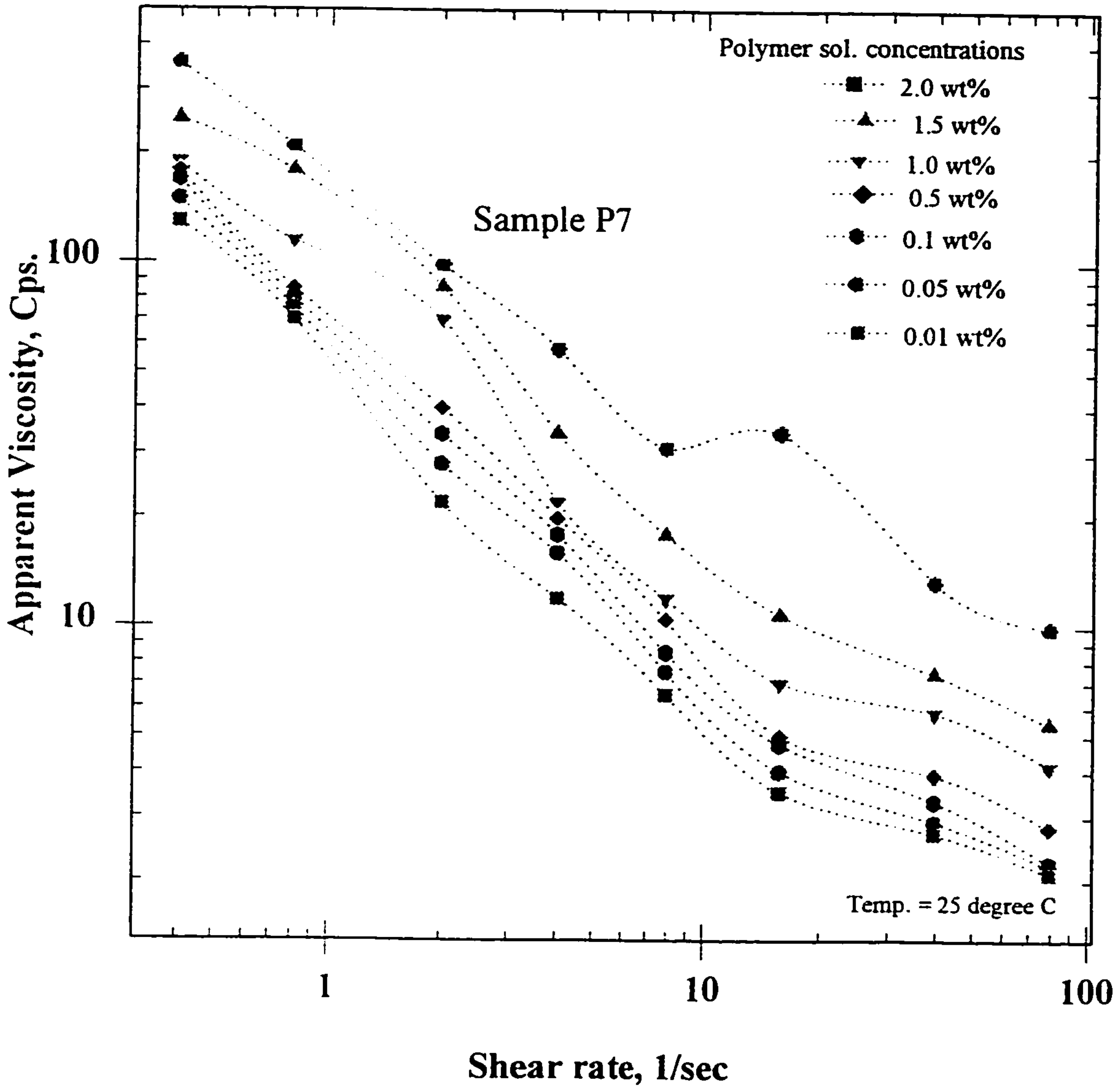


Figure 5-3; Effect of multi-block copolymer solution Poly (AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS,2 wt%), hydrophobe (ST, 6 mol%) by micellar copolymerization.

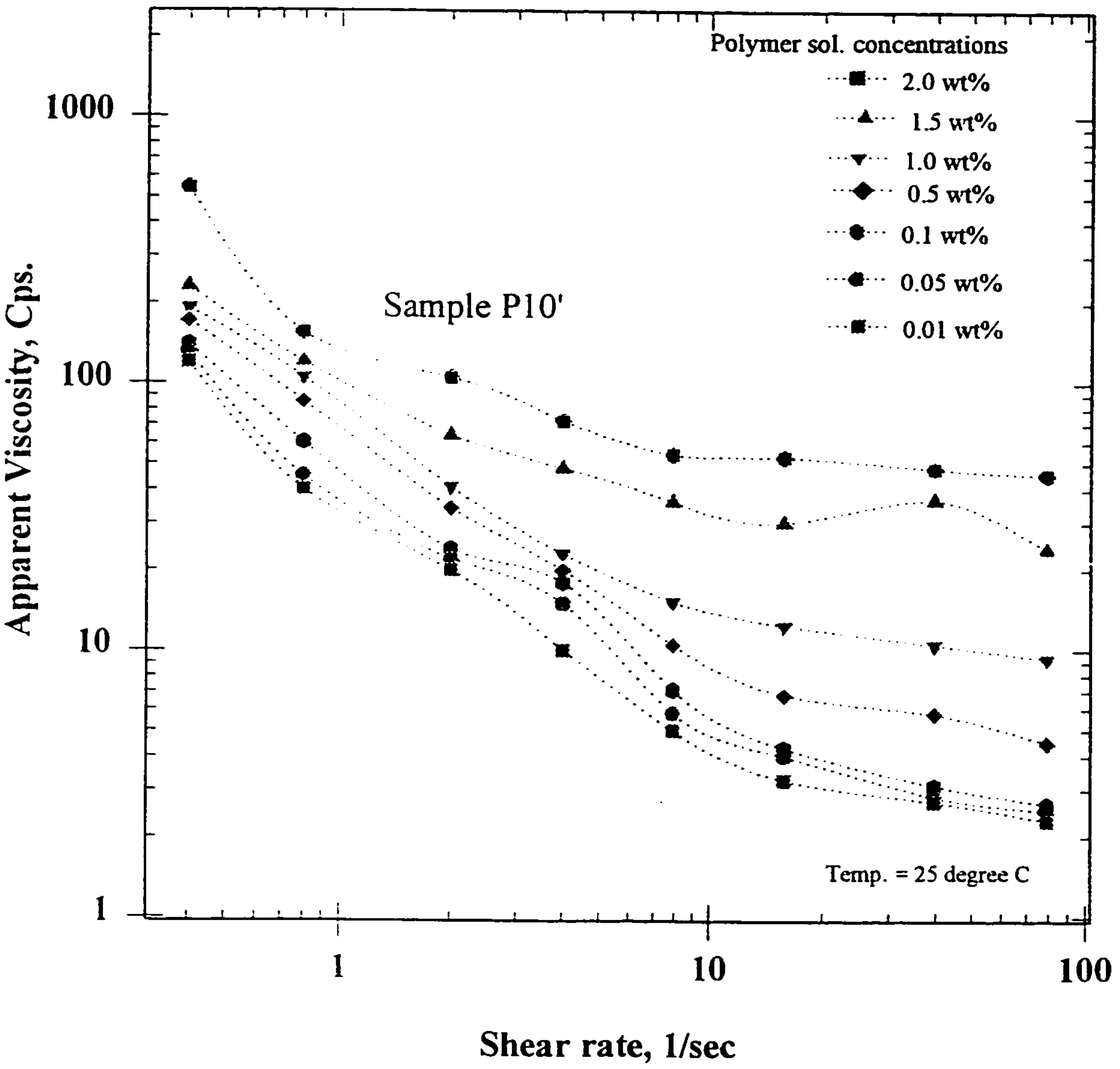


Figure 5-4; Effect of multi-block copolymer solution Poly (AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (CTAB 1.36 wt%), hydrophobe (ST, 3 mol%), by micellar copolymerization.

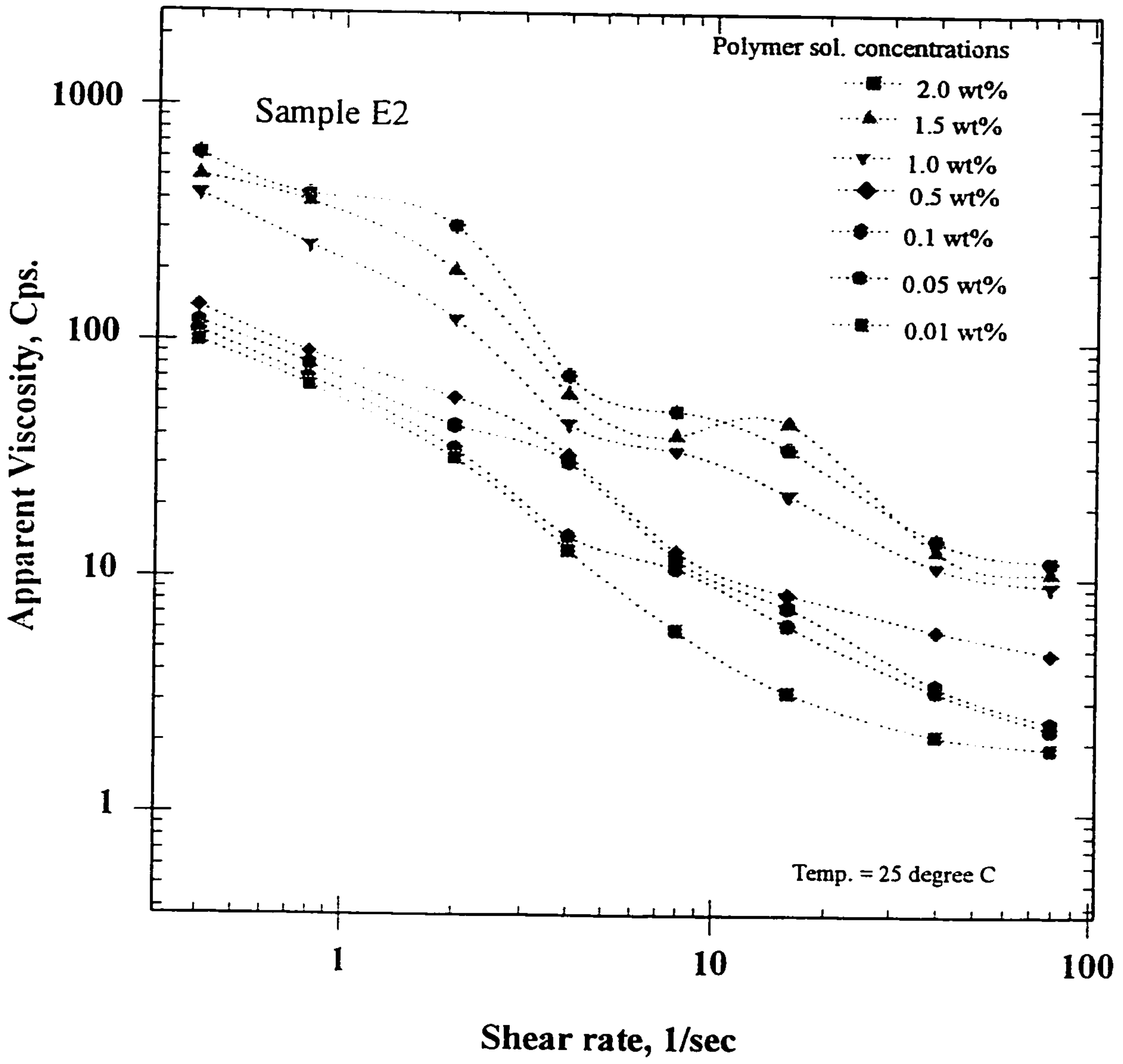


Figure 5-5; Effect of multi-block copolymer solution Poly (AM-b-C12) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS,3 wt%), hydrophobe (C12, 1 mol%) by micellar copolymerization.

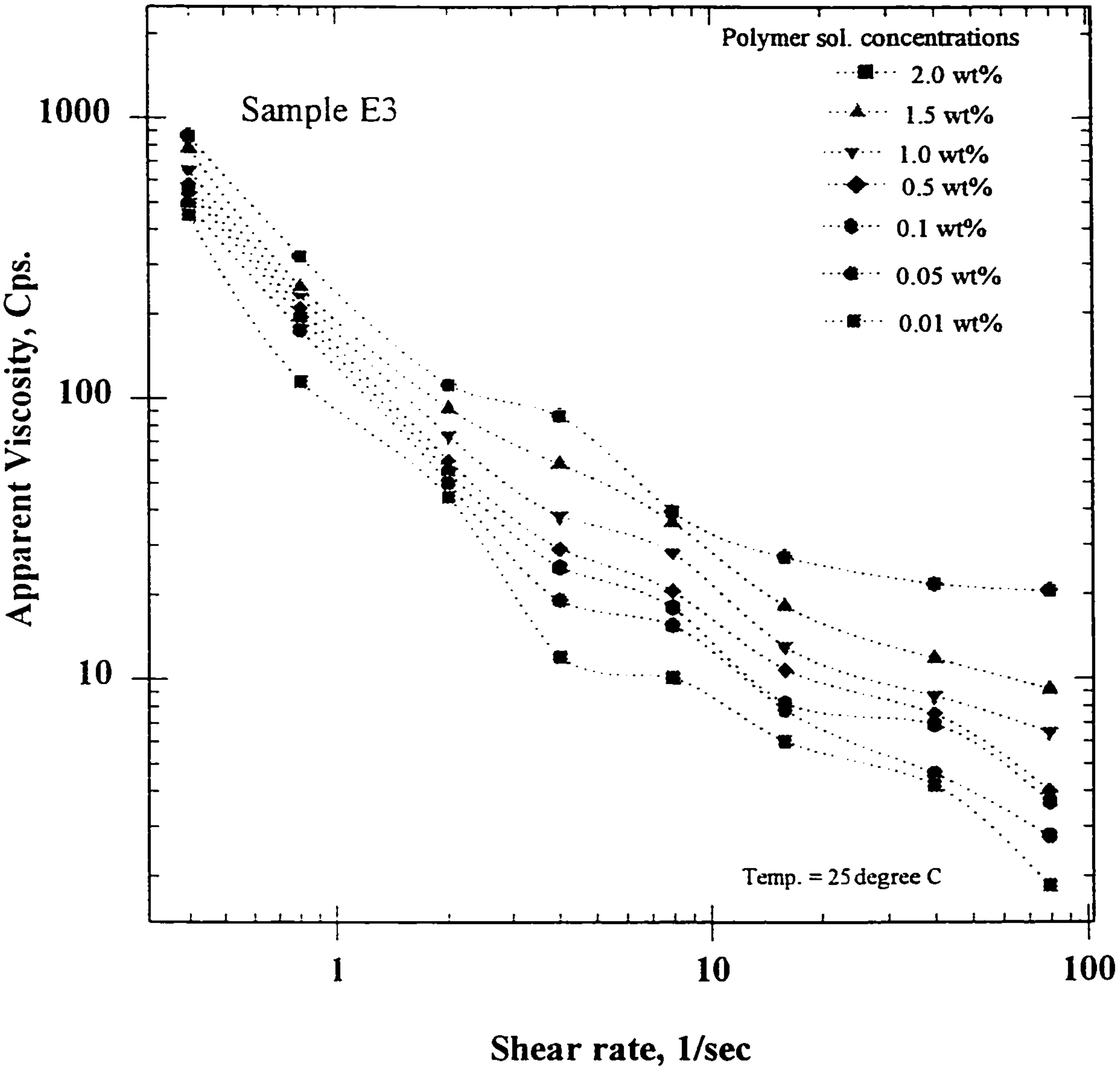


Figure 5-6; Effect of multi-block copolymer solution Poly (AM-b-C12) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS,3 wt%), hydrophobe (C12, 2 mol%) by micellar copolymerization.

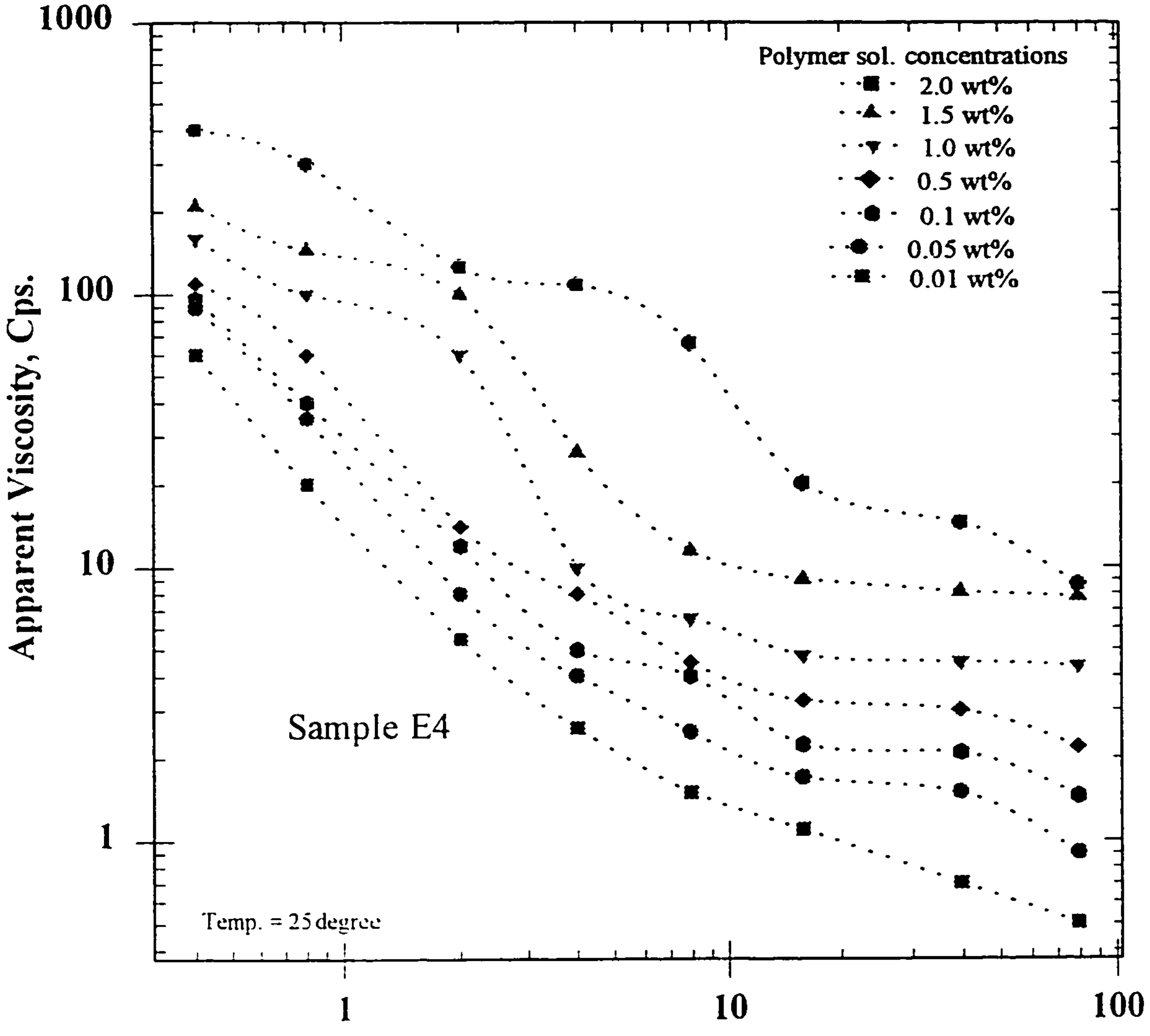


Figure 5-7; Effect of multi-block copolymer solution Poly (AM-b-C12) on the shear rate dependence of viscosity in deionized water. Surfactant (SDS, 3 wt%), Feed hydrophobe, 3.0 mol% C12. Micellar polymerization is used.

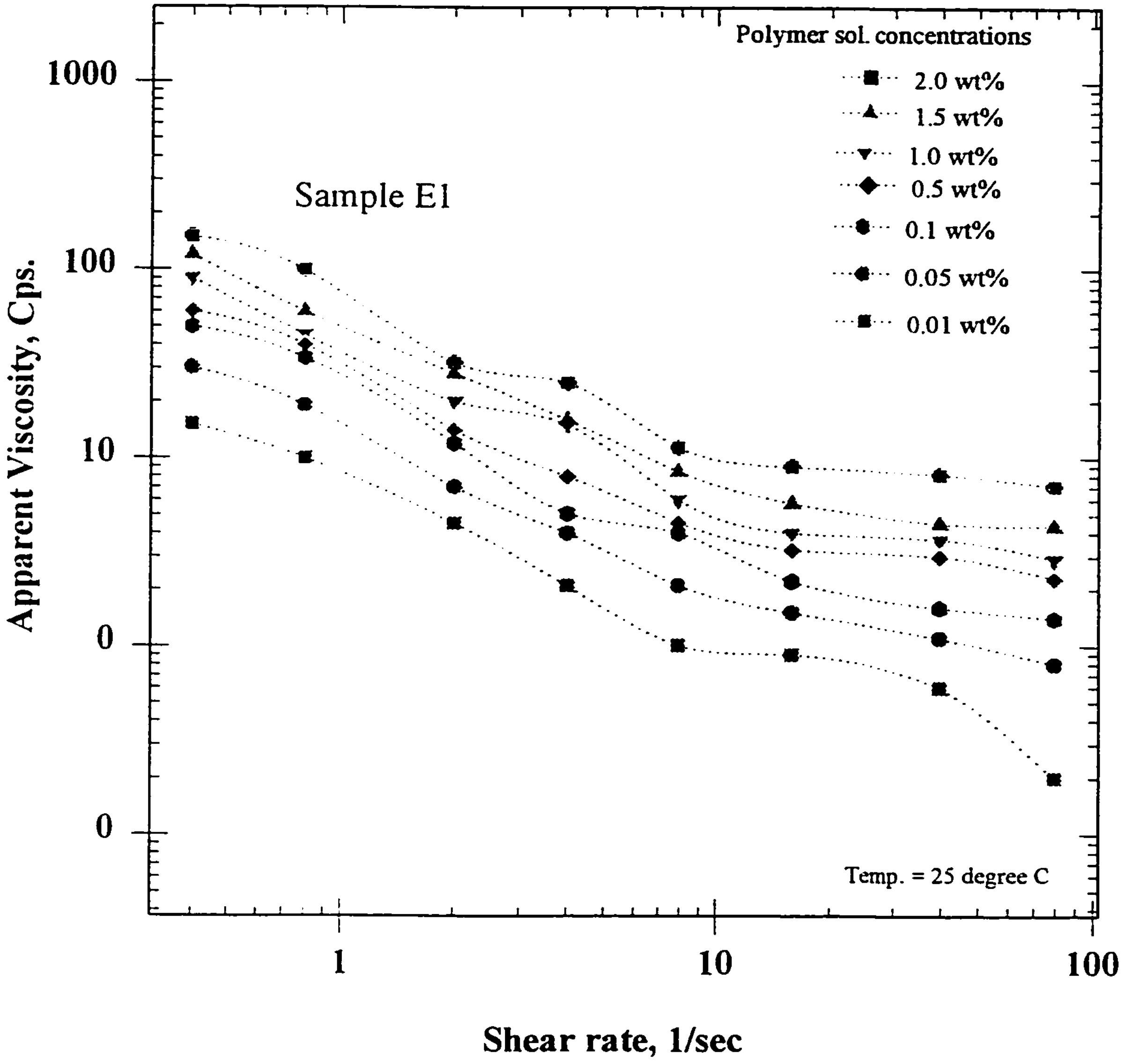


Figure 5-8; Effect of a homopolymer solution Poly (AM) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS,3 wt%), hydrophobe (C12, 0.0 mol%), by micellar polymerization.

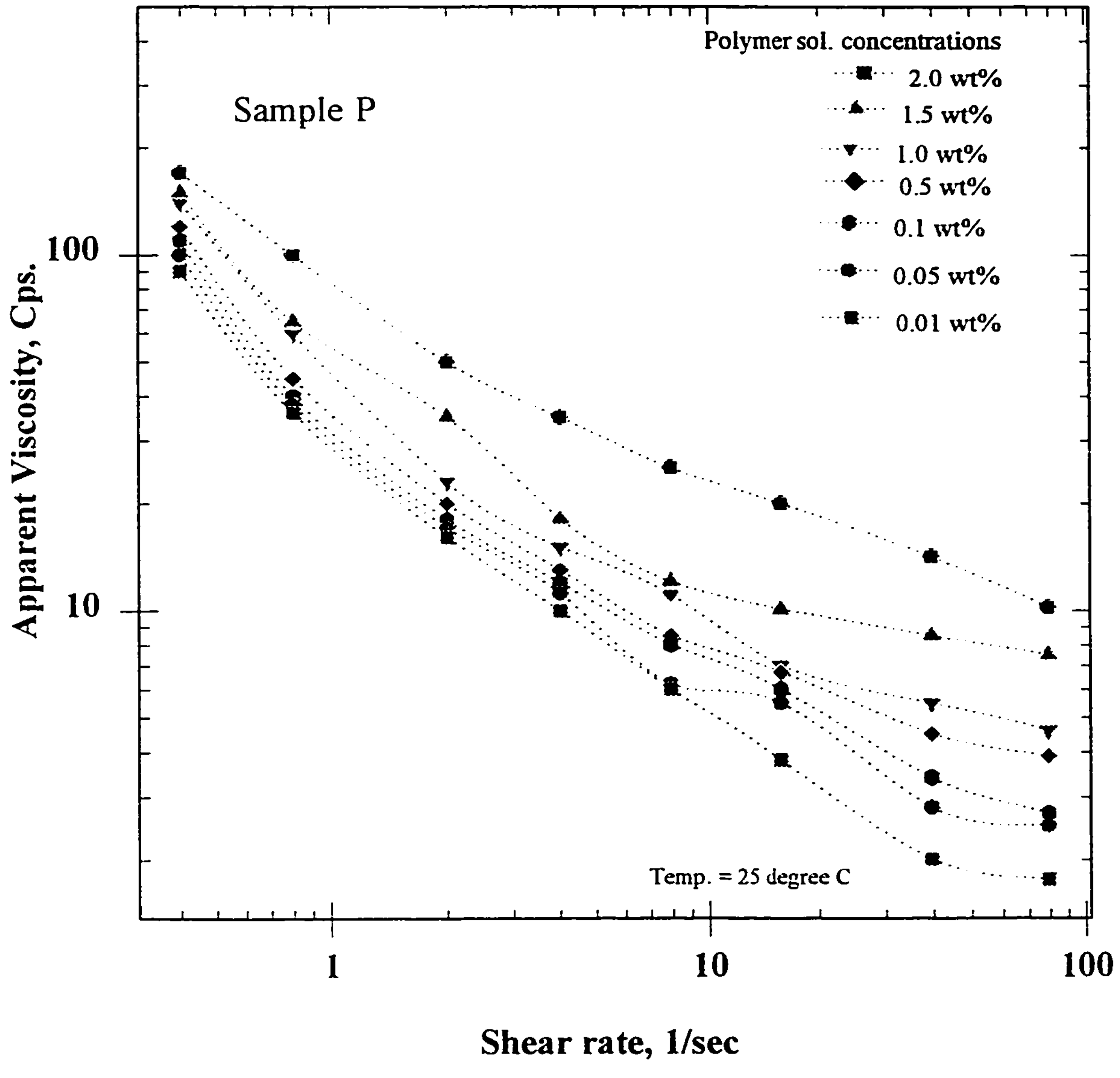


Figure 5-9; Effect of random copolymer solution Poly (AM-r-ST) on the shear rate of dependence of viscosity in deionized water at 25 °C. Formamide as a cosolvent. Hydrophobe (ST,3 mol %), by homogeneous copolymerization.

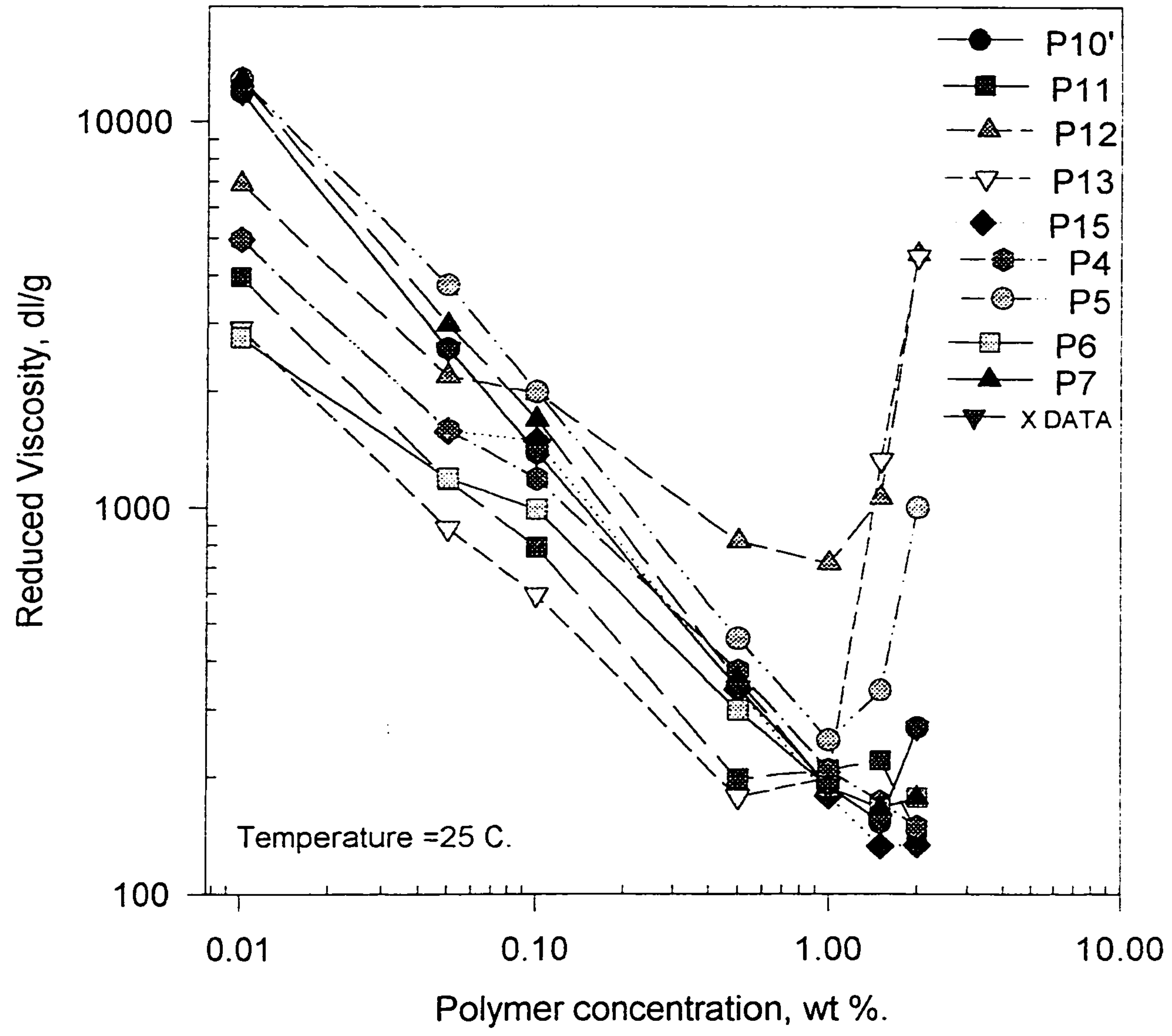


Figure 5-10; Reduced viscosity as a function of polymer concentration of multi-block copolymers, P10' to P7 as in the sequence of Table 5-4, Polyacrylamide-block-Polystyrene. Samples were prepared in deionized water at shear rate of 0.3 sec^{-1}.

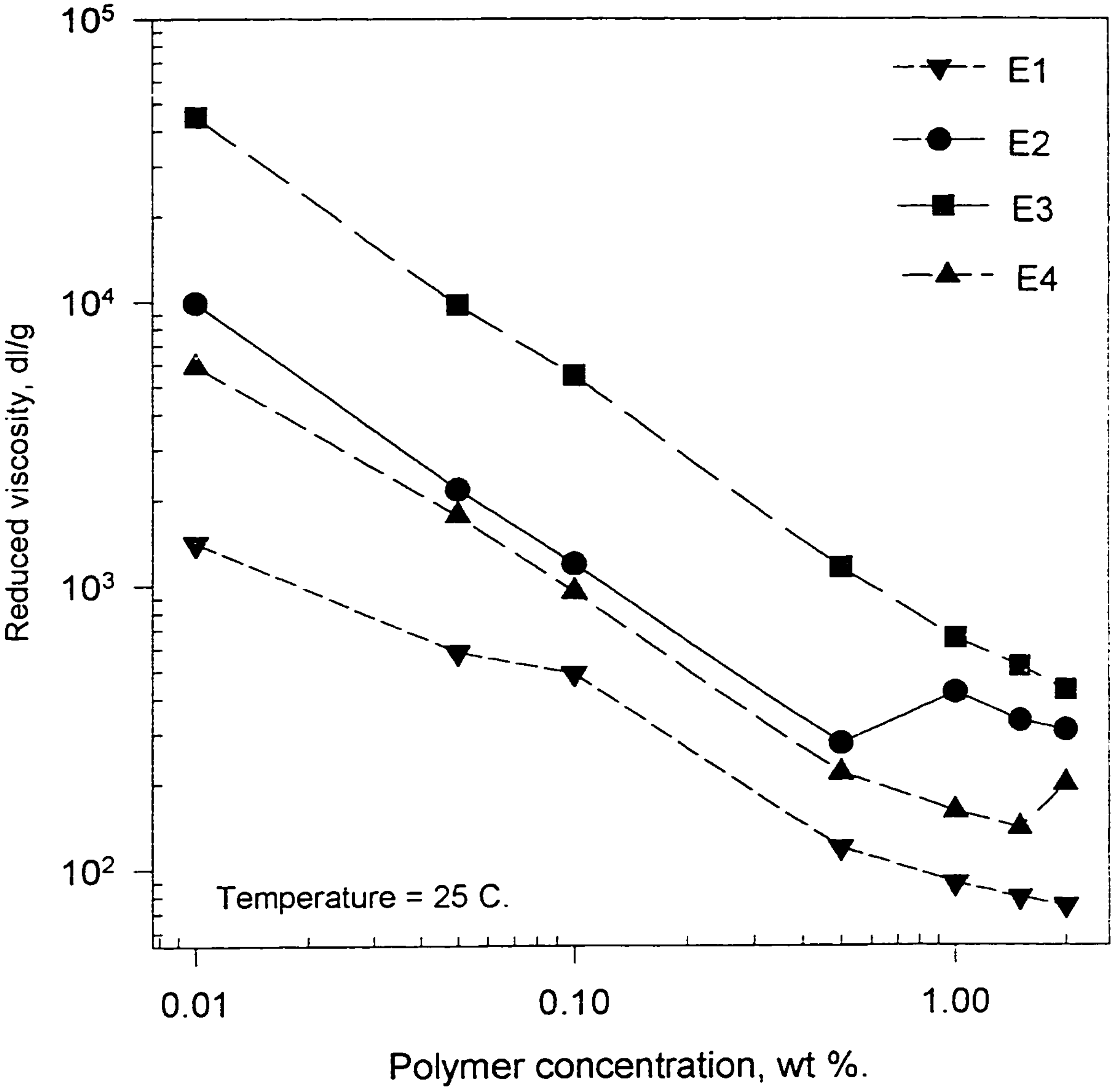


Figure 5-11; Reduced viscosity as a function of polymer concentration of non-ionic multi-block copolymers, Poly(AM-b-C12), except E1 stands for polyAM. Samples were prepared in deionized water at shear rate of 0.3 sec^{-1}.

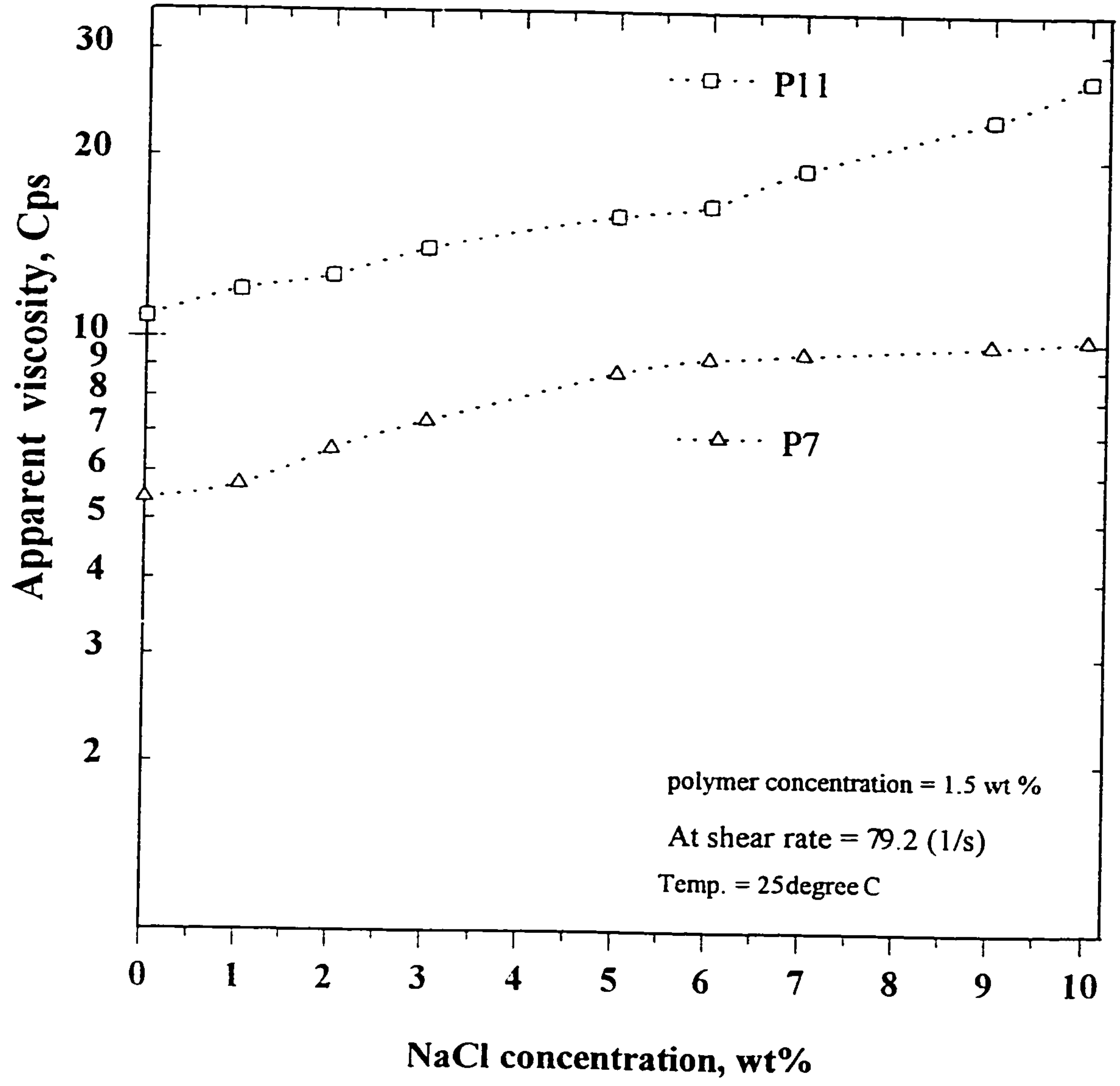


Figure 5-12; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer of P11 (poly AN-b-poly ST) with 6 mol% ST and P7 (poly AM-b-Poly ST) with 6mol% ST.

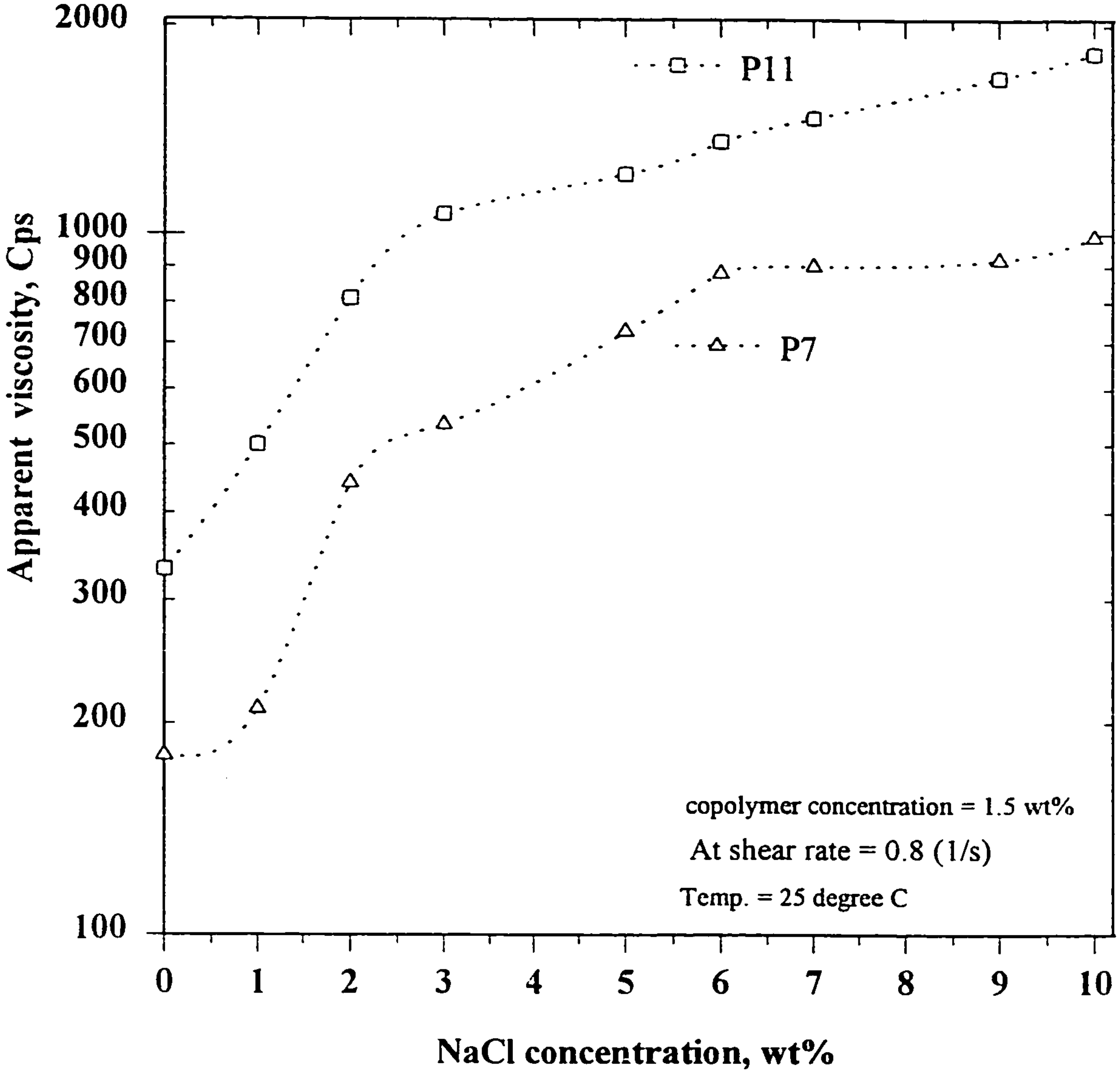


Figure 5-13; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer of P11 (poly AN-b-poly ST) with 6 mol% ST and P7 (poly AM-b-Poly ST) with 6mol% ST.

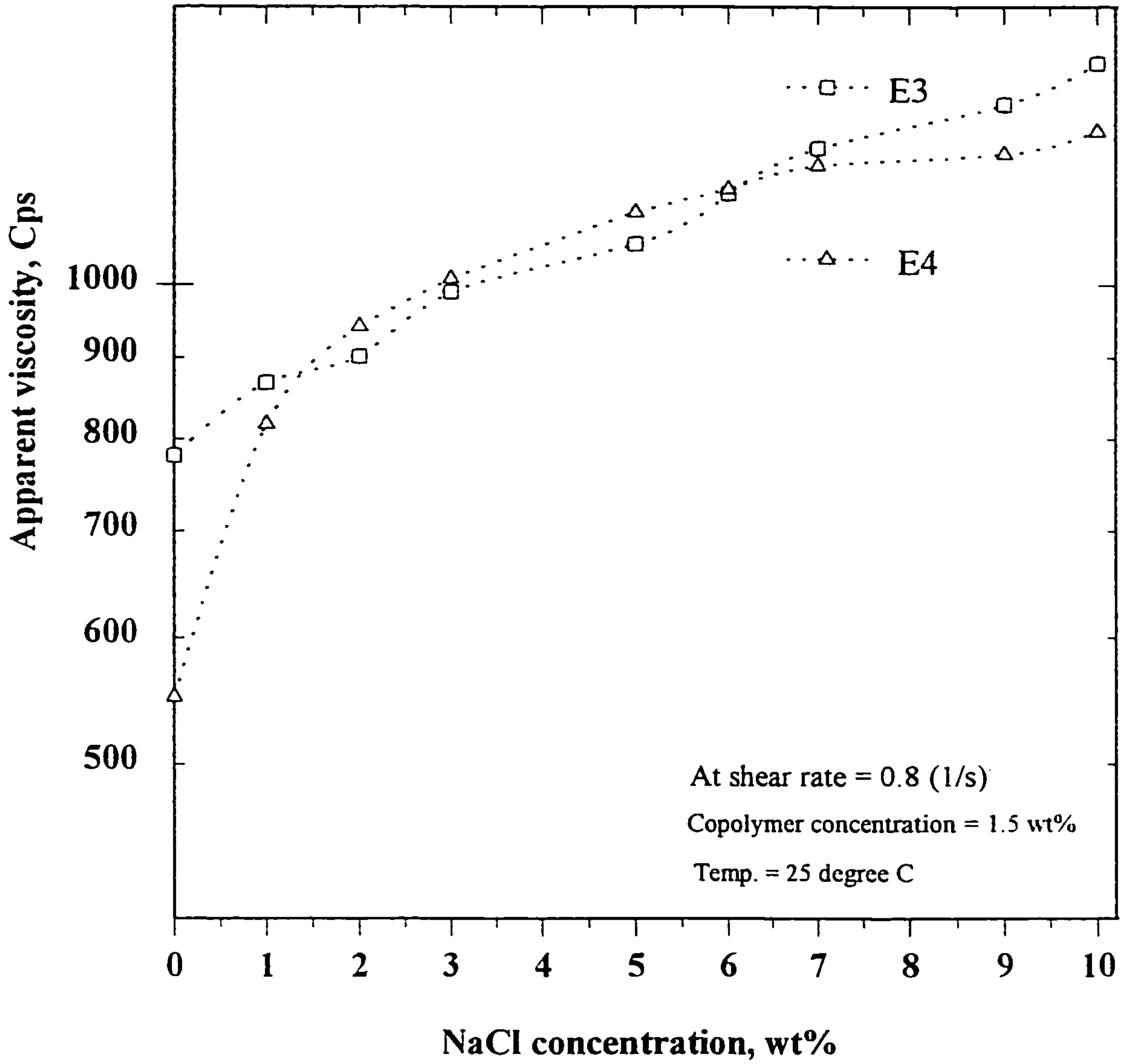


Figure 5-14; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer of E3 (poly AN-b-poly C12) with 2 % C12 and E4 (poly AM-b-Poly C12) with 3% C12.

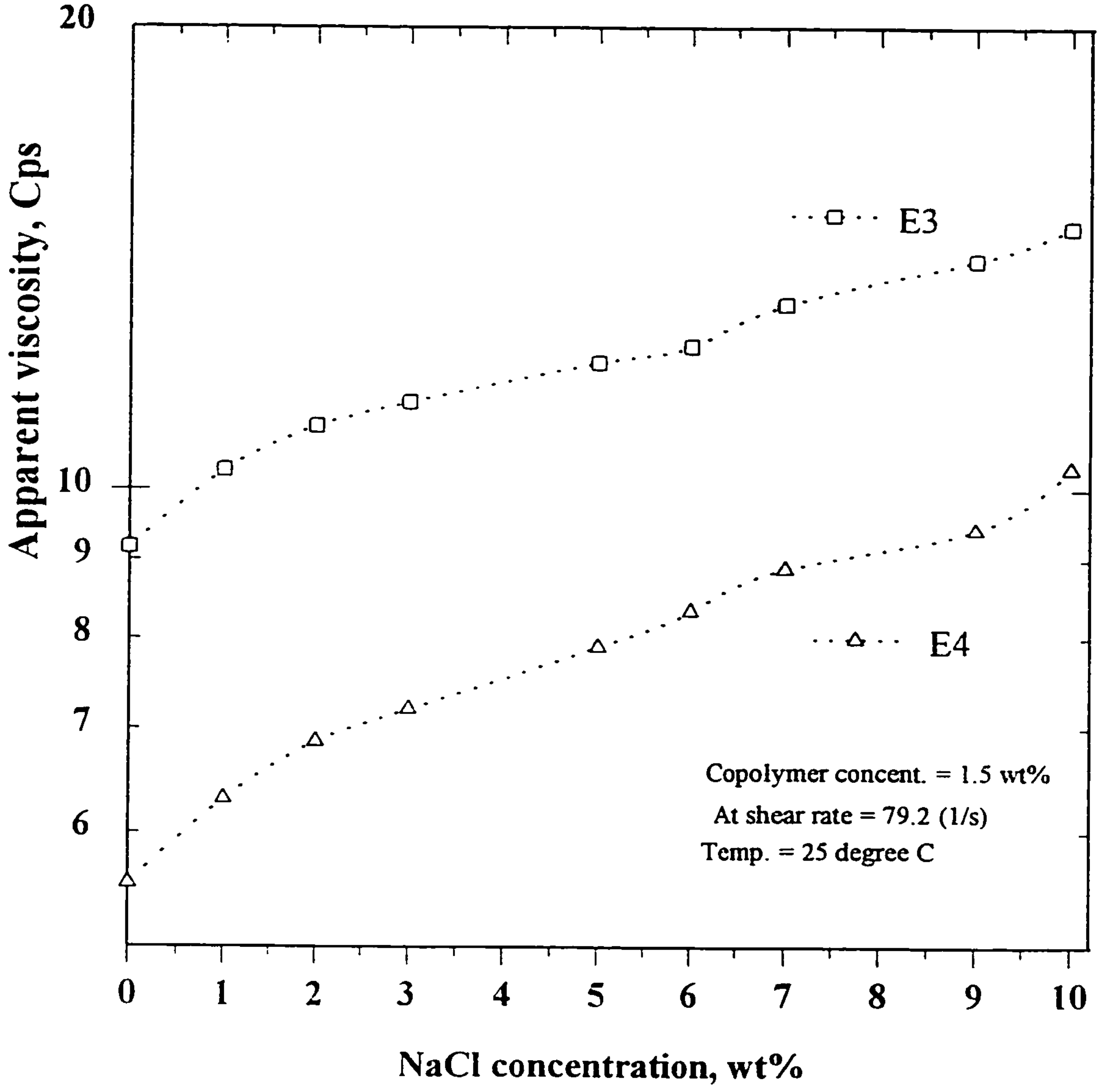


Figure 5-15; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer of E4 (poly AN-b-poly C12) with 3 % C12 and E3 (poly AM-b-Poly C12) with 2% C12.

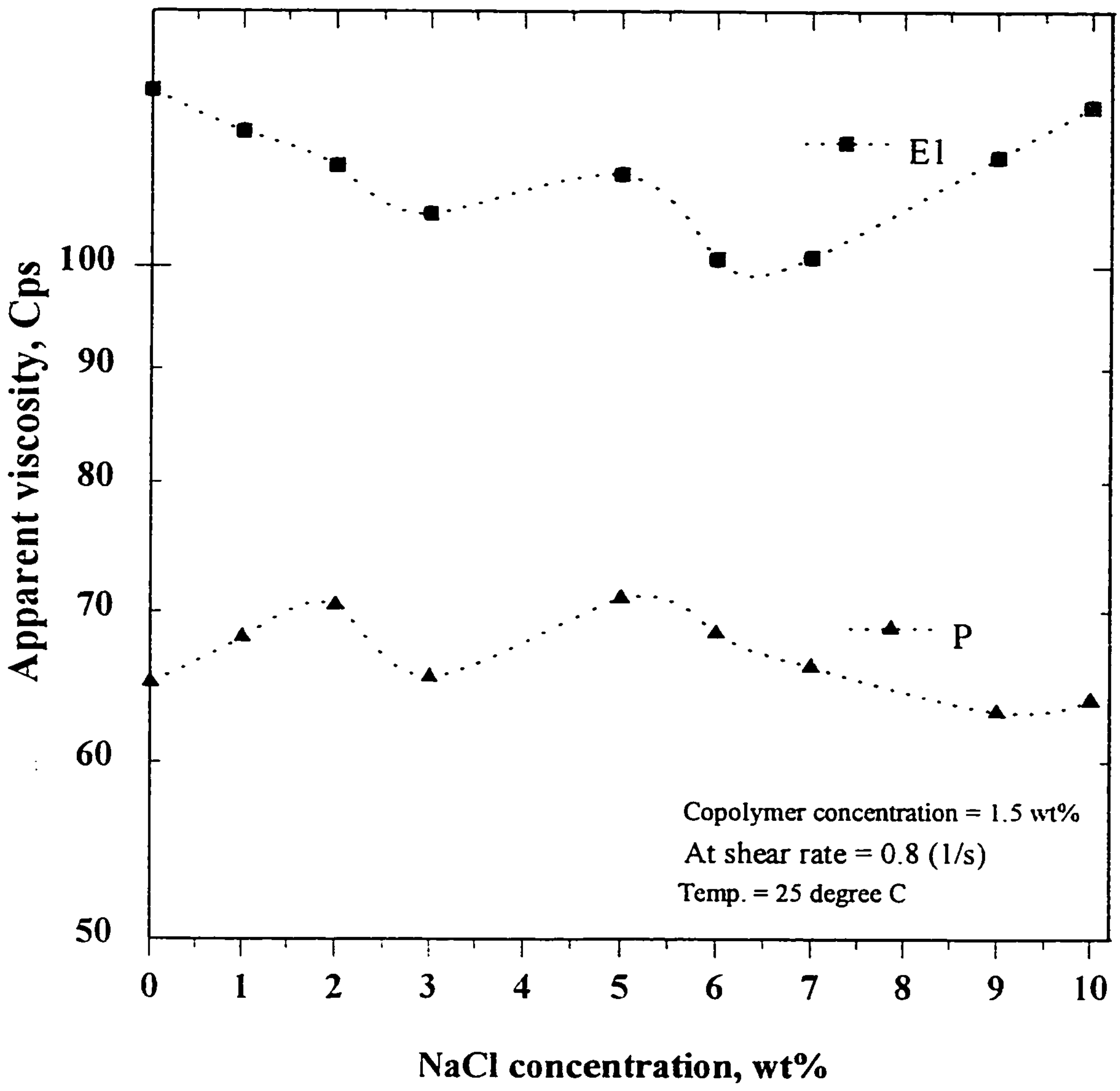


Figure 5-16; Effect of NaCl concentration on the apparent viscosity of a random copolymer, P or (poly AM-r-poly ST) with 3 mol% ST and E1 poly AM with 3 wt% SDS.

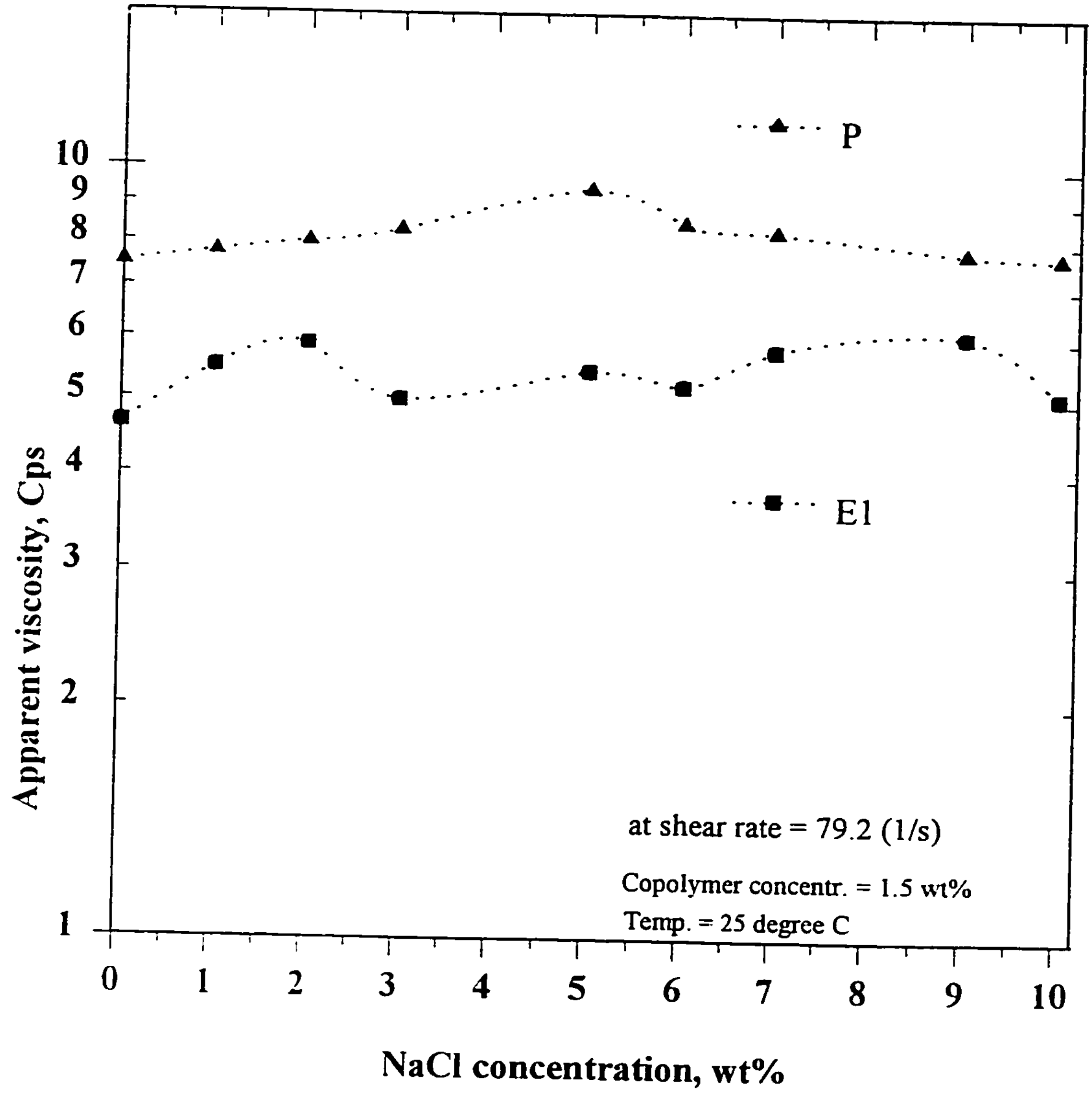


Figure 5-17; Effect of NaCl concentration on the apparent viscosity of a random copolymers P or (poly AM-r-poly ST) with 3% ST and EXP#1 homo-poly AM with 3 wt% SDS.

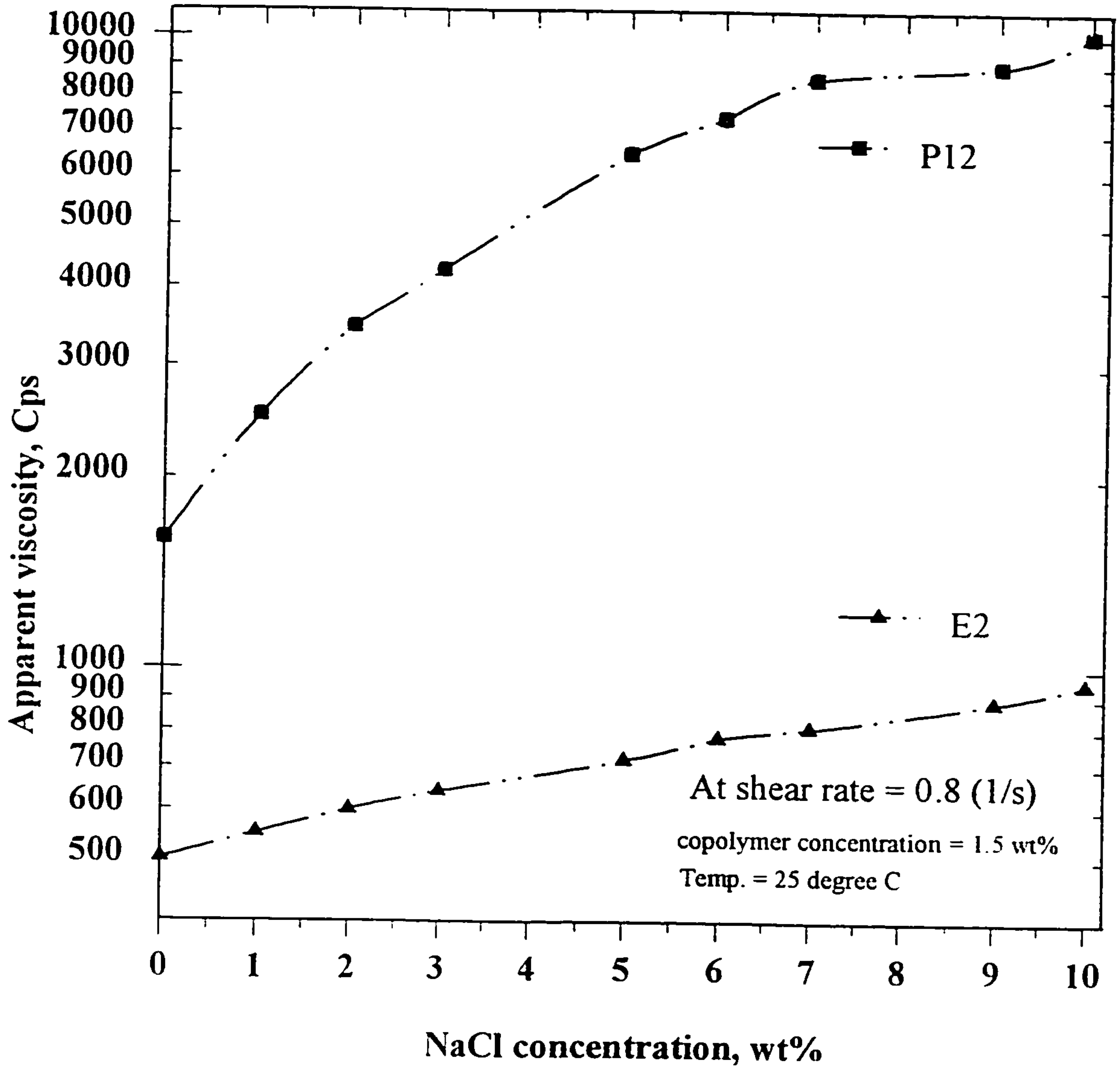


Figure 5-18; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer, P12(poly AM-b-poly ST) with 7% ST and E2 (poly AM-b-polyC12) with 1% C12.

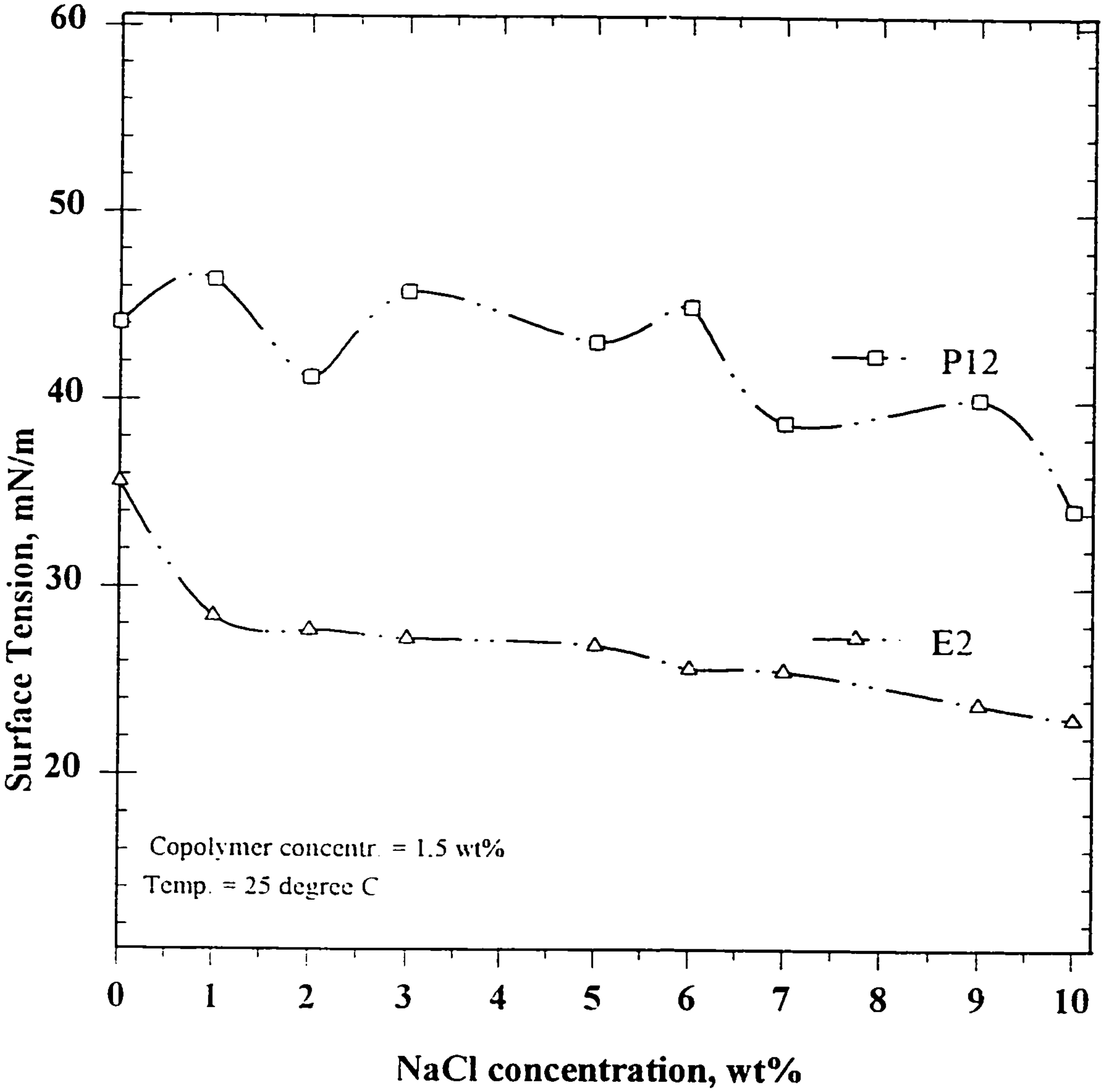


Figure 5-19; Effect of NaCl concentration on the surface tension of multi-block copolymer, P12(poly AM-b-poly ST) with 7% ST and E2 (poly AM-b-polyC12) with 1% C12.

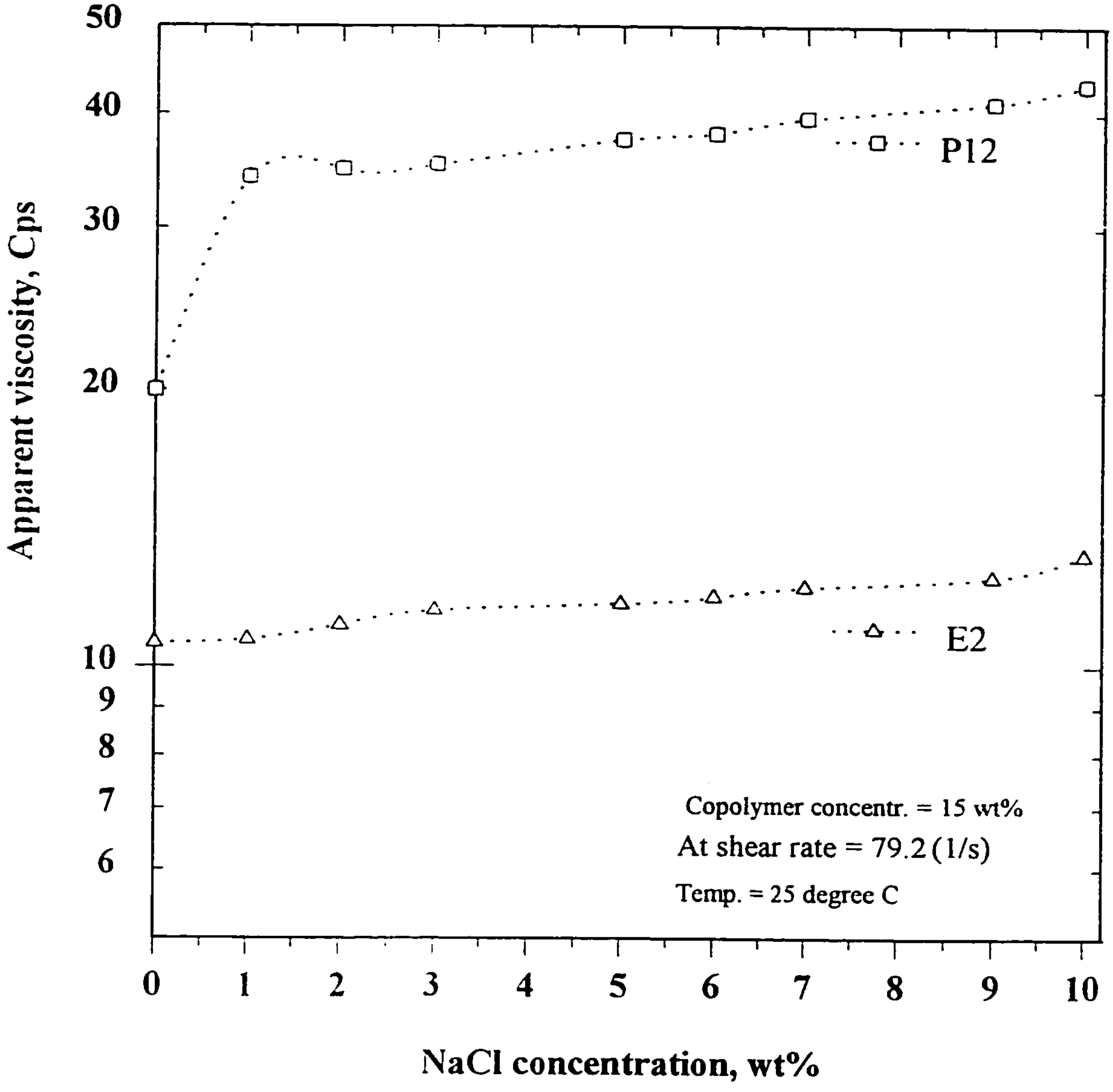


Figure 5-20; Effect of NaCl concentration on the apparent viscosity of multi-block copolymer, P12(poly AM-b-poly ST) with 7% ST and E2 (poly AM-b-polyC12) with 1% C12.

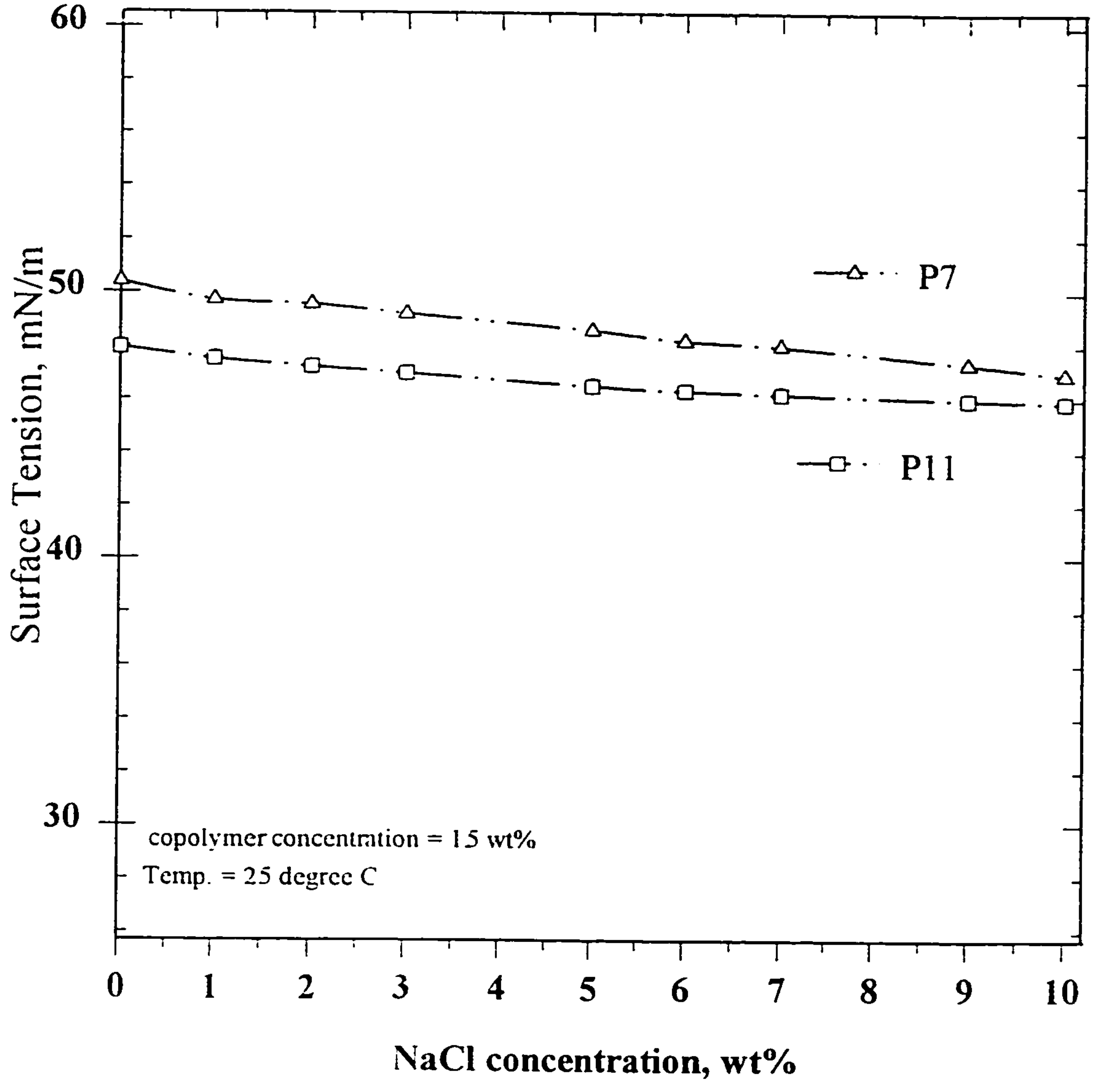


Figure 5-21; Effect of NaCl concentration on the surface tension of multi-block copolymer, P12(poly AM-b-poly ST) with 6% ST and P7 (poly AM-b-polyST) with 6mol%.

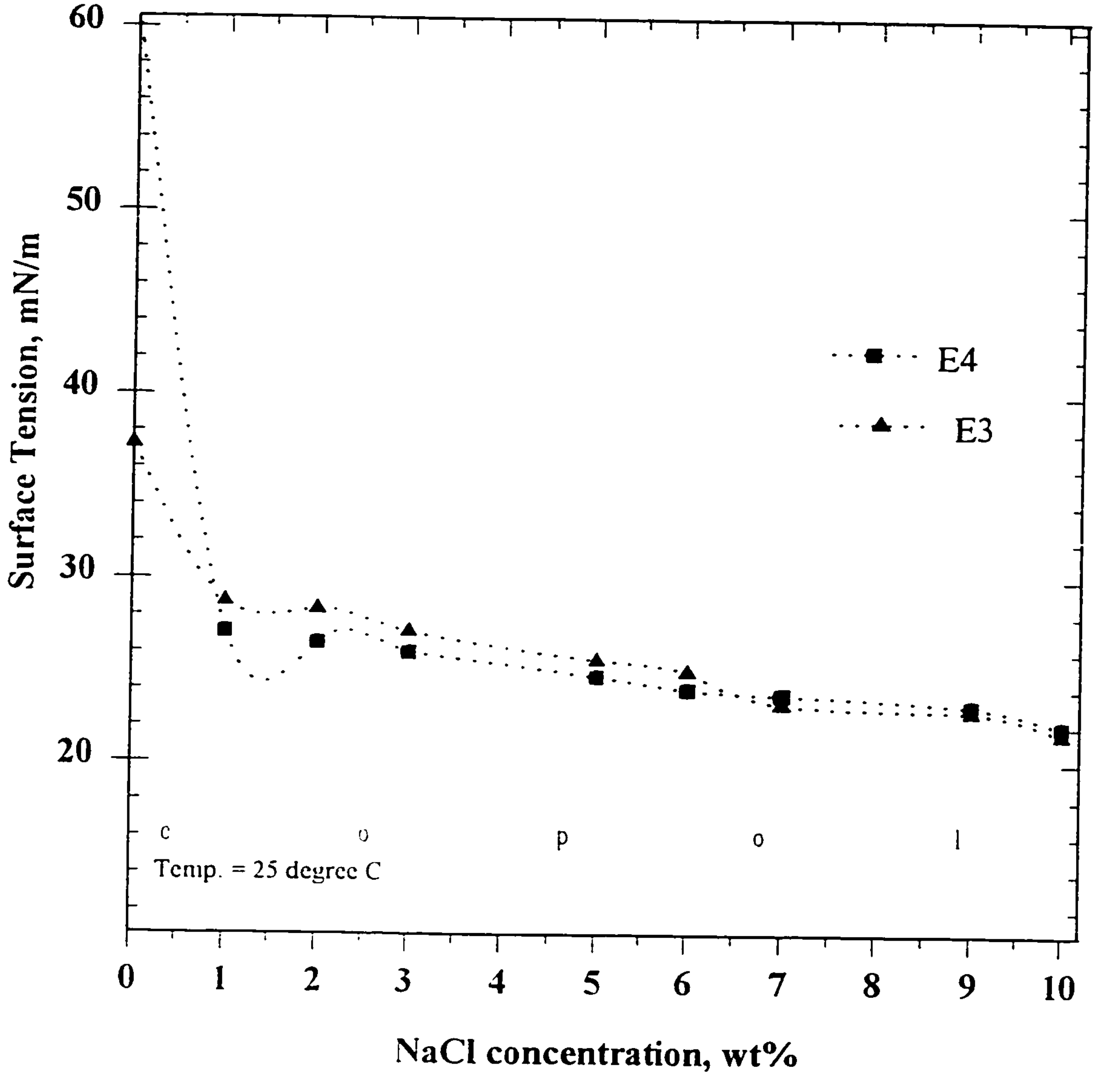


Figure 5-22; Effect of NaCl concentration on the surface tension of multi-block copolymer of E4 (poly AM-b-poly ST) with 3% C12 and E3 (poly AM-b-polyC12) with 2% C12.

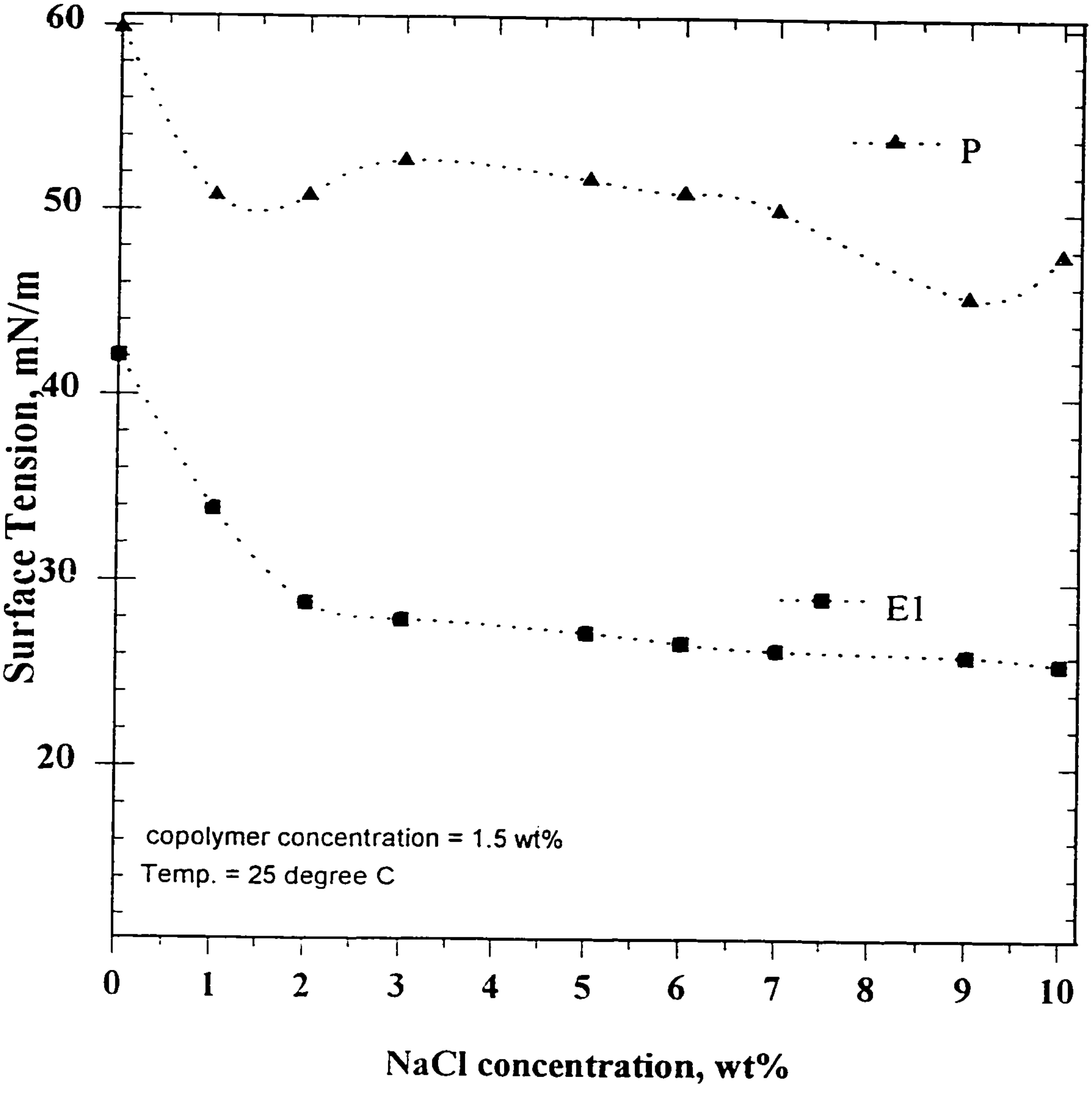


Figure 5-23; Effect of NaCl concentration on the surface tension of a random copolymer P (poly AM-r-polyST) with 3% ST and E1(homo-polyAM-) with 3% SDS.

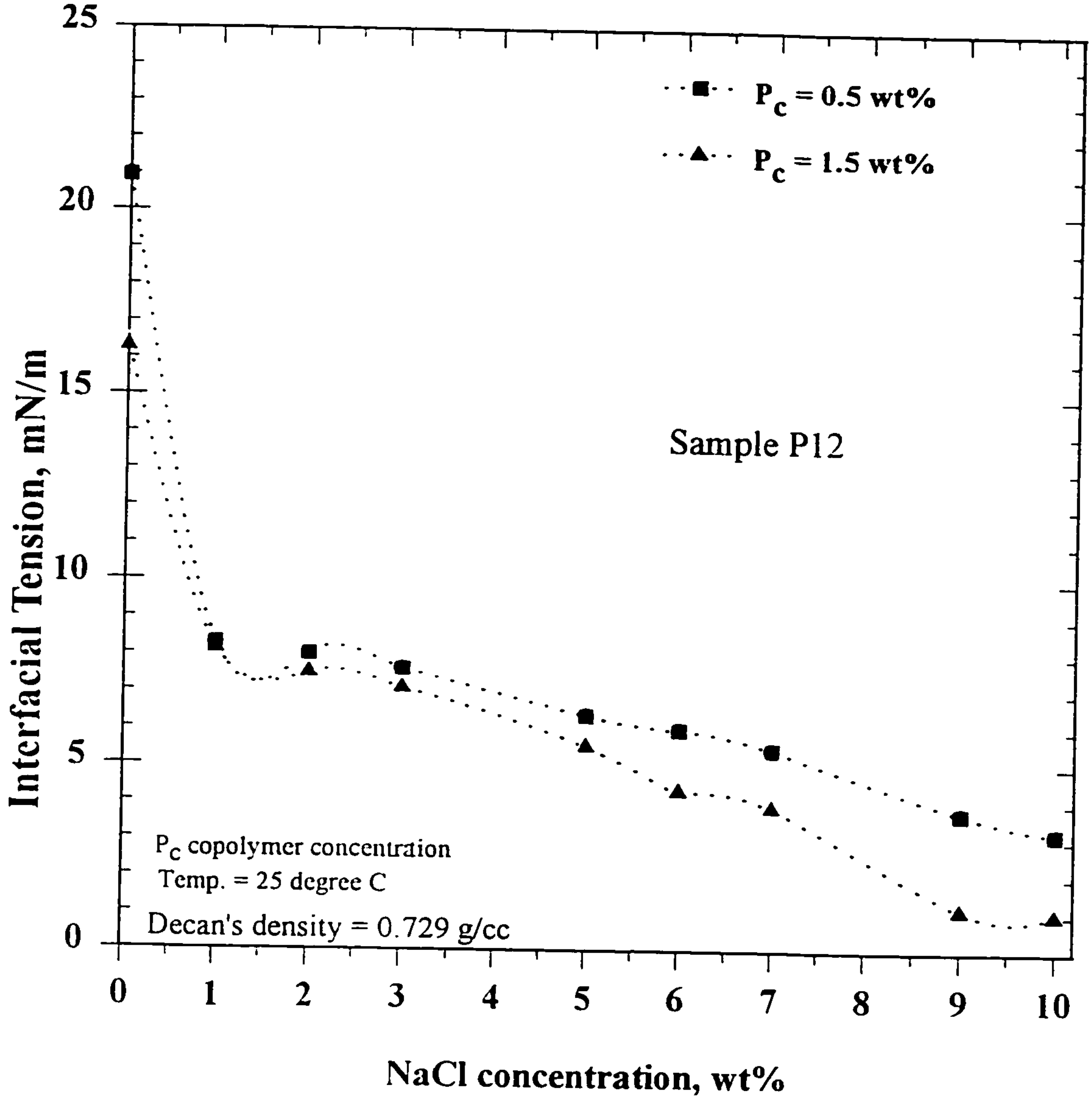


Figure 5-24; Effect of NaCl concentration on the interfacial tension of a multi-block copolymer P12 (poly AM-b-poly ST) with 7 mol% ST, polymer sol. Density = 1.071 g/cc.

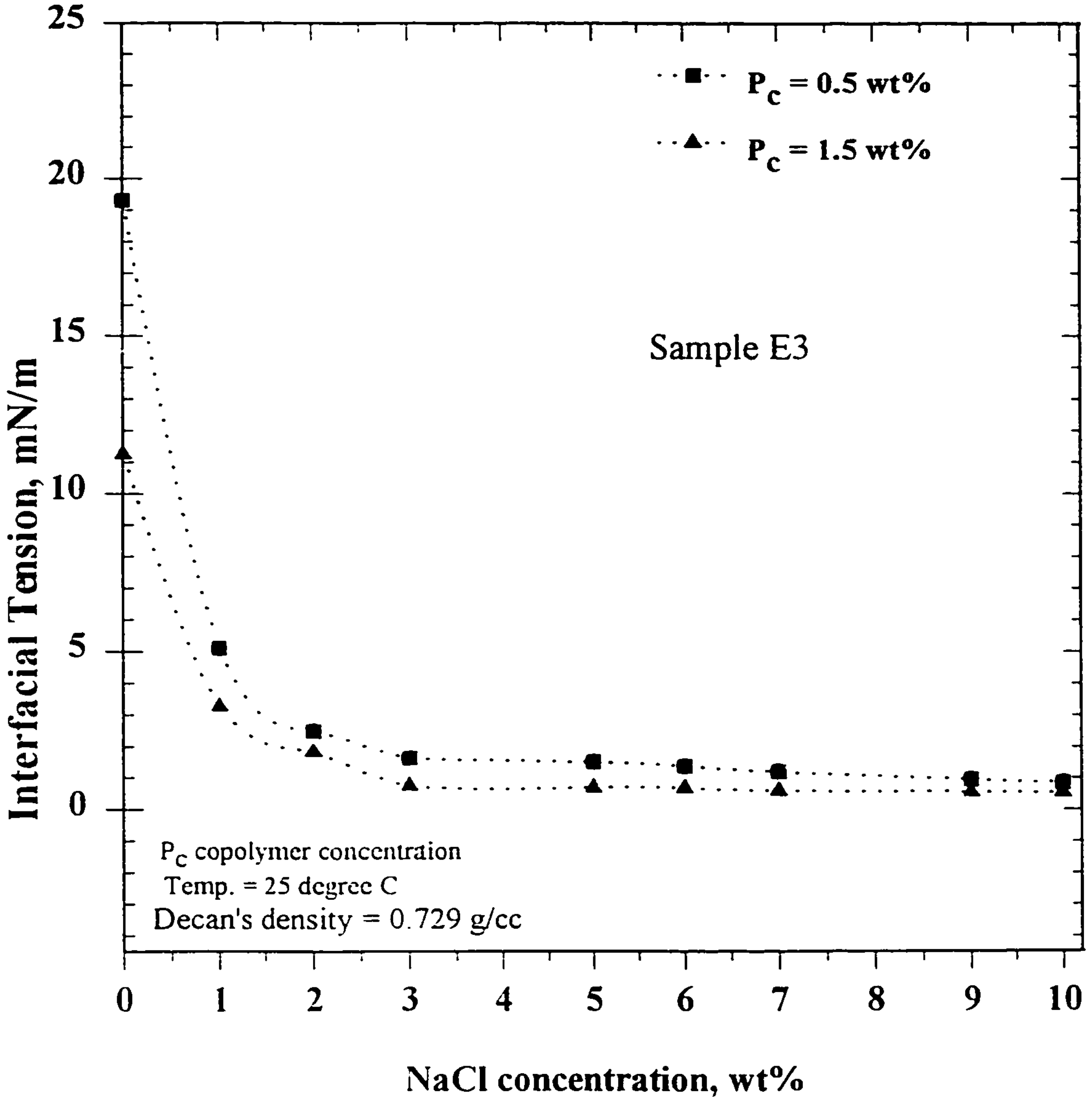


Figure 5-25; Effect of NaCl concentration on the interfacial tension of a multi-block copolymer of E3 (poly AM-b-poly C12, polymer sd.density 1.021 g/cc.

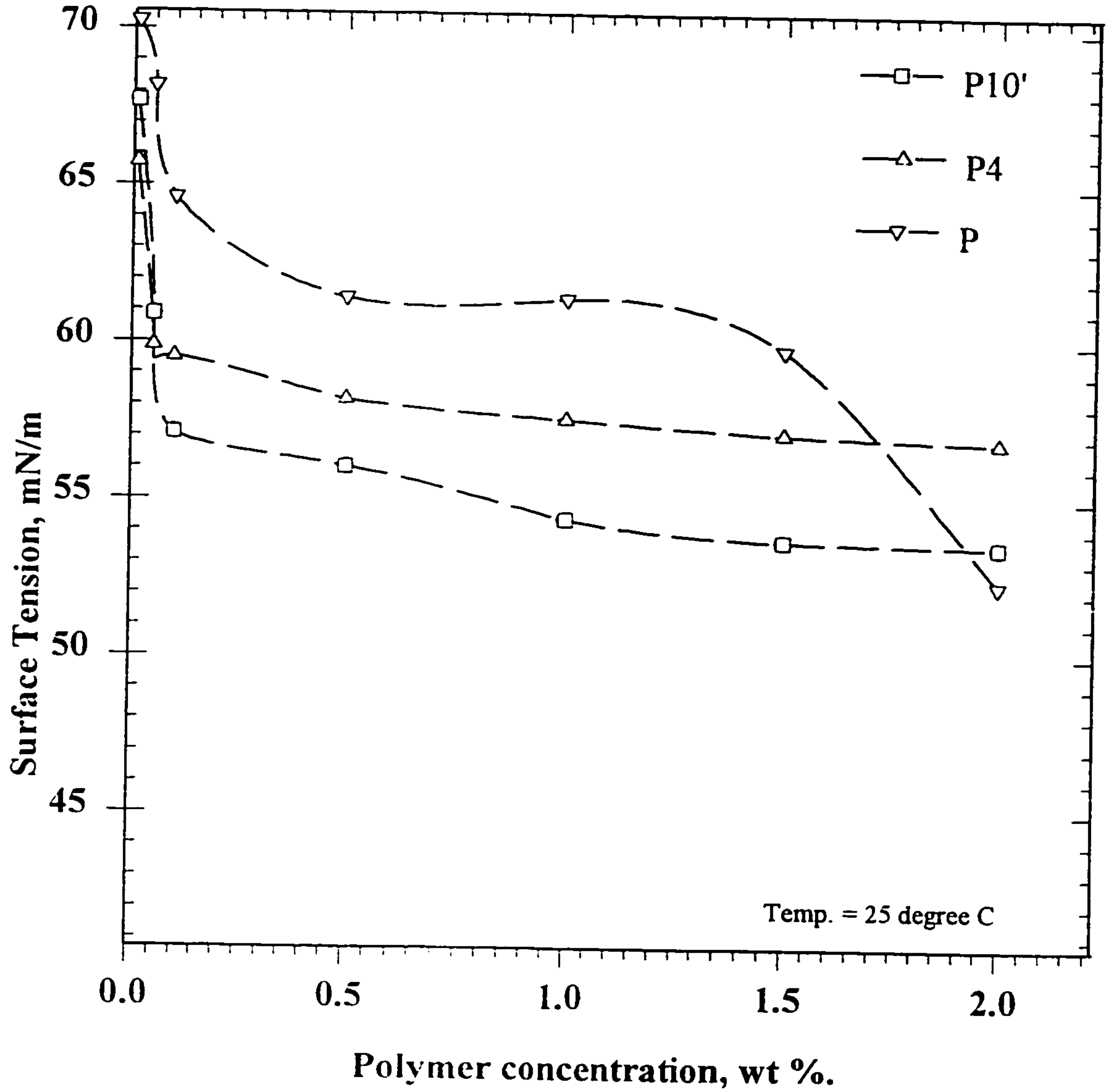


Figure 5-26; Effect of polymer concentration on the surface tension of a multi-block copolymer, P10 and P4 poly (ST-b-AM) with 3 mol% ST. Sample P: random copolymer with 3 mol % ST. Samples prepared in deionized water at 25 degree C.

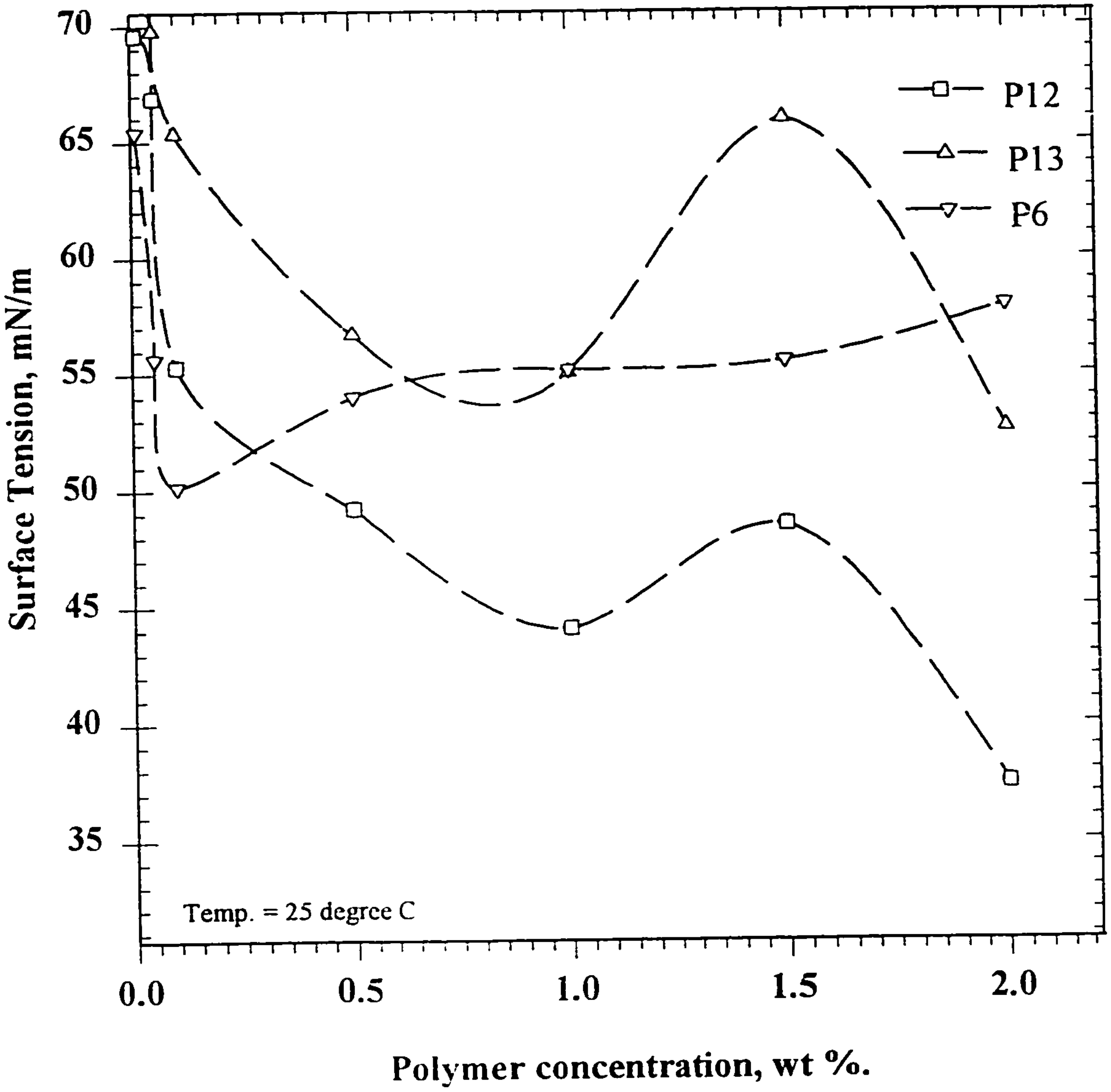


Figure 5-27a; Effect of polymer concentration on the surface tension of a multi-block copolymer, P12 P13 and P16 poly(ST-b-AM) with 7 mol% ST. Sample P6:prepared using CTAB. Both P12 and P13 synthesized in SDS. Samples prepared in d. water.

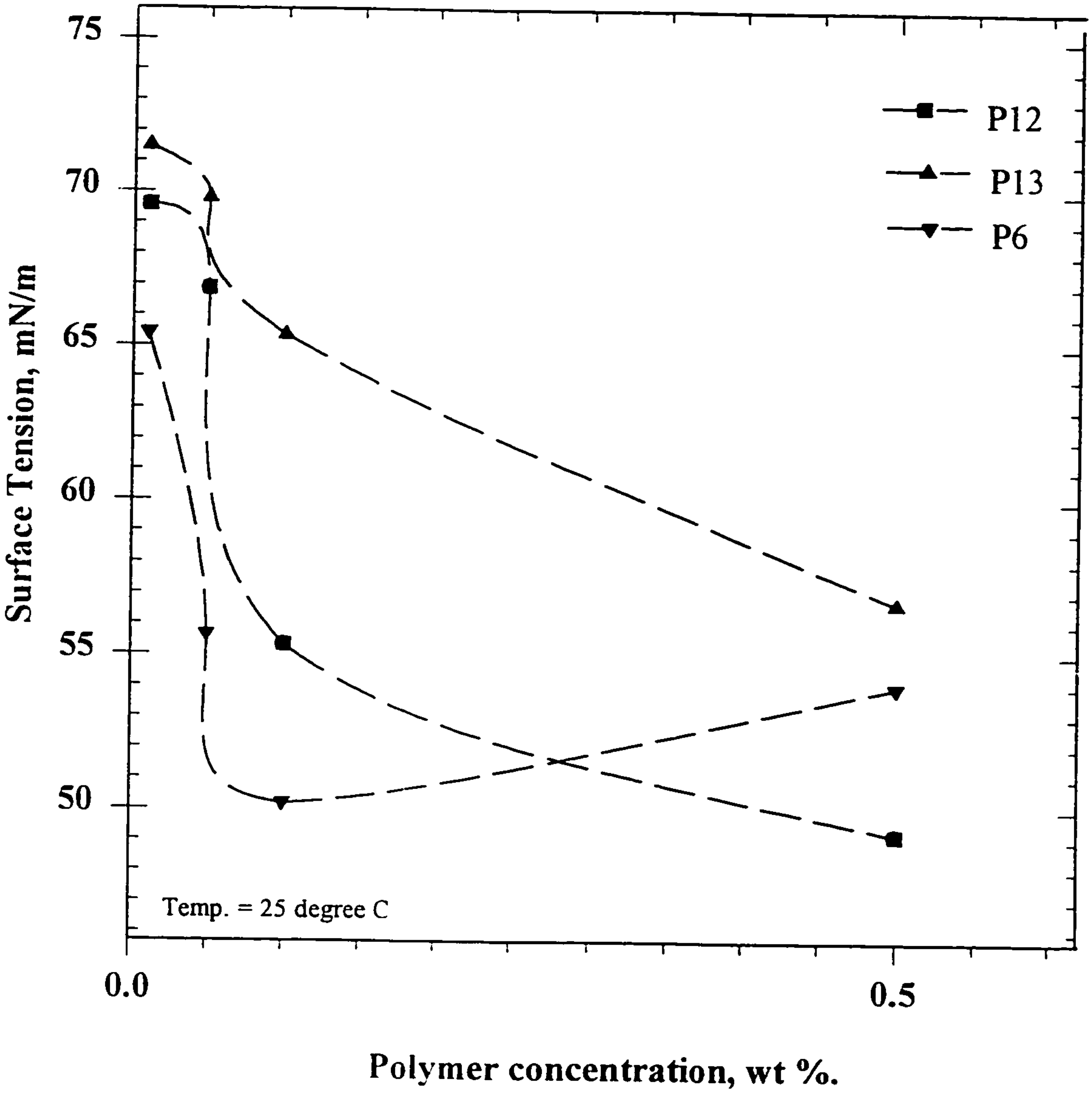


Figure 5-27b; Effect of polymer concentration on the surface tension of a multi-block copolymer, P12 P13 and P16poly (ST-b-AM) with 7 mol% ST. Sample P6:prepared using CTAB. Both P12 and P13 synthesized in SDS. Samples prepared in deionized water.

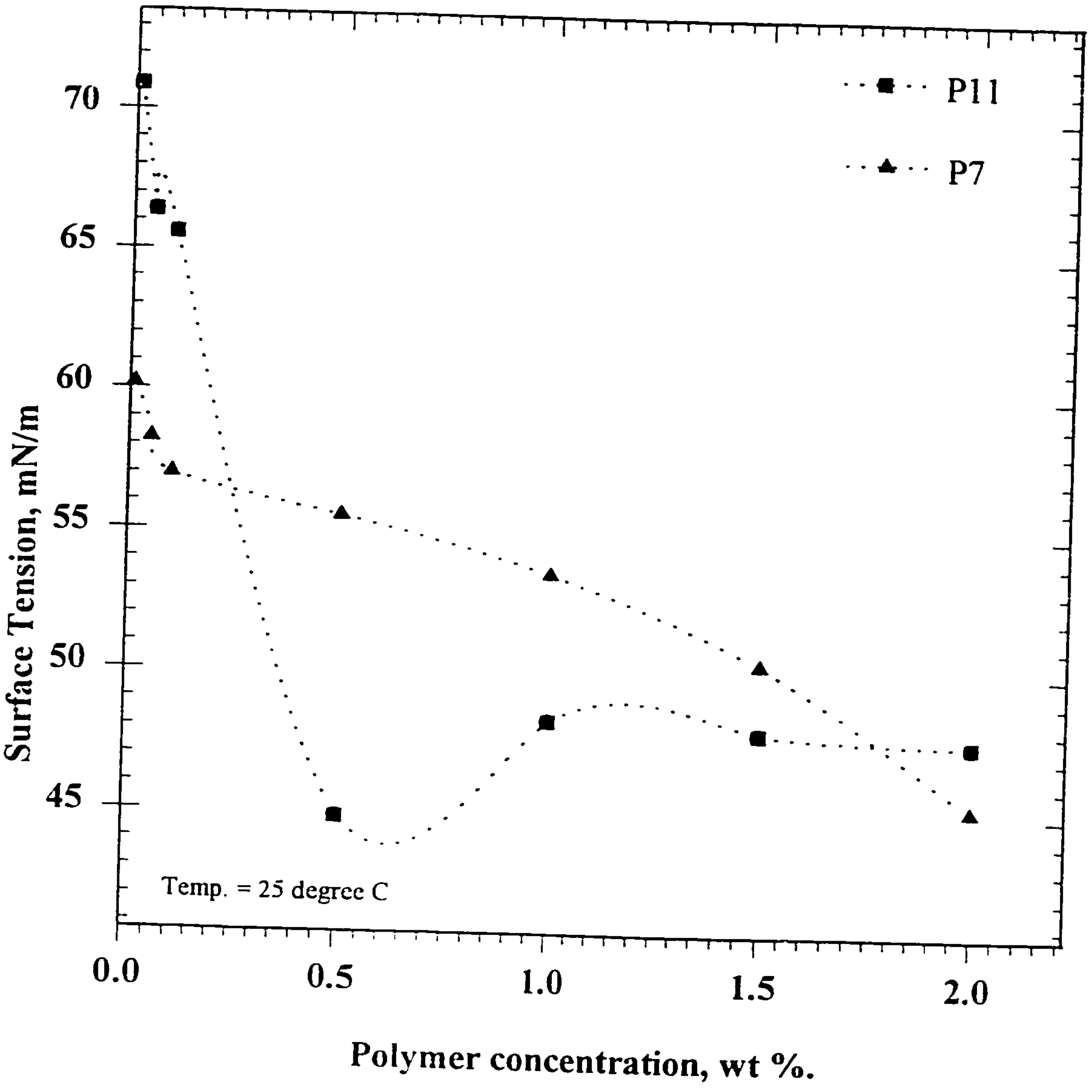


Figure 5-28; Effect of polymer concentration on the surface tension of a multi-block copolymer, P11and P7poly (ST-b-AM) with 6 mol% ST. Sample P11prepared using CTAB. Both P7 prepared using SDS. Samples prepared in deionized water.

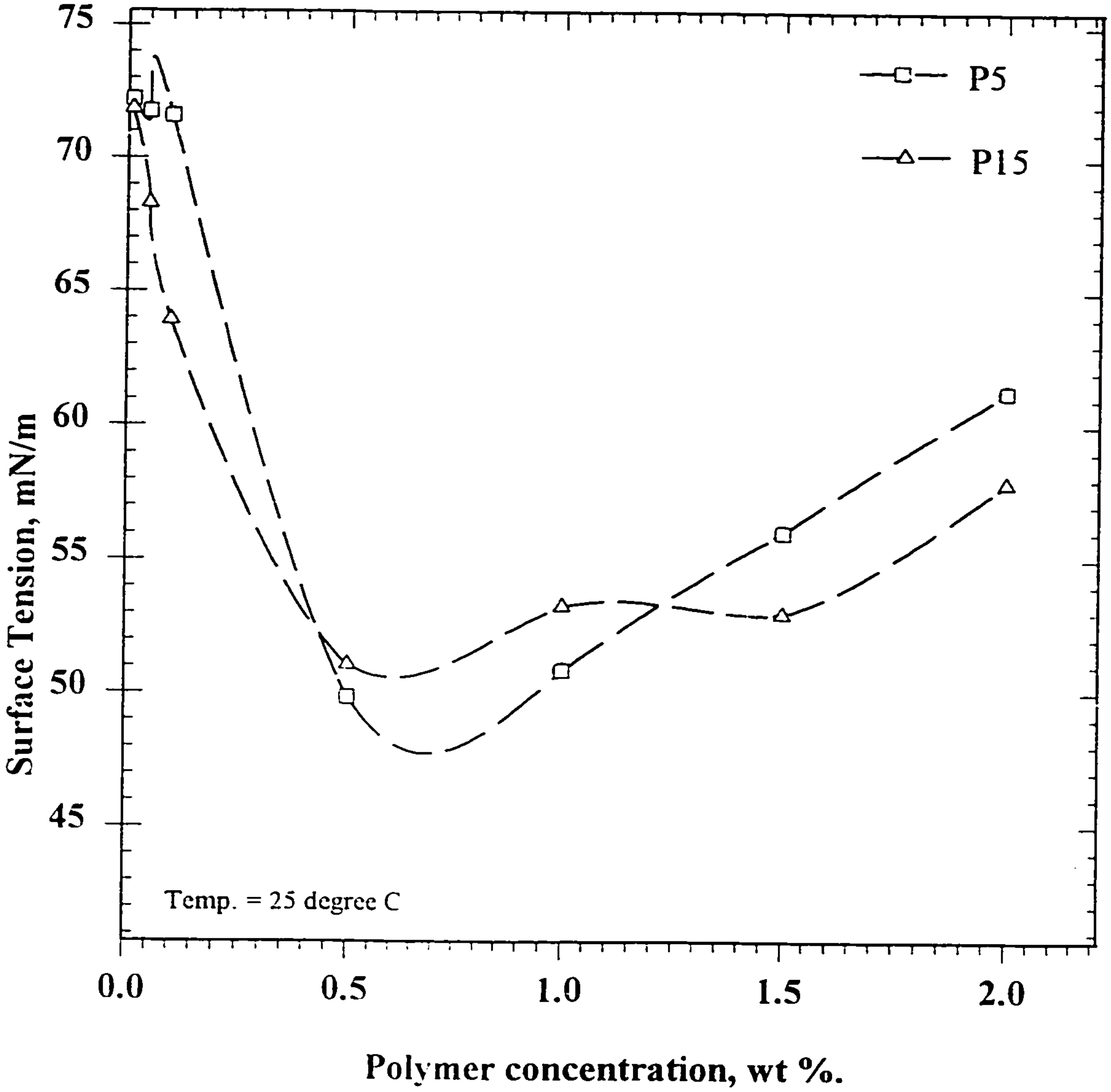


Figure 5-29; Effect of polymer concentration on the surface tension of a multi-block copolymer, P15 and P5 poly (ST-b-AM) with 1 mol% and 2 mol% ST respectively. P15 and P5 synthesized using CTAB and SDS, respectively. Samples prepared in deionized water.

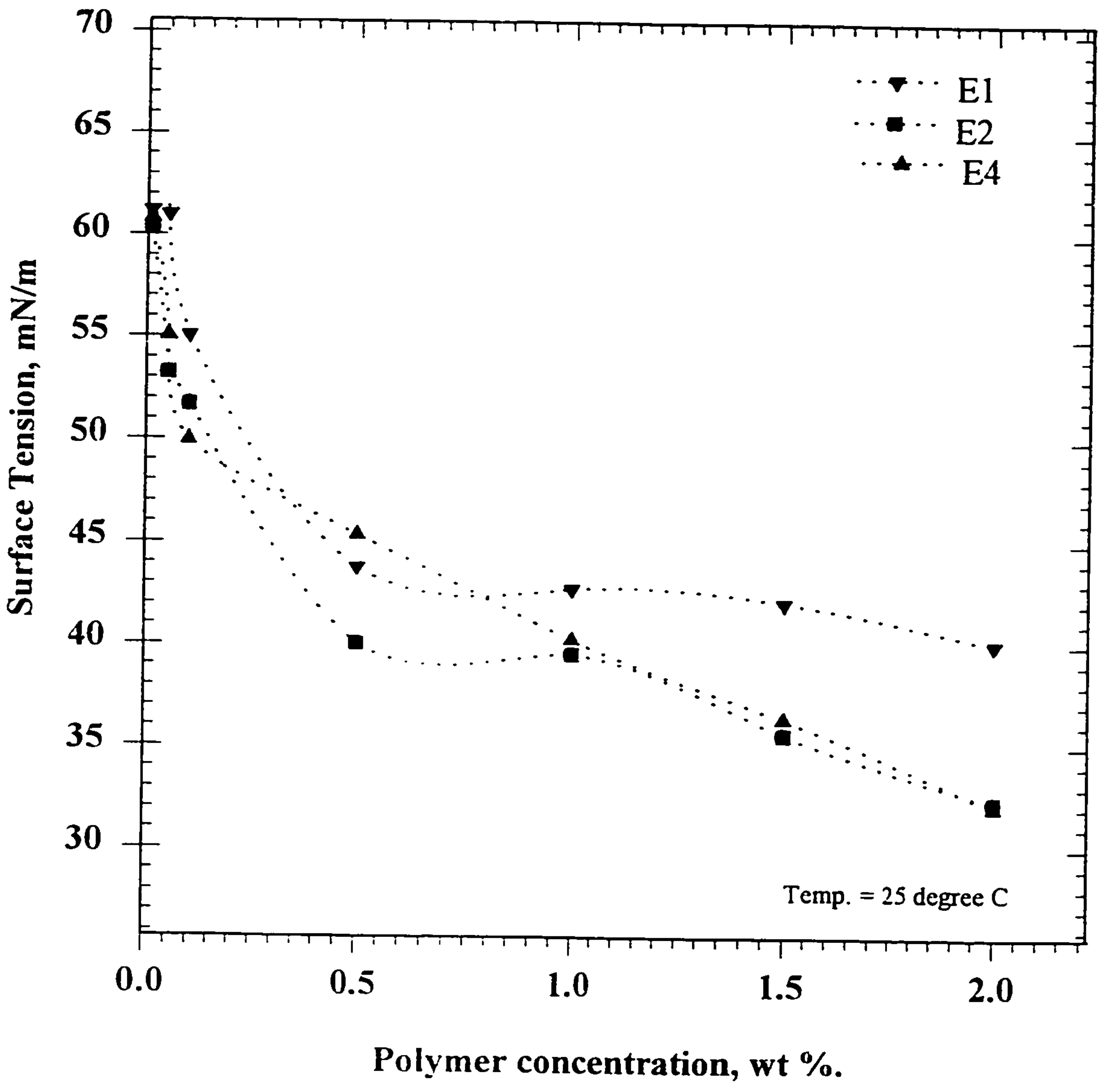


Figure 5-30; Effect of polymer concentration on the surface tension of a multi-block copolymer, E2and E4 poly (CT-b-AM) with 1 mol% and 2 mol% ST respectively. Comparison with homopoly AM, E1 at 3 wt SDS. Samples prepared in deionized water.

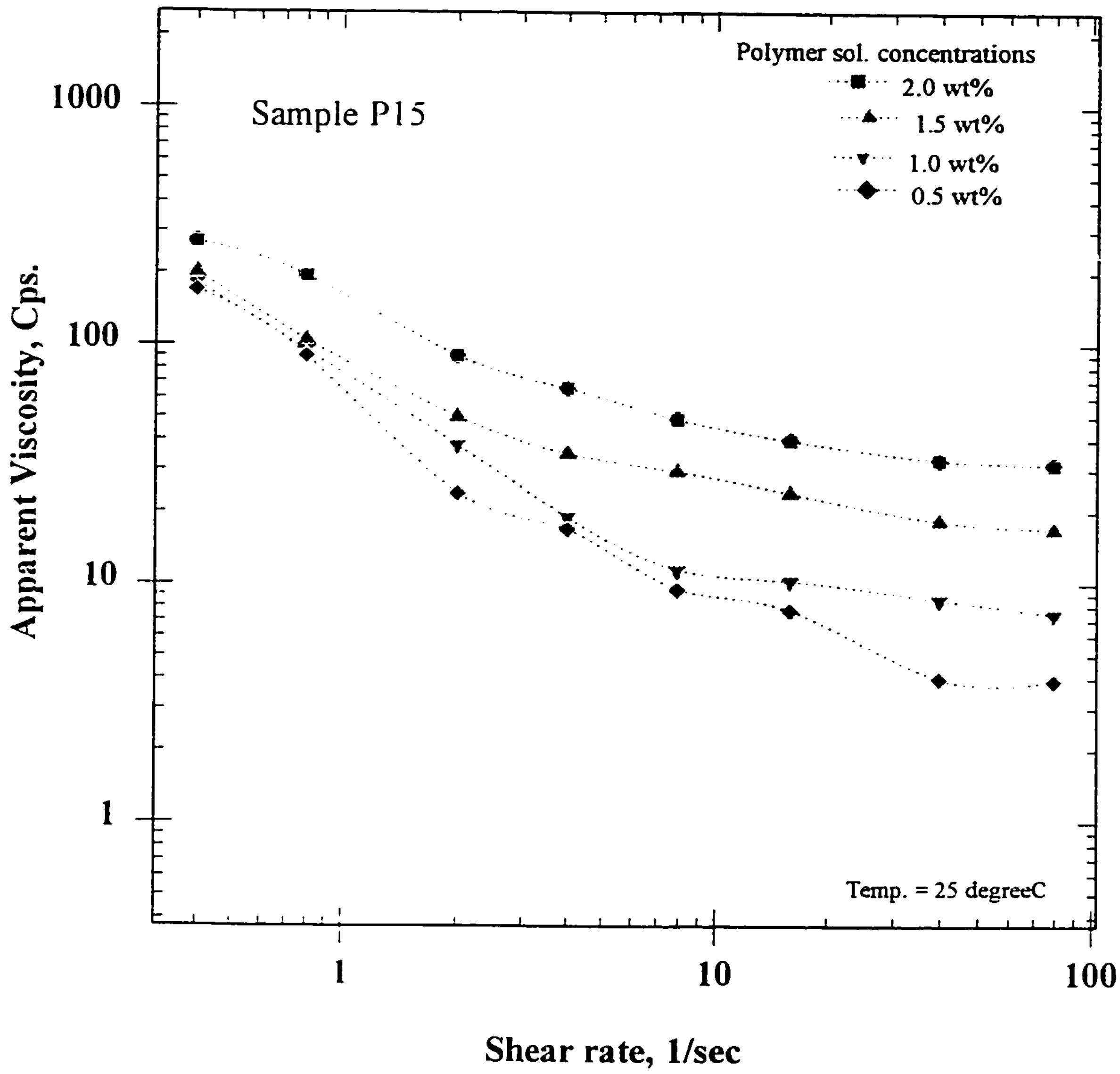


Figure 5-31; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (CTAB), 1 wt%), hydrophobe (ST, 1 mol%), by micellar copoly-merization.

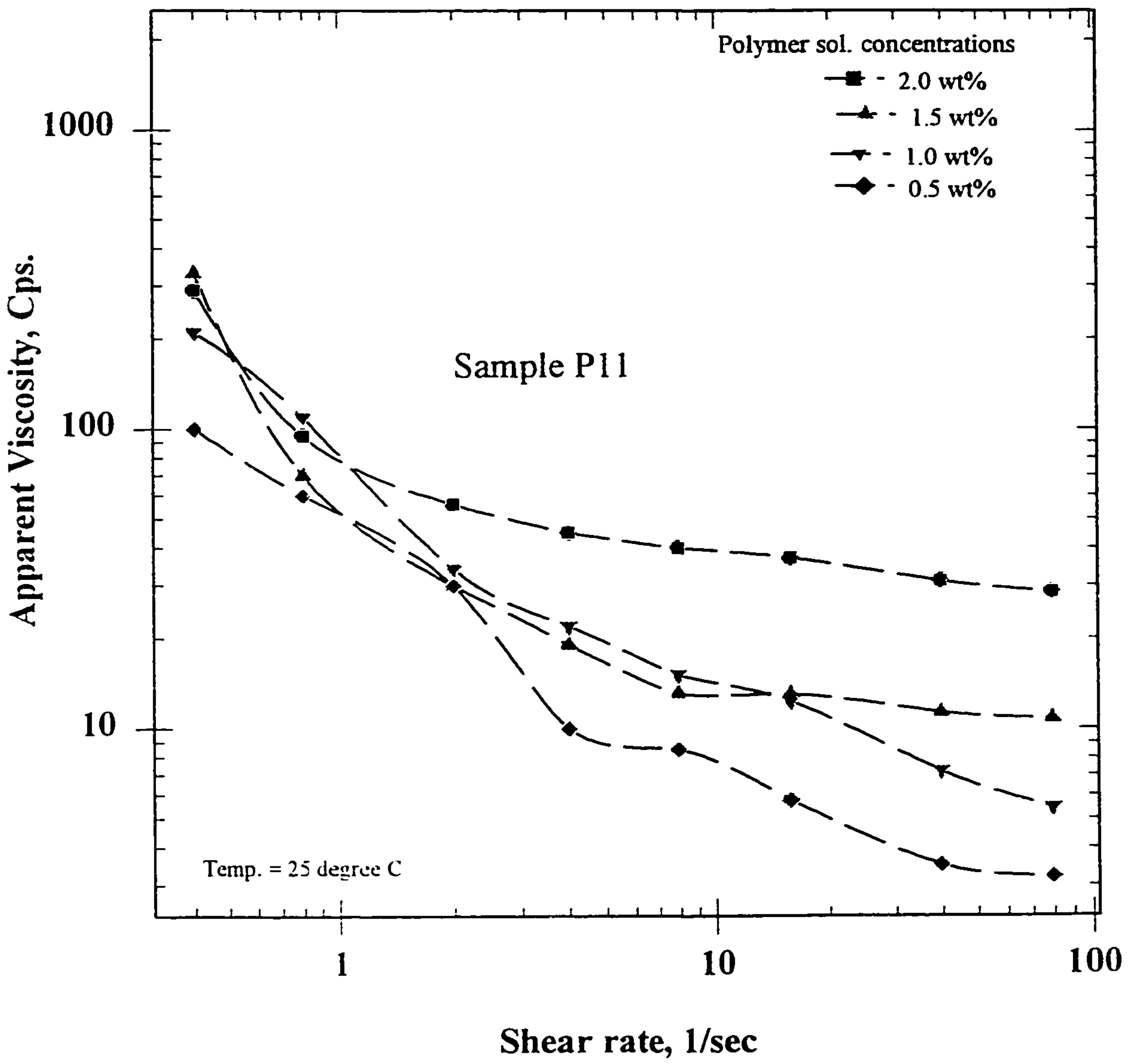


Figure 5-32; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate of viscosity in deionized water at 25 °C. Surfactant (CTAB, 2.68 wt %), hydrophobe (ST, 6 mol%), by micellar copolymerization.

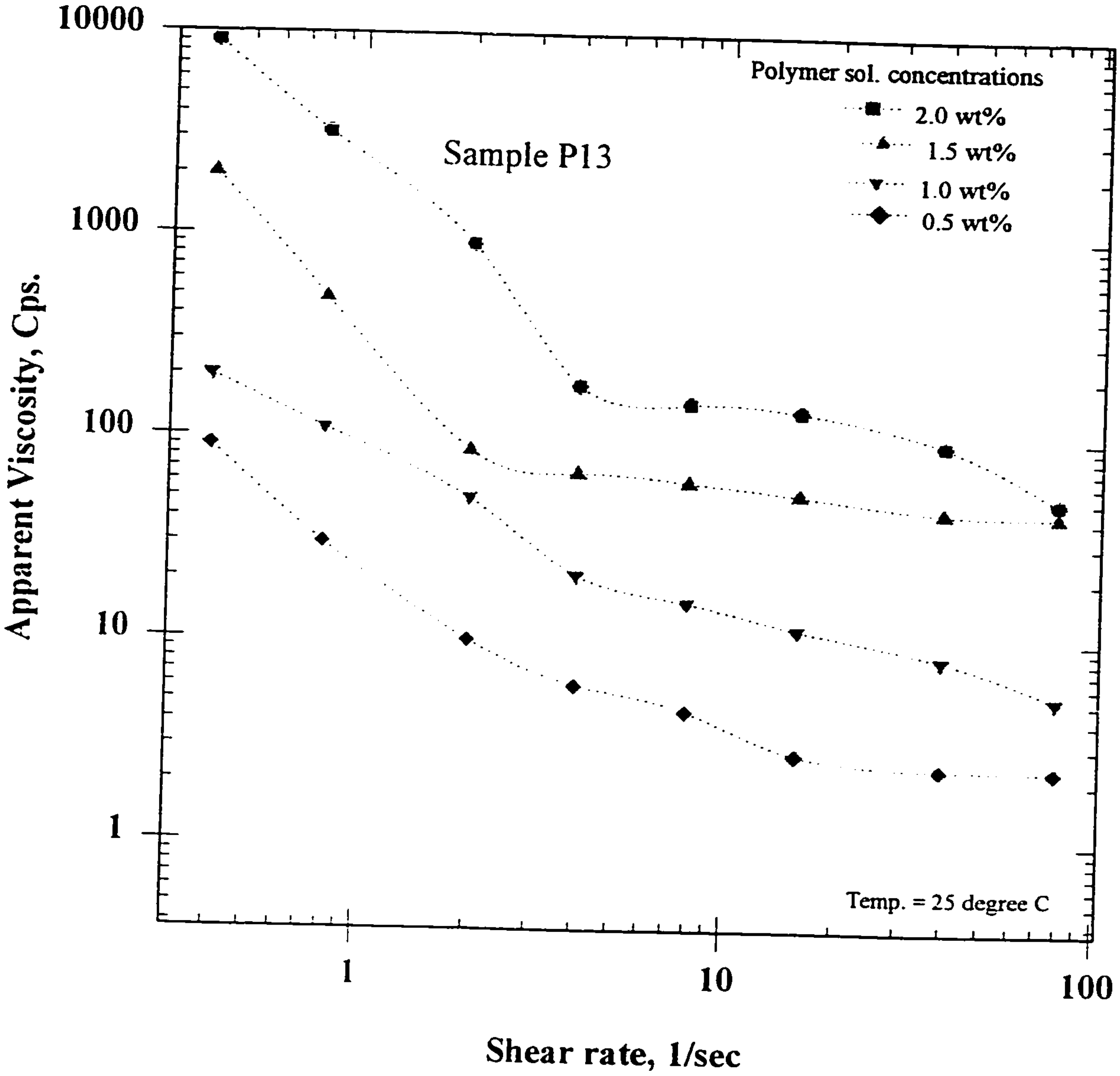


Figure 5-33; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (CTAB, 3.97 wt%), hydrophobe (ST, 7 mol%), by micellar copolymerization.

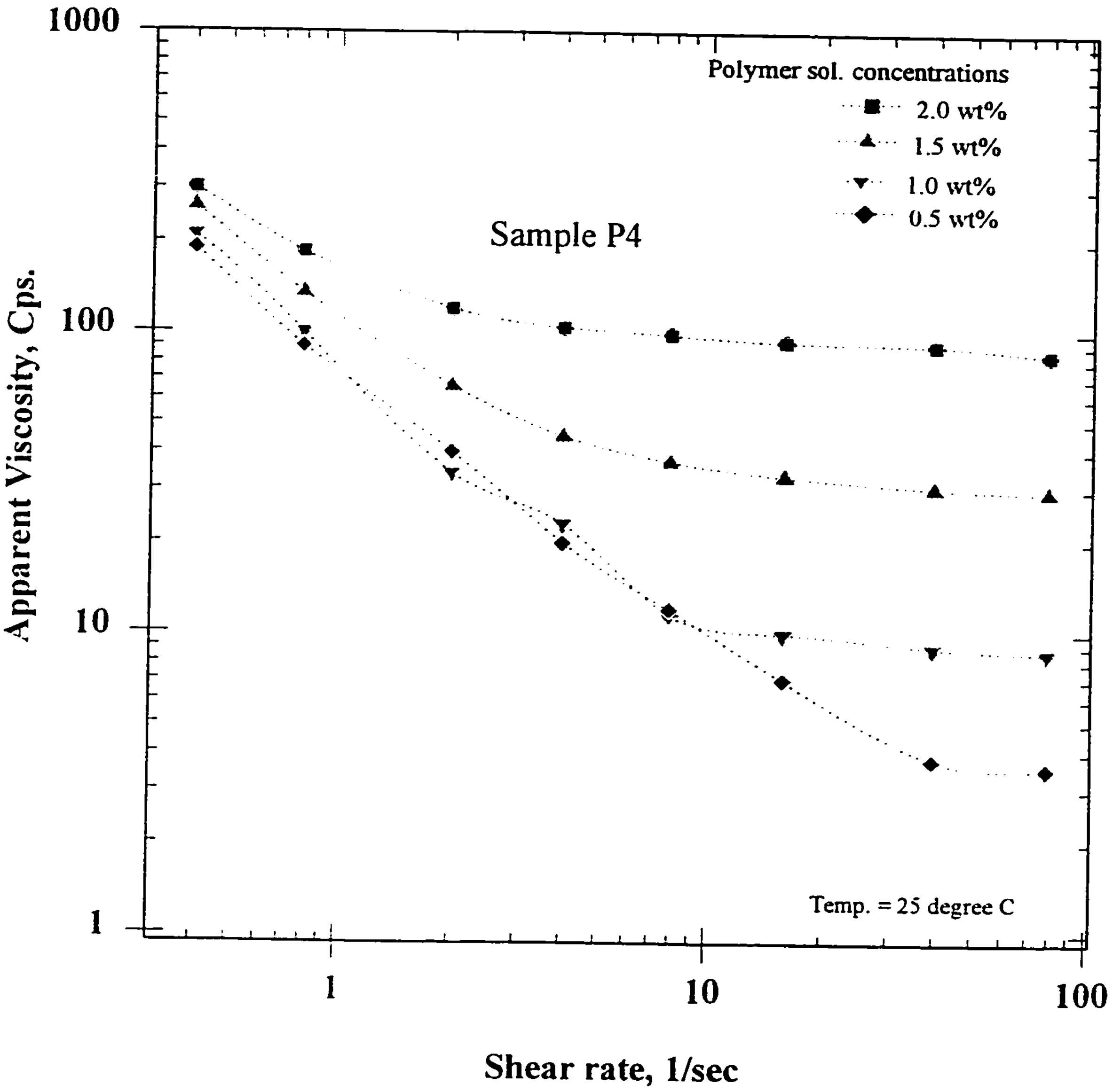


Figure 5-34; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS, 2 wt%), hydrophobe (ST, 3 mol%), by micellar copolymerization.

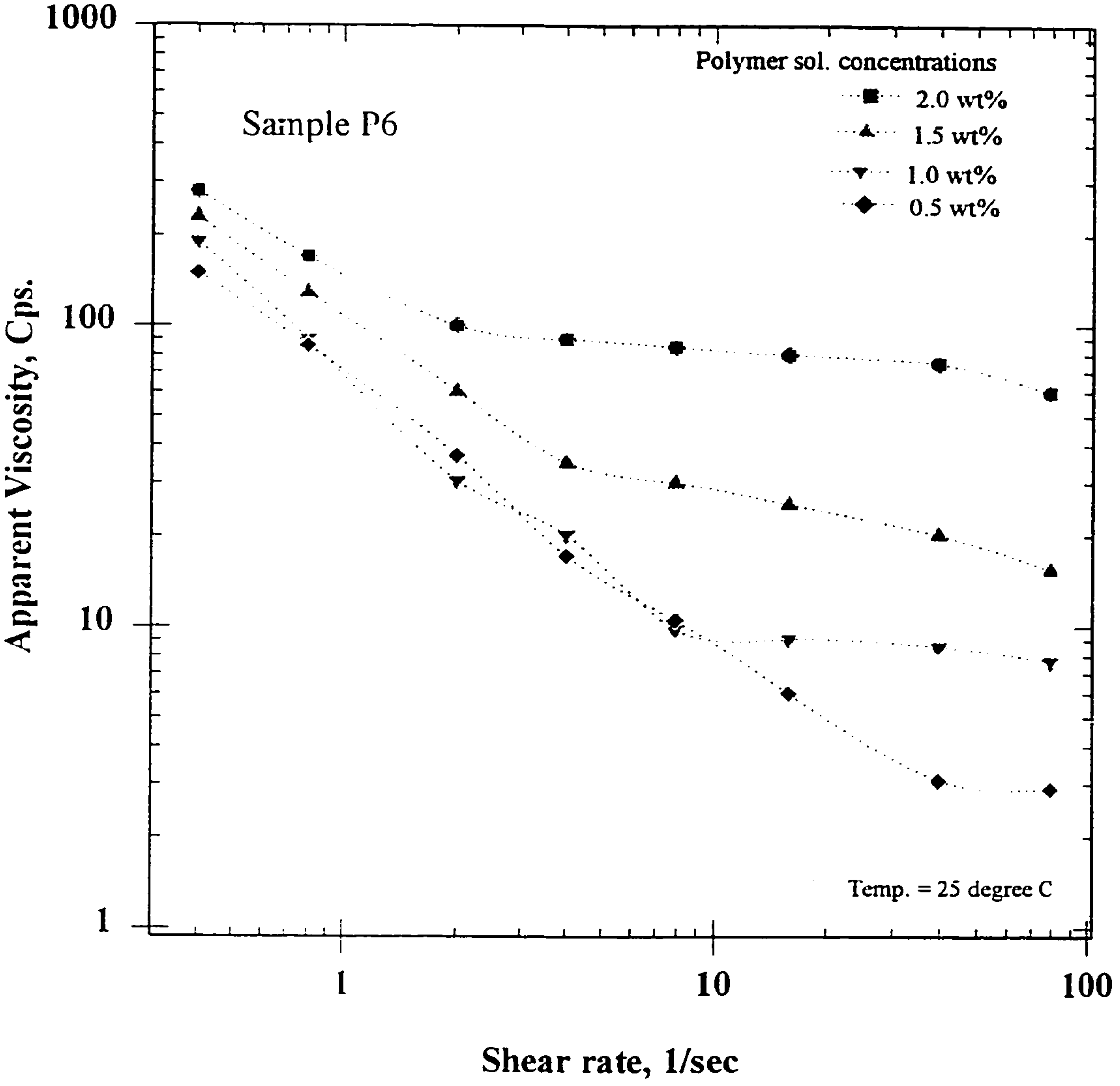


Figure 5-35; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (SDS, 3.15 wt%), hydrophobe (ST, 7 mol%), by micellar copolymerization.

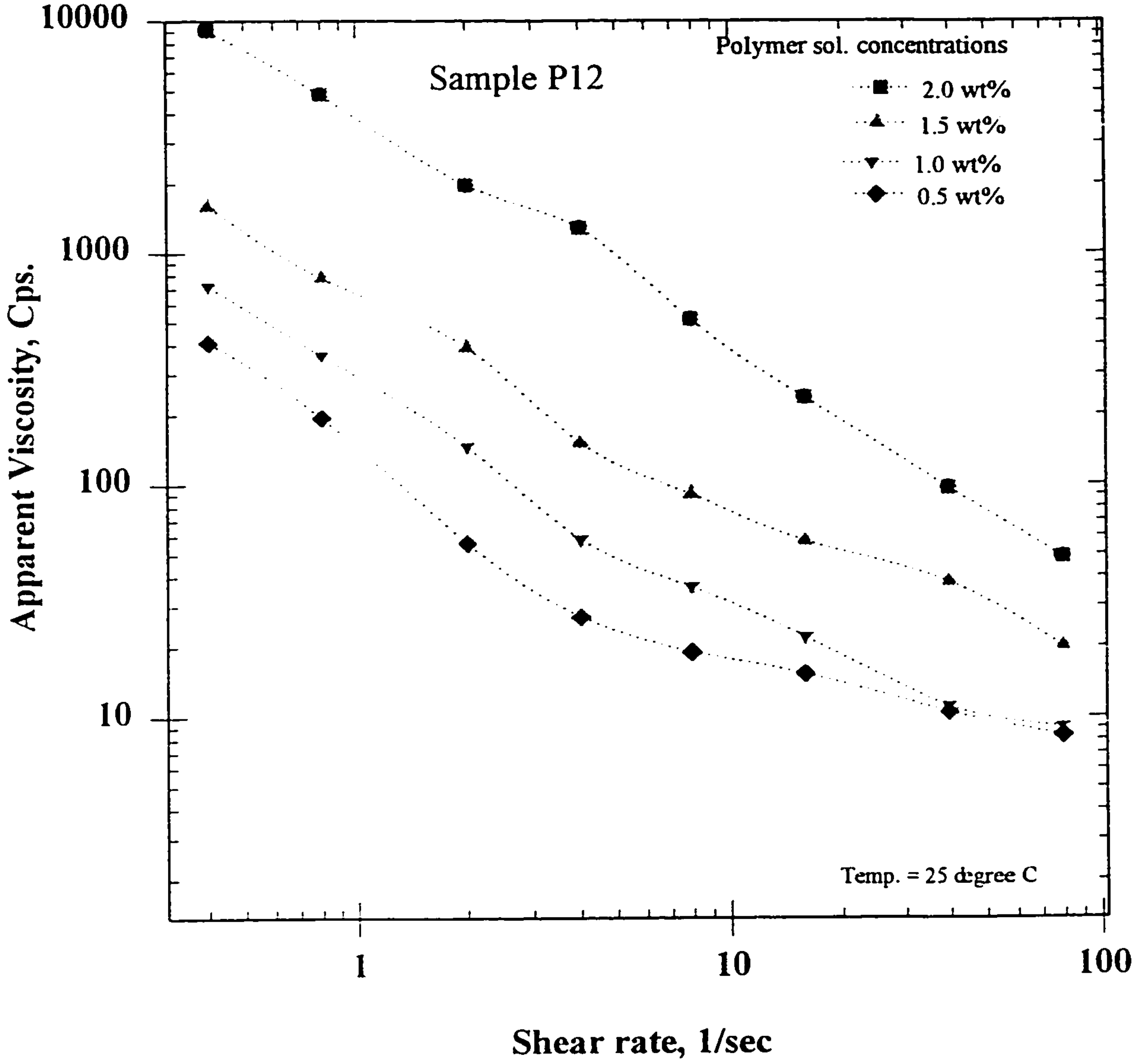


Figure 5-36; Effect of multi-block copolymer solution Poly(AM-b-ST) on the shear rate dependence of viscosity in deionized water at 25 °C. Surfactant (CTAB, 3.97 wt%), hydrophobe (ST, 7 mol%), by micellar copolymerization.

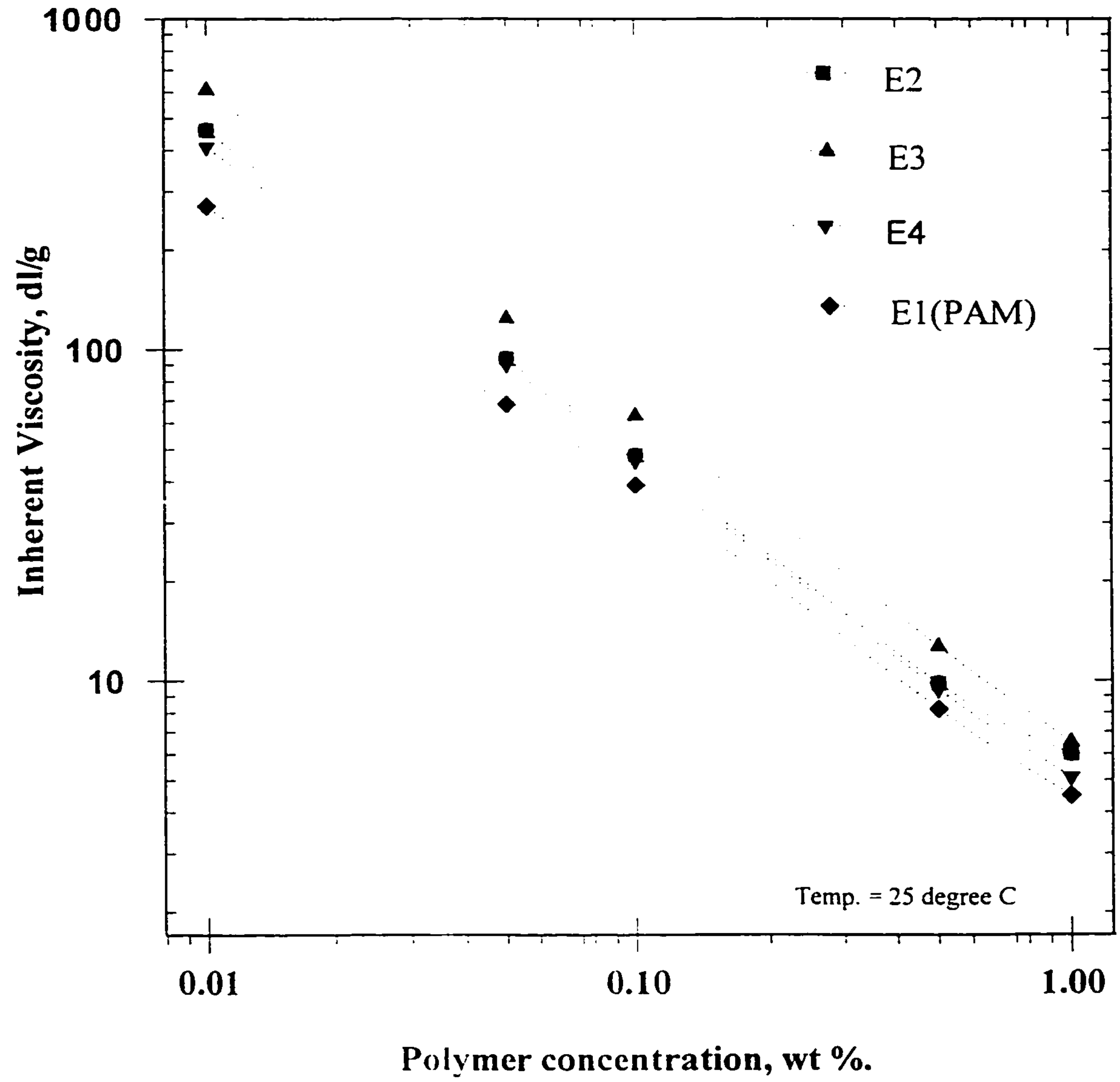


Figure 5-37; Effect of polymer concentration on the inherent viscosity of multi-block copolymers, E2, E3 and E4, poly(C12-b-AM) with 1, 2, 3 mol% C12. Sample E1 is homo-PAM. SDS in feed is 3 wt%. Samples prepared in deionized water at 25 °C and at shear rate 0.3 s^{-1}.

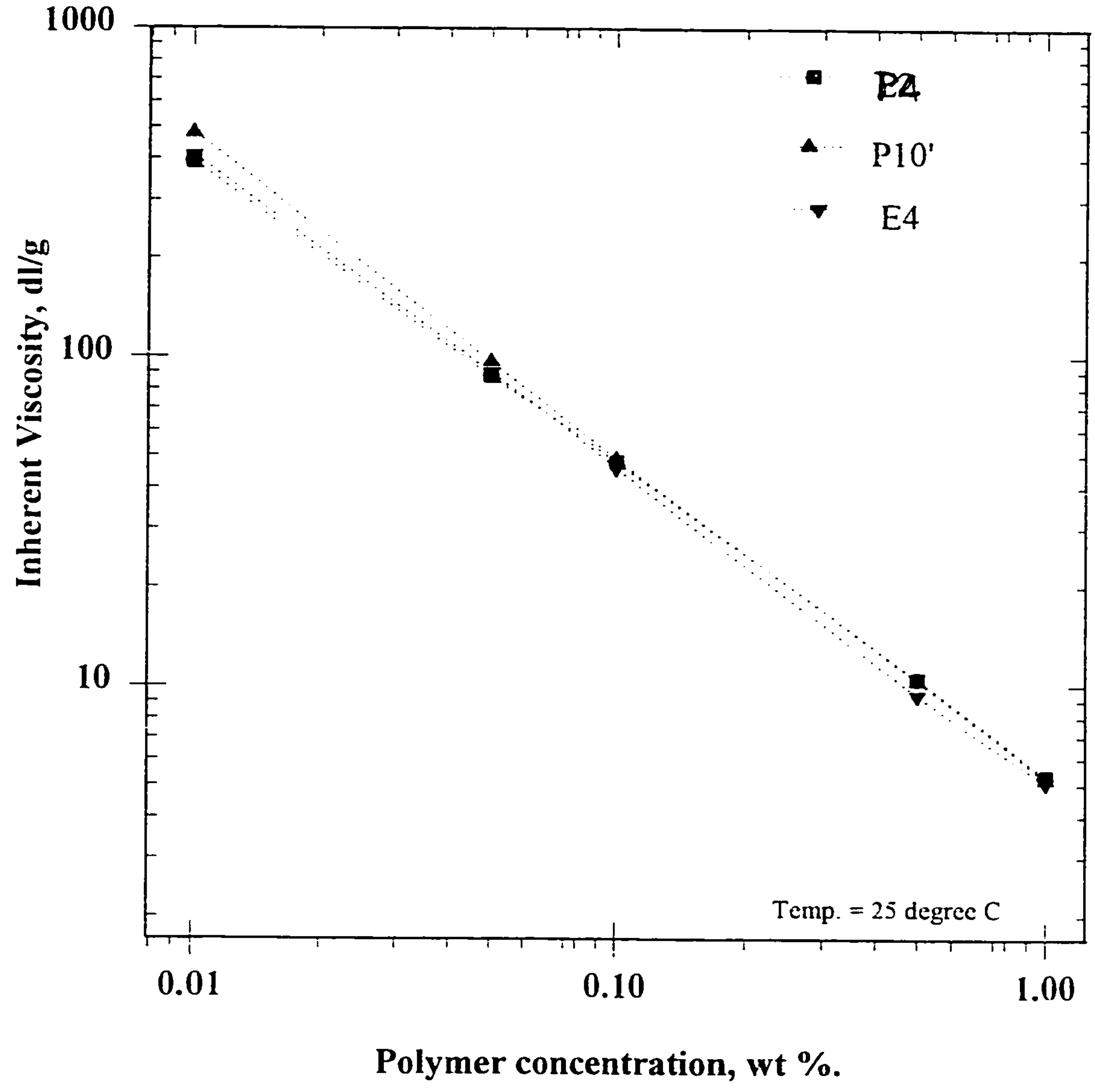


Figure 5-38; Effect of polymer concentration on the inherent viscosity of multi-block copolymers, P4, P10' poly(ST-b-AM) with 3 mol% ST and, E4 poly(C12-b-AM) with 3 mol% C12. Samples prepared in deionized water at 25 °C and at shear rate 0.3 s^{-1}.

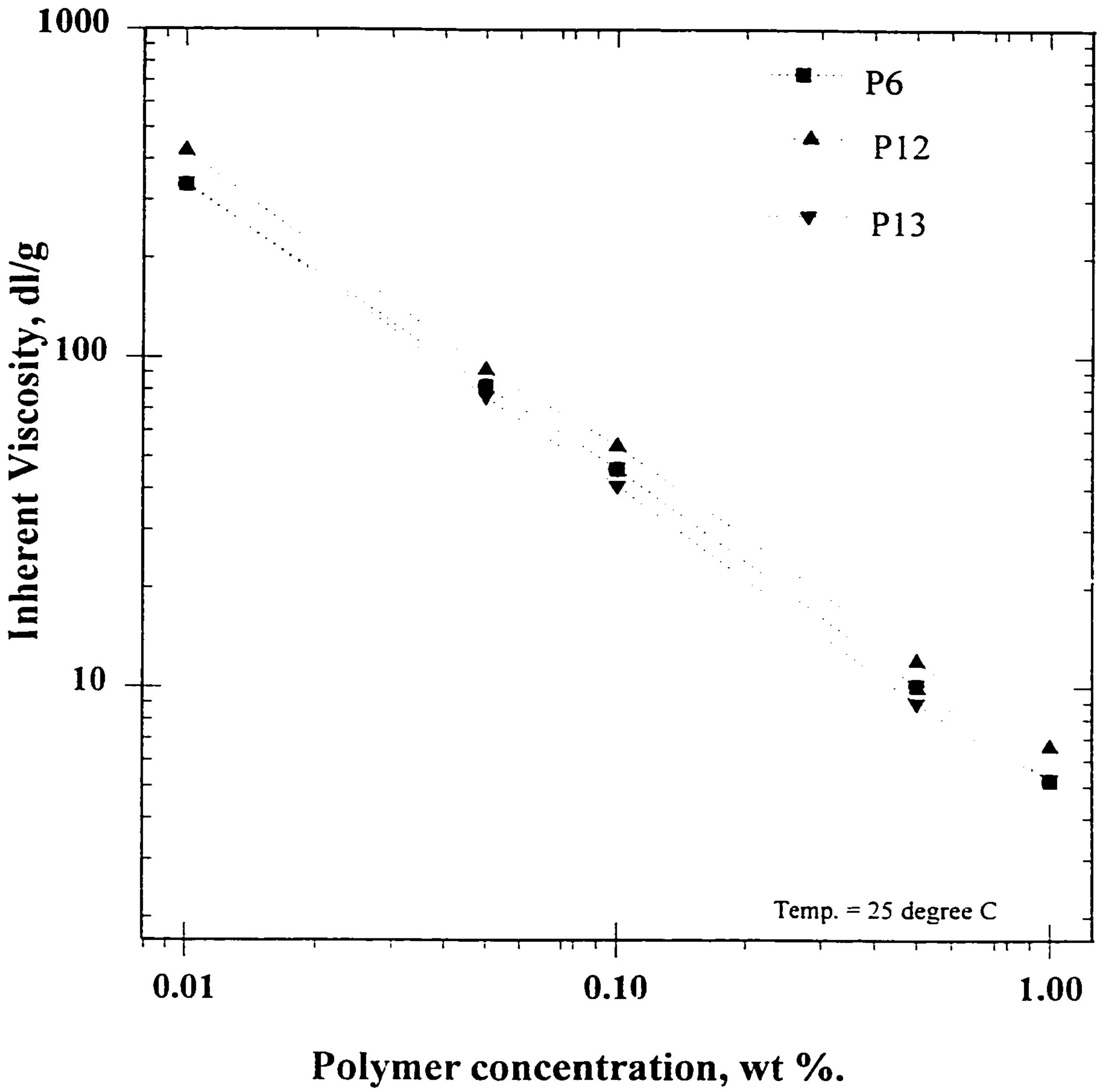


Figure 5-39; Effect of polymer concentration on the inherent viscosity of multi-block copolymers, P12, P13 and P6 poly(ST-b-AM) with 7 mol% ST. CTAB is used in synthesizing P12 and P13 samples. SDS is used in P6. Samples are prepared in deionized water at 25 °C and at shear rate 0.3 s^{-1}.

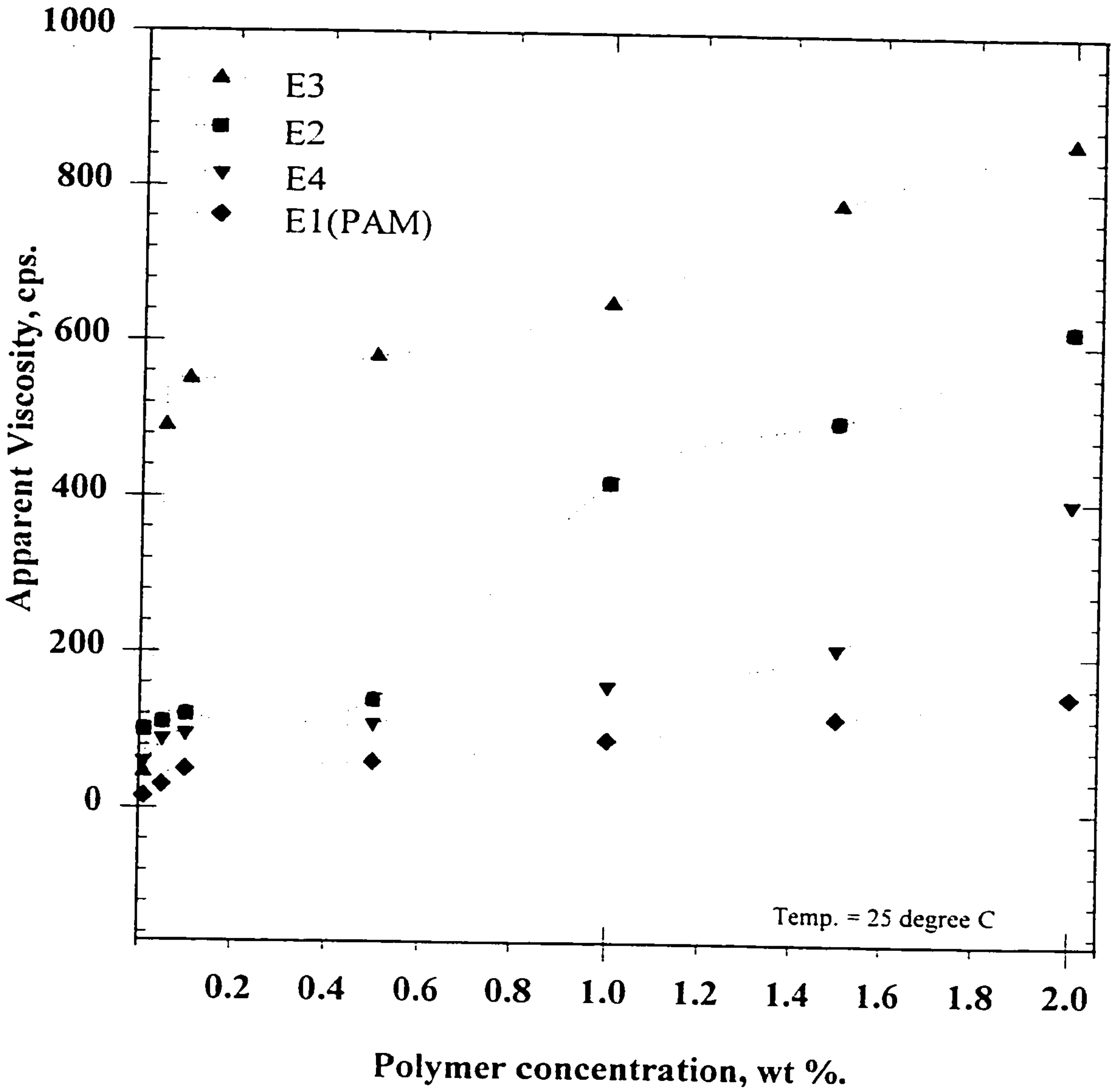


Figure 5-40; Effect of polymer concentration on the apparent viscosity of multi-block copolymers, E2, E3, and E4, poly(C12-b-AM) with 1, 2, 3 mol% C12. Sample E1 is a homo-PM. SDS in feed is 3 wt% in all. Samples are prepared in deionized water at 25 °C and at shear rate 0.4 s^{-1}.

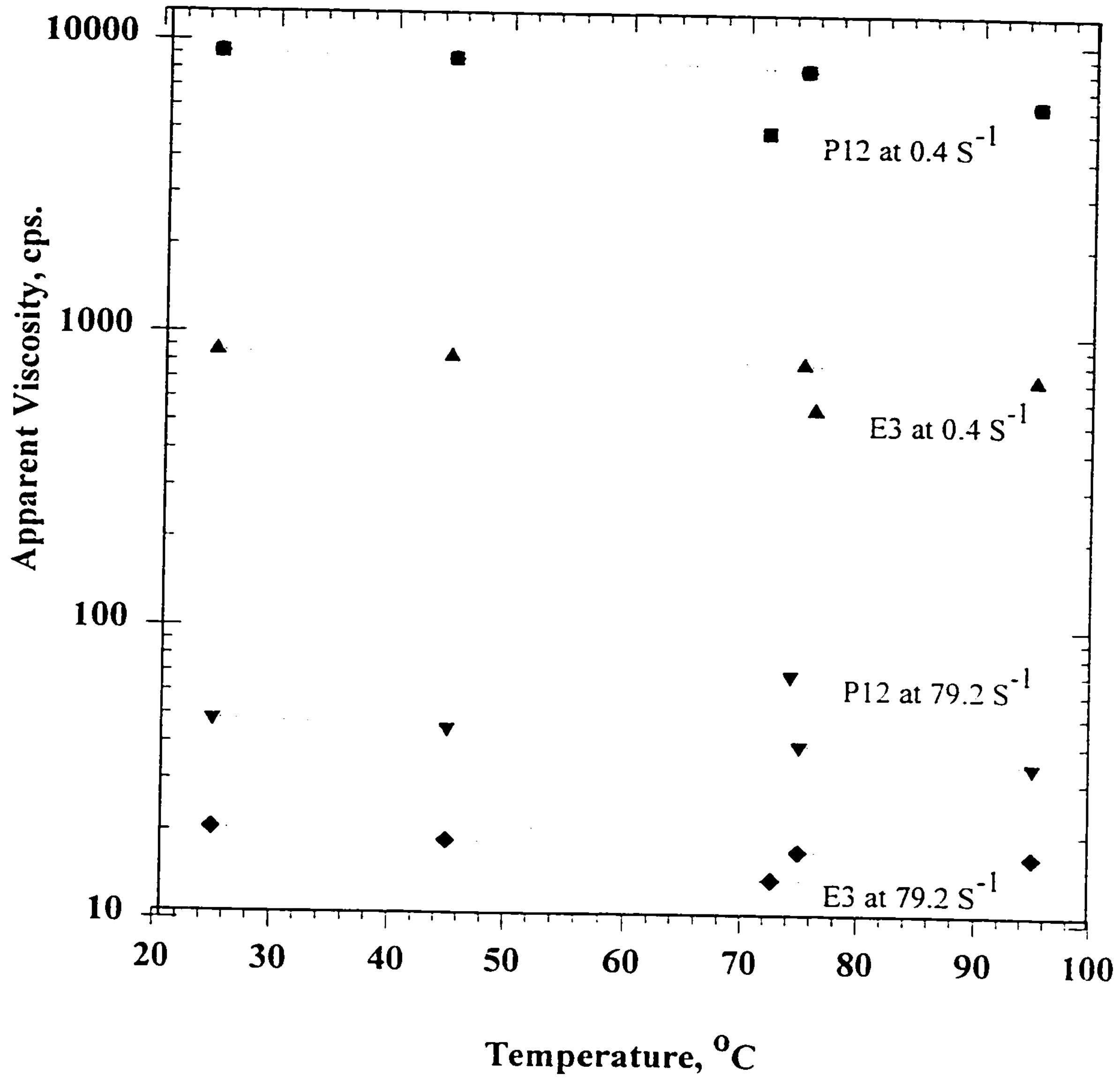


Figure 5-41; Effect of temperature on the apparent viscosity of multi-block copolymers; P12 poly(ST-b-AM) with 7 mol% ST and , E3 poly(C12-b-AM) with 2 mol% C12. Polymer concentration is 2 wt%. Samples are prepared in deionized water at 25 °C.

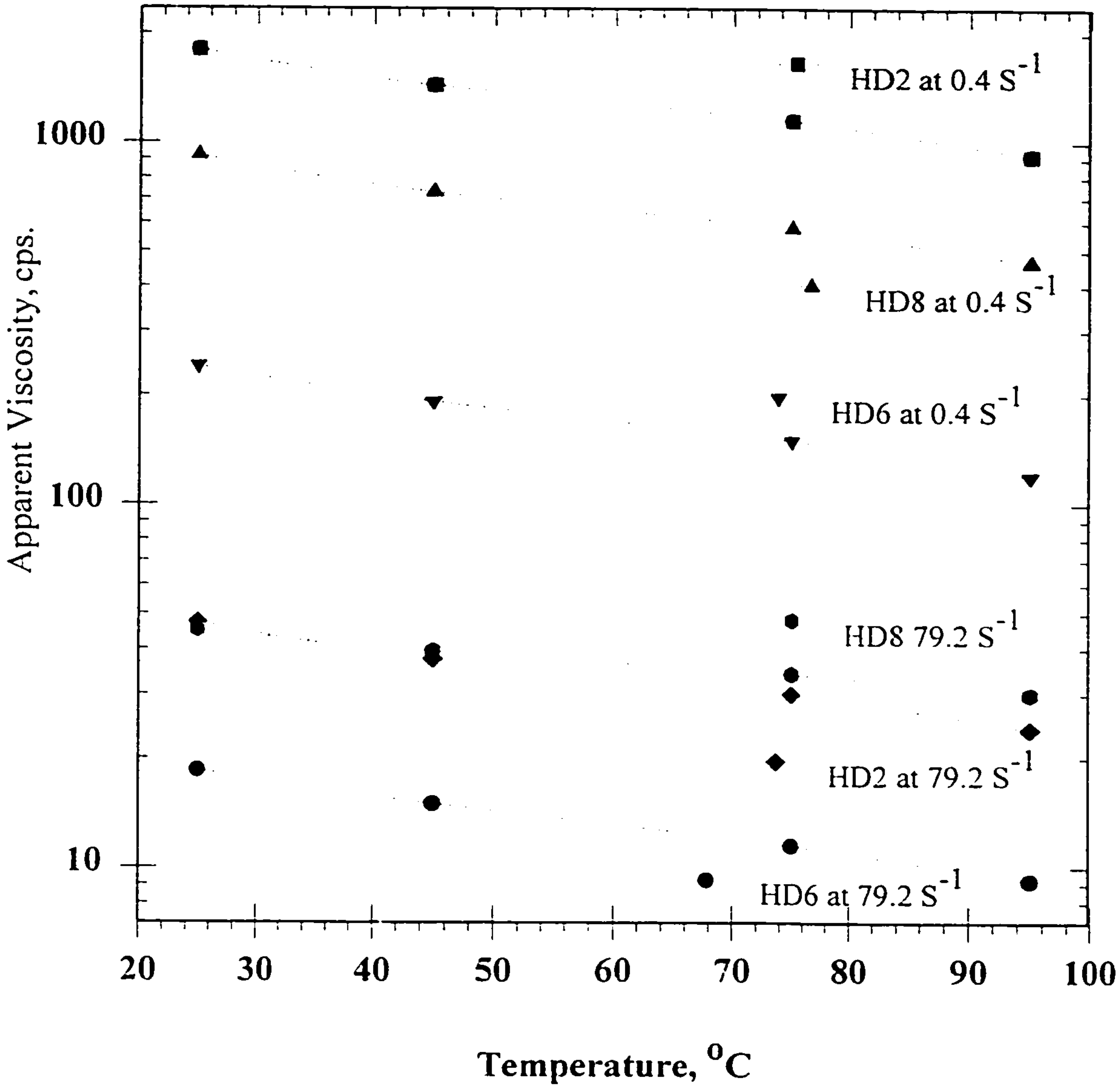


Figure 5-42; Effect of temperature on the apparent viscosity of di-block copolymers; HD2, HD6 poly(MMA-b-AN) with 38 mol% MMA and, HD8 poly (MMA-b-VI) with 34 mol% MMA. Polymer concentration is 2 wt%. Samples are prepared in deionized water at 25 °C.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Summary and General Conclusions

In this work, an attempt has been made to design novel series of amphiphilic ionic and nonionic associating block copolymers that can simultaneously provide high viscosity to pusher fluids (controlling the mobility) in reservoir flooding and also intra-low interfacial tension for enhanced microscopic displacement efficiency in enhanced oil recovery operations. In order to achieve this objective, two types of structures were successfully synthesized or modified including diblocks and multiblocks of copolymers having various interesting characteristics. The rheological solution behavior as well as surface and interfacial behaviors of the block copolymer solutions were studied with respect to their polymer concentrations, shear rates, temperature, salinity, molecular weight, and time history or storage. The aqueous solutions of the polymers exhibit reasonably high solution viscosity and, good surface and interfacial activity in brine solutions. Properties highly valuable in technological and industrial areas especially in enhanced oil recovery operations or any water-based systems.

It is worth mentioning that the only suitable classes of polymer candidates for investigations for enhanced oil recovery are: hydrophobically water-soluble copolymers (core-corona systems that produce regular micelles), amphiphilic block copolyelectrolytes, and possibly hydrophobically modified biopolymers. These systems would be the best possible areas of research for chemically enhanced oil recovery improvements.

6.2 Comparisons of the Di-blocks and Multi-blocks Copolymers

6.2.1 Viscosity Behavior

The results from this study indicate that ***viscosities*** of diblock copolymer solutions were found to be moderately low compared to viscosities imparted by associative thickeners. Large number of hydrophobic groups in hydrophobically associating polymers (ionic and nonionic) would usually results in lower thickening ability due to high intra-molecular hydrophobic association but with low surface and interfacial tension. The polymer solution of samples HD6 and HD8 exhibit lower thickening ability, relative to sample HD2, owing to hydrophobic association that it is predominantly intra-molecular in nature. HD2 copolymer, however, show greater thickening ability at low polymer concentrations. That's mainly due to longer inter-molecular hydrophobic association. So, it can be deduced that the longer the hydrophobic sequences (blocks) in the polymer structure, the higher is the viscosity. However, it should be pointed out that the number of hydrophobic associations should be reasonably low to maintain water solubility.

6.2.2 Surface and Interfacial Behavior

The results from this study indicate the ***surface and interfacial tension*** of diblock copolymer solutions were found to be moderately low compared to interfacial tensions imparted by conventional surfactants. For both types of block copolymers, a reasonable reduction of water surface tension is obtained. Surface and interfacial tensions decrease with increasing polymer concentrations for all the (co)polymer studied in this work. In the case of diblocks, sample HD8 (sodium poly(methacrylate-b-VI)) exhibits the highest surface and interfacial activity demonstrated by low values of surface and interfacial tensions (8.1 and 1.87 mN/m respectively) at polymer concentration of 1.5 wt % (15,000 PPM.). Moreover, this copolymer shows salt tolerancy beyond 10 wt % NaCl. For the other type of block copolymers, it was found that samples EXP3 and P12 exhibit higher surface and interfacial activities compared to the other copolymers studied. IFT of 0.5 mN/m at 10 wt % salt (NaCl) is obtained from EXP3 copolymer or poly(AM-b-C12) of 1.5 wt % concentration. No cmc or breakpoint resembling cmc by conventional surfactants is obtained the hydrophobically modified polyacrylamide.

Diblock copolyelectrolytes synthesized/modified in this study were found to suffer from the presence of electrolytes, especially divalents, due to charge shielding effects. The higher the charge density, the stronger is the suffering. It should pointed out, however, that multiblock copolymers behave differently because of their nonionic nature that allow high salt tolerancy. It was found that multiblock copolymer, P12, exhibits the highest thickening ability (10,110 cps.) at high salinity (10 wt %) among other copolymers investigated. At the same time the polymer (1.5 wt %) shows high surface and interfacial activity (43.1 and 1.01 mN/m respectively) at high salt content (10 wt %). Therefore, sample P12 considered to be *the most likely candidate* for EOR application among other polymers investigated. The viscosity of the random copolymer synthesized by homogenous process was found to be lower than the viscosity of the homopolyacrylamide, indicating that there is no significant hydrophobic association. However, both the homopolyacrylamide and the random copolymer exhibit close surface and interfacial tensions.

The results from this study indicate that diblock polyelectrolytes or hydrophobically modified sodium polymethacrylates give low viscosity and surface and interfacial tensions in the presence of salt. This class of amphiphilic block copolymers exhibit significant solution behaviors than the homopolymers comprising the copolymer. It is readily observed that the size of behavior is not enough for effective mobility control and/or displacement operations in enhanced oil recovery technology. However, sample HD2 exhibits moderate thickening ability and both surface and interfacial activity. Its 1.5 wt % concentration exhibits a viscosity of 1000 cps. at 0.8 s^{-1} compared to lower viscosity values imparted by HD6 and HD8 diblocks. Moreover high values of surface and interfacial tensions are exhibited by this type of polymers, as demonstrated by sample HD8, although the ultimate interfacial tension given by these polymers studied in this work does not fulfill the requirement of enhanced oil recovery operations. It is considered, however, a design matter not else because, as we believe, it is possible to obtain by proper designing polymers that have the ability to simultaneously provide and/or maintain high solution viscosity and ultra-low interfacial tension (IFT) to waterfloods environment used for enhanced oil recovery.

It is evident from the study that the rheological properties of hydrophobically associating water-soluble polymers (blocks and multiblocks) can be controlled by the nature/level of the hydrophobe, and the distribution of the hydrophobic groups (blocks). Most of the reported studies have concentrated only on investigating one polymer property regarding EOR property requirements, i.e., viscosity and interfacial activity. The results presented in this study show, however, that the dual properties in one polymer are of significant investigation for the process. It was demonstrated that by simply varying the experimental design conditions we were able to control the monomer sequence distribution of the copolymers and therefore to control their rheological properties. Moreover, foaming properties of copolymers prepared by micellar process support the amphiphilic nature of block copolymers that are usually synthesized to be used as polymeric surface active agents.

It can be observed that incorporating small amount of hydrophobic groups on the backbone of polyacrylamide leads to enhancements in its thickening ability and surface and interfacial activity as evidence from the values of viscosity and IFT of the block copolymers (ionic and nonionic). The thickening ability of the copolymers is attributed to strong intermolecular hydrophobic association. In addition, balance between the hydrophilic and hydrophobic forces on the polymer backbone promotes interfacial activity and soluibilization power. Adsorption and reorientation of amphiphilies at the interface are responsible for lowering the IFT as well. It was also found that addition of salt to the nonionic multiblock copolymer solutions promote aggregation of micelles and this results in high thickening ability manifested by higher values of viscosity. On the hand, amphiphilic block copolyelectrolytes exhibit lower salt tolerance owing to their polyelectrolytes nature where electrostatic charge-charge shielding causes the macromolecular coil to collapse leading to smaller hydrodynamic volume and hence low viscosification efficiency.

6.3 Recommendations

For any effectiveness in a polymer system, different tests (characterizations) should be carried out following the synthesis part to gain a lot from the synthesis, but sometimes it is not affordable. Great body of data definitely supports the work for modeling purposes. For example, it is necessary to develop afterwards a molecular model that can predict exactly the interfacial tension behavior of the copolymer solutions in an aqueous/brine media. Similarly in order to test the data generated in this study a proper rheological/viscometric model should be developed and allows for predicting the behavior of the polymer solutions subjected to different additives and conditions.

Moreover, a study of phase behavior for these two types of block copolymers with different hydrocarbons should be carried out to elucidate the conditions of change in the middle phase microemulsions that it is responsible for ultra-low interfacial tension.

The sample storage stability should be also investigated thoroughly by modifying the polymer structure or segments that are responsible for physical hydrolysis. The aging behavior of hydrophobically modified (co)polyacrylamides is attributed to the hydrolysis of the amide groups to polyacrylic acid counterpart.

Also making injectibility tests on sandstone and/or carbonate rock samples resembling the flooding operations in enhanced oil recovery is recommended, since it would provide more confidence in the effectiveness of the polymer properties.

Preparation of the polymer solutions by different methods such as freezing/thawing, freeze drying/redissolution and dialysis would greatly affect the properties of the polymer solutions. From this prospective the polymers should be investigated as well. In this study only the precipitation/redissolution cycles of sample preparations were employed.

Finally, by considering all conclusions and recommendations cited at this work, improved polymers, that can effectively provide favorable and desirable solution properties to waterfloods used for enhancing oil recovery from subterranean formations, could be designed at the probable theoretical region located in-between hydrophobicity and hydrophilicity regions.

APPENDIX - A

Rheological/Viscosity Behavior

Table 5.5, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P11 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	290	332	210	100
0.6	0.8	95.0	70.1	110	60.1
1.5	2.0	56.1	30.0	34.1	30.1
3.0	4.0	45.1	19.0	22.0	10.0
6.0	7.9	40.1	13.1	15.1	8.52
12	15.8	37.1	13.0	12.3	5.76
30	39.6	31.1	11.3	7.21	3.51
60	79.2	28.6	10.8	5.46	3.21

Table 5.6, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P13 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	9020	2000	200	90.2
0.6	0.8	3200	485	110	30
1.5	2.0	910	86.2	50.2	10
3.0	4.0	183	67.1	21.0	6.0
6.0	7.9	150	60.8	15.5	4.51
12	15.8	138	53.2	11.5	2.76
30	39.6	96	44.4	8.32	2.40
60	79.2	50	43.0	5.31	2.35

Table 5.7, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P4 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	300	260	210	190
0.6	0.8	185	135	100	90.2
1.5	2.0	120	66.3	34.1	40.1
3.0	4.0	104	45.1	23.1	20.0
6.0	7.9	98.5	37.1	11.5	12.0
12	15.8	93.5	33.2	10.0	7.01
30	39.6	91.5	30.6	9.02	3.81
60	79.2	85	29.6	8.67	3.56

η_a ; Apparent viscosity, RPM; Revolution Per Minute

Table 5.8, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P6 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	280	230	190	150
0.6	0.8	170	129	90	86.0
1.5	2.0	100	60.5	30.5	37.1
3.0	4.0	90	35	20.2	17.2
6.0	7.9	85	30	9.8	10.5
12	15.8	80	25.5	9.1	6.01
30	39.6	75	20.2	8.6	3.1
60	79.2	60	15.5	7.7	2.9

Table 5.9, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P15 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	270	200	180	170
0.6	0.8	195	105	95.1	90.2
1.5	2.0	90.2	50.1	38.1	24.0
3.0	4.0	66.1	35.1	19.0	17.0
6.0	7.9	49.1	29.6	11.5	9.52
12	15.8	40.0	24.0	10.3	7.77
30	39.6	33.2	18.4	8.62	4.01
60	79.2	31.6	17.0	7.46	3.91

Table 5.10, The viscosity-shear rate relationship for multi-block copolymer of polyAM-block-polyST or P12 for specified polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	9150	1600	721	411
0.6	0.8	4830	782	361	195
1.5	2.0	1970	391	146	56.1
3.0	4.0	1280	151	58.1	27.0
6.0	7.9	515	91.0	36.1	19.0
12	15.8	237	57.0	22.0	15.3
30	39.6	96.5	38.0	11.1	10.5
60	79.2	48.4	20.0	9.01	8.32

η_a ; Apparent viscosity, RPM; Revolution Per Minute

Table 5.11, The viscosity-shear rate relationship for a multi-block copolymer of polyAM-block-polyST or (sample P5) for polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt%, in Cps	η_a of 0.01wt%, in Cps
0.3	0.4	2010	505	251	230	200	190	130
0.6	0.8	1250	325	182	150	102	90.2	65.1
1.5	2.0	615	120	80.0	52.1	36.1	24.1	22
3.0	4.0	181	50.1	41.8	30.1	13	10.1	8.02
6.0	7.9	92.5	36.0	26.0	15.5	6.01	5.51	5.01
12	15.8	73.2	29.2	17	9.52	3.51	2.5	2.25
30	39.6	57.0	23.5	13	5.41	2.6	2.3	2.1
60	79.2	35.0	22.1	12.1	4.56	1.8	1.66	1.5

Table 5.12, The viscosity-shear rate relationship for a multi-block copolymer of polyAM-block-polyST or (sample P7) for polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt%, in Cps	η_a of 0.01wt%, in Cps
0.3	0.4	356	250	190	180	170	150	130
0.6	0.8	210	180	115	85.2	80.2	75.2	70.1
1.5	2.0	98.6	86.1	70.0	40.1	34.0	28.1	22.0
3.0	4.0	58.2	34.1	22.1	20.0	18.0	16.0	12.0
6.0	7.9	31.1	18.0	12.0	10.5	8.52	7.52	6.51
12	15.8	34.3	10.8	7.01	5.01	4.76	4.01	3.51
30	39.6	13.3	7.41	5.81	3.92	3.32	2.91	2.7
60	79.2	9.92	5.41	4.16	2.81	2.25	2.20	2.1

Table 5.13, The viscosity-shear rate relationship for a multi-block copolymer of polyAM-block-polyST or (sample P10') for polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	540	230	191	172	140	130	120
0.6	0.8	155	120	105	85.3	60.1	45.1	40.1
1.5	2.0	105	63.8	41.0	34.2	24.0	22.0	20.0
3.0	4.0	72.0	48.1	23.0	20.0	18.0	15.0	10.0
6.0	7.9	54.1	36.1	15.2	10.5	7.1	5.8	5.0
12	15.8	53.0	30.1	12.4	6.80	4.3	4.01	3.26
30	39.6	48.0	36.7	10.5	5.76	3.11	2.82	2.7
60	79.2	45.5	24.0	9.30	4.51	2.65	2.50	2.30

η_a; Apparent viscosity, RPM; Revolution Per Minute

Table 5.14, The viscosity-shear rate relationship for a random copolymer of polyAM-*random*-polyST or (sample P) for polymer concentrations at 25 °C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	170	150	140	120	110	100	90.2
0.6	0.8	100	65.0	60.1	45.1	40.1	38.0	36.0
1.5	2.0	50.0	35.1	23.0	20.0	18.0	17.1	16.1
3.0	4.0	35.0	18.1	15.1	13.0	12.0	11.2	10.0
6.0	7.9	25.2	12.1	11.1	8.52	8.02	6.2	6.01
12	15.8	20.1	10.1	7.01	6.72	6.01	5.51	3.81
30	39.6	14.2	8.51	5.50	4.51	3.41	2.81	2.01
60	79.2	10.2	7.50	4.60	3.91	2.70	2.50	1.76

Table 5.15, The viscosity-shear rate relationship for a polyAM or (sample EXP1) for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	150	120	90.1	60.5	50.1	30.2	15.1
0.6	0.8	100	60.1	45.2	40.1	34.1	19.1	10.0
1.5	2.0	32.1	28.1	20.01	14.1	12.01	7.02	4.50
3.0	4.0	25.2	16.01	15.1	8.02	5.10	4.01	2.10
6.0	7.9	11.4	8.51	6.01	4.56	4.01	2.10	1.01
12	15.8	9.01	5.76	4.01	3.26	2.21	1.50	0.9
30	39.6	8.2	4.51	3.71	3.01	1.6	1.10	0.6
60	79.2	7.1	4.34	2.91	2.30	1.4	0.81	0.2

Table 5.16, The viscosity-shear rate relationship for a multiblock copolymer of polyAM-block-polyST or (sample EXP2) for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	620	501	421	140	120	110	100
0.6	0.8	420	391	256	90.2	80.1	70.2	65.1
1.5	2.0	310	200	125	58.1	44.1	35.1	32.1
3.0	4.0	72.1	60.1	45.1	33.1	61.0	15.0	13.1
6.0	7.9	51.1	40.1	34.6	13.0	12.01	11.0	6.01
12	15.8	35.1	45.6	22.5	8.52	7.51	6.27	3.26
30	39.6	14.6	13.1	11.2	6.01	3.51	3.32	2.15
60	79.2	11.8	10.6	9.35	4.81	2.45	2.3	1.9

η_a ; Apparent viscosity
RPM; Revolution Per Minute

Table 5.17, The viscosity-shear rate relationship for a multiblock copolymer of polyAM-block-polyST or (sample EXP3) for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	862	781	651	581	550	490	450
0.6	0.8	321	250	230	210	195	175	115
1.5	2.0	112	92.1	73.8	60.2	55.1	50.1	44.6
3.0	4.0	86.2	58.2	38.1	29.1	25.0	19.0	12.0
6.0	7.9	39.4	36.1	28.1	20.5	18.0	15.5	10.1
12	15.8	27.1	18.2	13.0	10.8	8.20	7.77	6.01
30	39.6	21.7	11.8	8.68	7.51	6.91	4.61	4.21
60	79.2	20.5	9.17	6.46	4.01	3.67	2.76	1.85

Table 5.18, The viscosity-shear rate relationship for a multiblock copolymer of polyAM-block-polyST or (sample EXP4) for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps	η_a of 0.1 wt%, in Cps	η_a of 0.05wt% , in Cps	η_a of 0.01wt% , in Cps
0.3	0.4	400	210	160	110	96.3	89.2	60.1
0.6	0.8	301	145	100	60.1	40.1	35.1	20.1
1.5	2.0	126	100	60.2	14.1	12.01	8.02	5.50
3.0	4.0	108	26.2	10.01	8.02	5.01	4.02	2.60
6.0	7.9	66.0	11.5	6.51	4.51	4.01	2.50	1.50
12	15.8	20.2	9.02	4.76	3.26	2.25	1.70	1.10
30	39.6	14.5	8.12	4.51	3.01	2.10	1.50	0.7
60	79.2	8.62	7.77	4.34	2.20	1.45	0.9	0.5

Table 5.19, The storage time-viscosity-shear rate relationship for a multiblock copolymer of polyAM-block-polyST or (sample P15) after 10 monthes from the initial mixing for different concentrations at 25°C.

RPM	Shear rate, S^{-1}	η_a of 2.0 wt%, in Cps	η_a of 1.5 wt%, in Cps	η_a of 1.0 wt%, in Cps	η_a of 0.5 wt%, in Cps
0.3	0.4	180	115	110	100
0.6	0.8	115	80.0	55.1	55.1
1.5	2.0	58.1	42.1	30.0	18
3.0	4.0	40.1	34.1	12.02	11.1
6.0	7.9	35.1	24.5	9.02	8.52
12	15.8	31.7	21.2	7.77	7.01
30	39.6	30.2	17.9	7.62	6.3
60	79.2	28.1	16.7	7.16	4.1

η_a ; Apparent viscosity, RPM; Revolution Per Minute

APPENDIX - B

Surface/ Interfacial Activity

Table 4-14 ; Surface Tensions in mN/m of Ionic Di-block Copolymers @ 25 °C and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt %.

Sample code	Structure	at 0.01 wt %	at 0.05 wt %	at 0.1 wt %	at 0.5 wt %	at 1.0 wt %	at 1.5 wt %	at 2.0 wt %
HD2	Hydrolized Poly(AN-b-MMA)	68.62	66.70	58.79	57.67	57.30	54.10	48.73
HD6	Hydrolized Poly(AN-b-MMA)	70.86	68.61	63.65	52.88	46.16	51.02	49.06
HD8	Hydrolized Poly(VI-b-MMA)	66.20	65.71	64.43	58.73	55.83	51.48	50.18

* A stock solution of 2 wt % of each sample is used to make the solutions by dilution.

& The surface tension of distilled water at air-water interface was found to be 72.21 mN/m.

Master Table 4-15: Rheology and Surface Activity of Amphiphilic Ionic Diblock Copolymer Solutions of 1.5 wt % in (1.0 wt % to 10 wt %) NaCl Concentrations at 25 °C.

Sol. Poly. conc., 1.5 wt % ⇓	Effect of NaCl Concentration on polymer solutions, in (wt %) NaCl								
NaCl Conc., wt % ⇒	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample Code: **HD2** Surface Tension at 25 °C vs. salt %	54.10	52.34	49.10	47.17	45.98	44.82	43.06	42.86	41.01
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	1000	551	381	300	250	200	190	150	140
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	32.2	9.72	9.18	8.42	6.94	6.61	5.51	4.91	4.84
Sample Code: **HD6** Surface Tension at 25 °C vs. salt%	51.02	50.51	50.91	49.36	48.81	43.92	42.41	40.50	40.00
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	210	205	200	190	170	160	140	120	100
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	14.6	10.6	8.56	7.86	6.31	5.91	4.81	4.34	4.16
Sample Code: **HD8** Surface Tension at 25 °C vs. salt%	51.48	45.11	40.66	39.21	38.60	37.34	36.20	35.74	35.00
Viscosity in cps. at shear rate of 0.8 (1/s) vs. salt%	812	721	710	651	550	500	441	381	332
Viscosity in cps. at shear rate 79.2 (1/s) vs. salt%	43.1	21.7	18.5	17.2	14.2	11.1	9.75	8.32	8.10

Note; a 1.5 wt % of HD8 copolymer shows good salt tolerancy at 10 wt % NaCl, 332 cps. at 25 °C.

Table 4-16 : The Effect of NaCl Concentration on the IFT of Aqueous Solutions of Ionic Di-block Copolymer HD8 and HD6 for 0.5 and 1.5 wt % Polymer Concentration at 25 °C.

NaCl conc, wt %	IFT[a], (mN/m) of Copolymer Sample **HD6**, at Poly. Conc. of		IFT, (mN/m) of Copolymer Sample **HD8**, at Poly. Conc. of	
	0.5 wt %	**1.5 wt %**	**0.5 wt %**	**1.5 wt %**
0.0	21.12	11.56	19.60	10.09
1.0	10.35	7.25	6.65	4.73
2.0	8.51	6.82	5.96	4.50
3.0	7.43	5.23	5.10	4.00
5.0	6.18	4.81	4.52	3.87
6.0	5.83	4.43	4.12	3.54
7.0	5.15	4.01	3.93	3.27
9.0	4.21	3.51	3.21	2.51
10.0	4.01	3.28	3.10	1.87

a IFT at (deionized water/n-decane) interface at 25 °C. = 45.64 mN/m.

Table 5-24; Surface Tensions (in mN/m) of Nonionic Multi-block Copolymers at 25°C and it's Dependence on Polymer Solution Concentration Ranging from 0.01 to 2.0 wt %.

Sample code	Structure	at 0.01 (wt %)	at 0.05 (wt %)	at 0.1 (wt %)	at 0.5 (wt %)	at 1.0 (wt %)	at 1.5 (wt %)	at 2.0 (wt %)
P10'*	Poly(AM-b--ST)	67.69	60.86	57.09	56.05	54.39	53.71	53.57
P11	Poly(AM- b--ST)	70.88	66.38	65.59	44.82	48.30	47.93	47.59
P12	Poly(AM- b--ST)	69.58	66.87	55.33	49.20	44.10	48.52	37.44
P13	Poly(AM- b--ST)	71.47	69.80	65.37	56.70	55.06	65.93	52.61
P15	Poly(AM- b--ST)	71.85	68.31	63.93	51.04	53.25	52.96	57.88
P4*	Poly(AM- b--ST)	65.72	59.85	59.50	85.20	57.58	57.12	56.89
P5*	Poly(AM- b--ST)	72.20	71.76	71.60	49.82	50.83	56.02	61.30
P6	Poly(AM- b--ST)	65.43	55.66	5020	54.01	55.17	55.53	57.91
P7*	Poly(AM- b--ST)	60.16	58.23	56.99	55.58	53.57	50.39	45.29
E1*	Poly(AM)	61.20	61.02	55.05	43.80	42.76	42.10	40.10
E2*	Poly(AM- b--C12)	60.32	53.24	51.69	40.04	39.54	35.60	32.33
E3	Poly(AM- b--C12)	50.68	52.95	48.18	47.41	39.02	37.21	34.67
E4*	Poly(AM- b--C12)	60.82	55.05	49.96	45.39	40.25	36.38	32.11
P*	Poly(AM-R-ST)	70.25	68.19	64.60	61.45	61.43	59.83	52.36

* A stock solution of 2 wt % of each sample was used to make the solutions by dilution, other solutions were prepared individually.

Master Table 5-25: Rheology (Viscosity vs Shear Rate) and Surface Activity of Amphiphilic Non-ionic Multi-block[a] Copolymer Solutions of 1.5 wt % in NaCl Concentrations Ranging from 1.0 wt % to 10 wt % at 25°C.

Sol. Poly. Conc., 1.5 wt %	Effects of NaCl Concentration on polymer solutions, in wt %								
NaCl Conc., wt %	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample Code: **P11** Surface Tension at 25°C vs. salt	47.93	47.51	47.22	46.98	46.51	46.34	46.21	46.01	45.89
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	332	501	811	1070	1220	1360	1470	1680	1820
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	10.8	12.0	12.7	14.1	16.0	16.7	19.2	23.4	27.2
Sample Code: **P7** Surface Tension at 25°C vs. salt	50.39	49.72	49.56	49.21	48.61	48.21	48.01	47.35	46.93
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	180	210	441	535	728	882	901	920	990
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	5.41	5.71	6.56	7.31	8.82	9.32	9.52	9.90	10.12
Sample Code: **P12** Surface Tension at 25°C vs. salt	48.52	46.40	41.21	45.81	43.10	45.01	38.81	40.11	34.18
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	1600	2510	3470	4270	6520	7430	8590	9010	10110
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	20.0	34.1	34.8	35.2	37.5	38.1	39.6	41.2	43.1
Sample Code: **E2** Surface Tension at 25°C vs. salt	35.60	28.43	27.70	27.26	26.90	25.67	25.55	23.78	23.00
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	501	550	600	642	720	780	810	890	952
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	10.6	10.7	11.1	11.5	11.7	11.9	12.2	12.5	13.2
Sample Code: **E3** Surface Tension at 25°C vs. salt	37.21	28.73	28.34	27.12	25.62	24.96	23.21	22.82	21.61
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	781	868	902	990	1062	1142	1220	1300	1380
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	9.17	10.3	11.0	11.4	12.1	12.4	13.2	14.1	14.8
Sample Code: **E4** Surface Tension at 25°C vs. salt	36.38	27.09	26.51	26.00	24.71	24.00	23.72	23.12	22.01
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	551	818	942	1010	1112	1150	1190	1210	1250
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	5.56	6.31	6.87	7.21	7.91	8.34	8.89	9.42	10.32

continued....

Contd...Table 5-25: Rheology and Surface Activity of Amphiphilic Non-ionic Multi-block$^{b, c}$ Copolymer Solutions of 1.5 wt % in 1.0 wt % to 10 wt % NaCl at 25°C.

Sol. Poly. Conc., 1.5 wt %	Effects of NaCl Concentration on polymer solutions, in wt %								
NaCl Conc., wt %	**0.0**	**1.0**	**2.0**	**3.0**	**5.0**	**6.0**	**7.0**	**9.0**	**10.0**
Sample: **P, Random** Surface Tension at 25°C vs. salt	59.83	50.76	50.80	52.72	51.73	53.89	50.11	45.45	47.74
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	65.1	68.2	70.5	65.5	71.0	68.5	66.2	63.2	63.9
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	7.50	7.77	8.02	8.32	9.4	8.5	8.3	7.82	7.72
Sample : **E1, PAM** Surface Tension at 25°C vs. salt	42.10	33.88	28.83	27.92	27.23	26.58	26.31	26.04	25.58
Viscosity in Cps at shear rate of 0.8 (1/s) vs. salt	120	115	111	105.6	110	100.8	101	112	118
Viscosity in Cps at shear rate of 79.2 (1/s) vs. salt	4.64	5.51	5.91	5.01	5.46	5.23	5.83	6.11	5.10

a : Sample codes of E2, E3, and E4 are block copolymers of AM/C12, others represent AM/ST block copolymers.

b E1 : homopolyacrylamide, PAM.

c P sample is a random copolymer, poly(AM-r-ST).

Table 5-26: The Effect of NaCl Concentration on the IFT of Aqueous Solutions of Nonionic Multi-block Copolymers (P12 and E3) at 25°C.

NaCl conc., wt %	IFT, (mN/m) of Copolymer Sample P12, at Poly. Conc. of		IFT, (mN/m) of Copolymer Sample E3, at Poly. Conc. of	
	0.5 wt %	1.5 wt %	0.5 wt %	1.5 wt %
0.0	20.93	16.29	19.31	11.26
1.0	8.29	8.14	5.11	3.27
2.0	8.01	7.50	2.48	1.83
3.0	7.62	7.10	1.63	0.75
5.0	6.37	5.53	1.51	0.70
6.0	5.98	4.32	1.37	0.68
7.0	5.46	3.88	1.20	0.60
9.0	3.75	1.14	0.95	0.56
10.0	3.21	1.01	0.86	0.53

P12 ; poly(AM-b-ST)
E3 ; poly(AM-b-C12)

Table 5-27 Surface tensions of ALL non-ionic and ionic di- and multi-block copolymers in mN/m @ 20 C at different polymer concentrations

Sample code	Structure	0.01 wt%	0.05 wt%	0.1 wt%	0.5 wt%	1.0 wt%	1.5 wt%	2.0 wt%
HD2	Hpoly(AN-co-MMA)	68.62	66.70	58.79	57.67	57.30	54.10	48.73
HD6	Hpoly(AN-co-MMA)	70.86	68.61	63.65	52.88	46.16	51.02	49.06
HD8	Hpoly(VI-co-MMA)	66.20	65.71	64.43	58.73	55.83	51.48	50.18
P10*'	Poly(AM-co-ST)	67.69	60.86	57.09	56.05	54.39	53.71	53.57
P11	Poly(AM-co-ST)	70.88	66.38	65.59	44.82	48.30	47.93	47.59
P12	Poly(AM-co-ST)	69.58	66.87	55.33	49.20	44.10	48.52	37.44
P13	Poly(AM-co-ST)	71.47	69.80	65.37	56.70	55.06	65.93	52.61
P15	Poly(AM-co-ST)	71.85	68.31	63.93	51.04	53.25	52.96	57.88
P4	Poly(AM-co-ST)	65.72	59.85	59.50	85.20	57.58	57.12	56.89
P5*	Poly(AM-co-ST)	72.20	71.76	71.60	49.82	50.83	56.02	61.30
P6	Poly(AM-co-ST)	65.43	55.66	5020	54.01	55.17	55.53	57.91
P7	Poly(AM-co-ST)	60.16	58.23	56.99	55.58	53.57	50.39	45.29
E1	Homo-Poly(AM)	61.20	61.02	55.05	43.80	42.76	42.10	40.10
E2*	Poly(AM-co-C12)	60.32	53.24	51.69	40.04	39.54	35.60	32.33
E3	Poly(AM-co-C12)	50.68	52.95	48.18	47.41	39.02	37.21	34.67
E4*	Poly(AM-co-C12)	60.82	55.05	49.96	45.39	40.25	36.38	32.11
P*	Poly(AM-R-ST)	70.25	68.19	64.60	61.45	61.43	59.83	52.36

* A stock solution of 2 wt % of each sample was used to make the solutions by dilution, other solutions were prepared individually.

APPENDIX - C

Characterization Charts (FTIR)

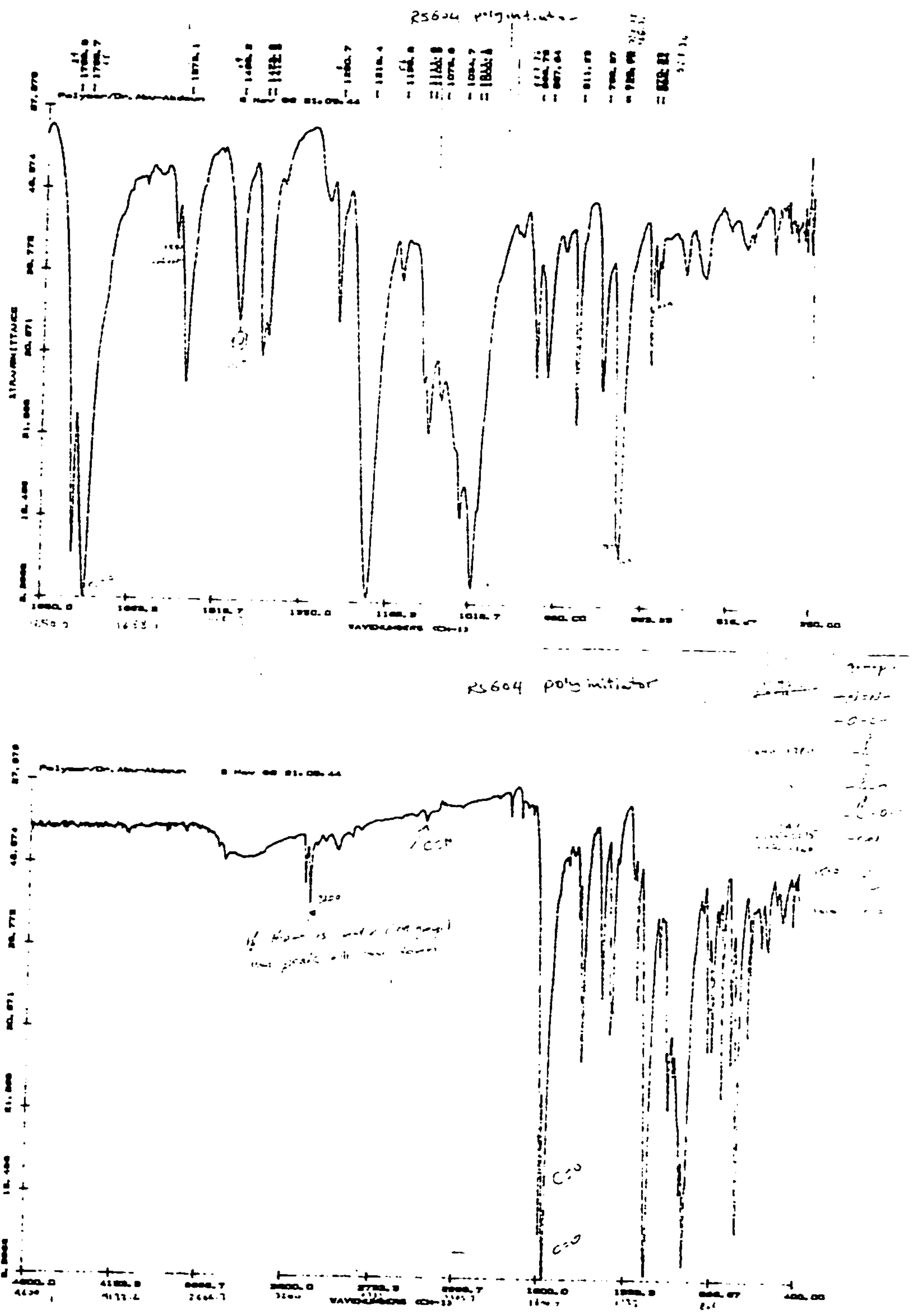


Figure 4-20 : FTIR spectrum of polyinitiator **RS604** using Perkin-Elmer Spectrometer from 250 cm^-1 to 4600 cm^-1 as wavenumbers.

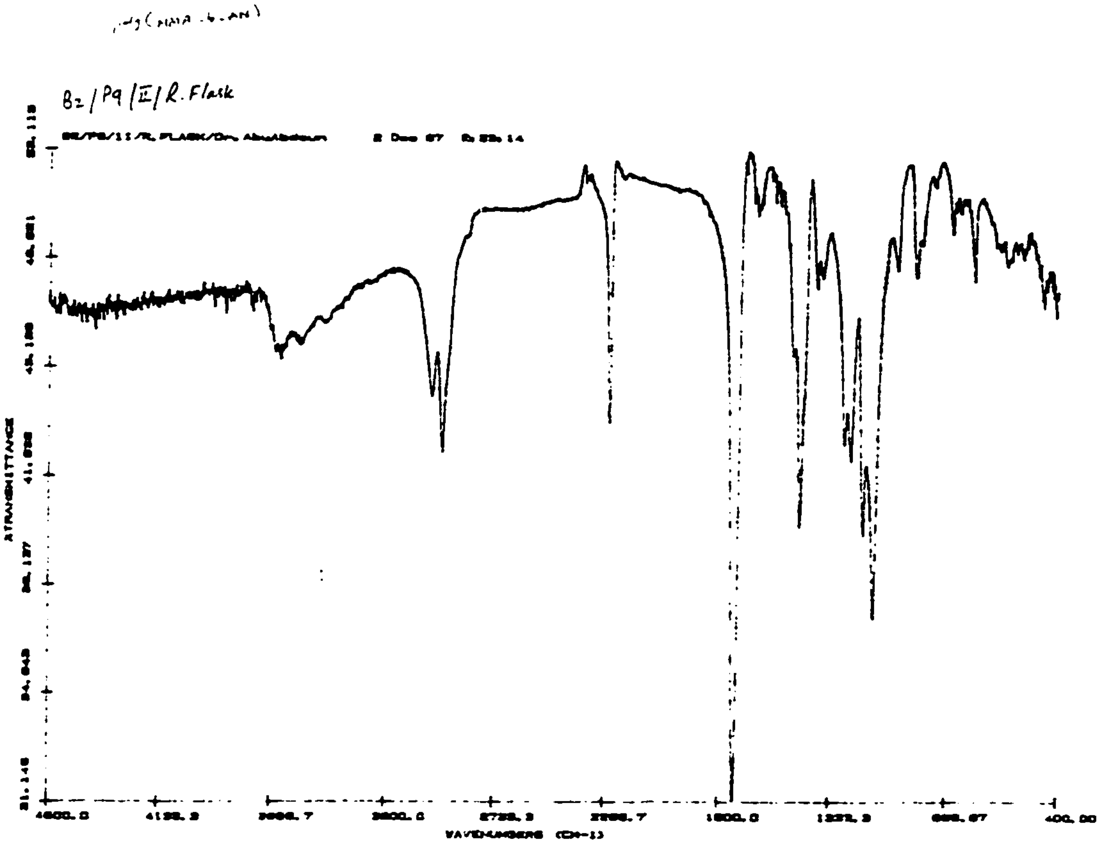


Figure 4-21 : FTIR spectrum of sample P9 II R or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 4600 cm^-1 as Wavenumbers.

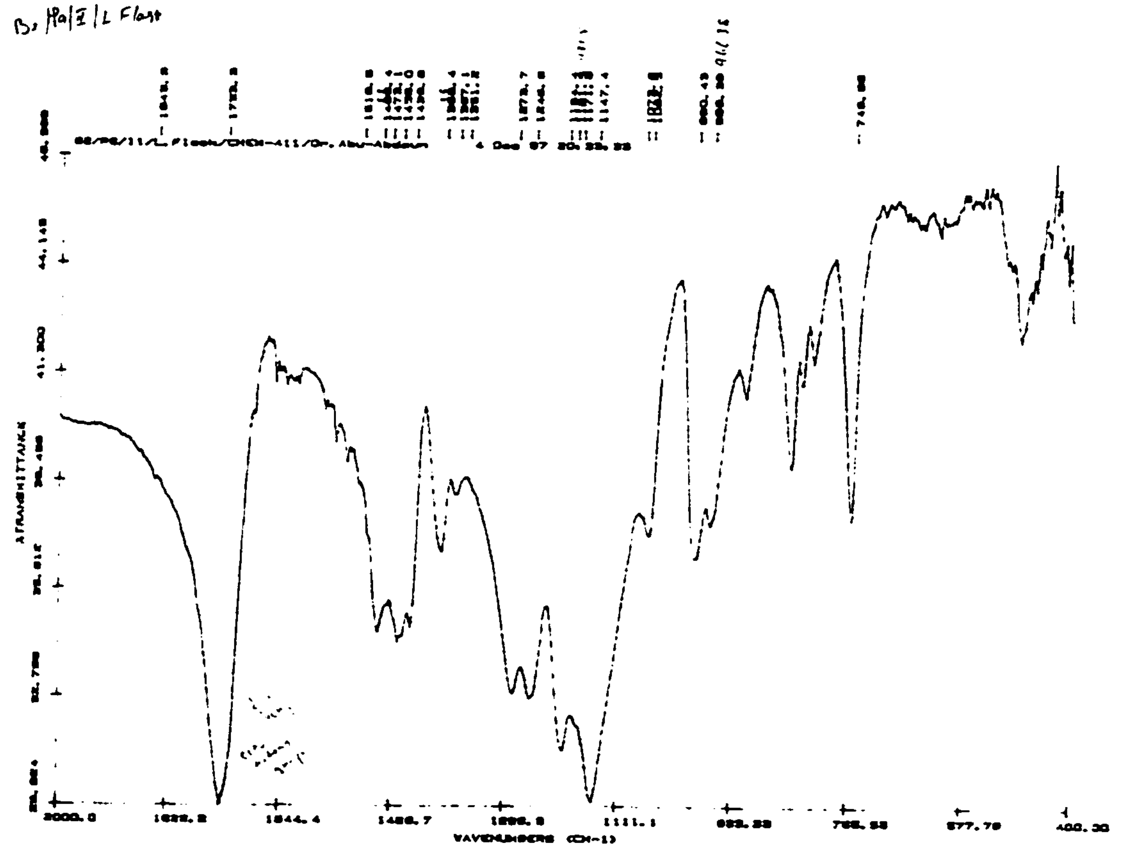


Figure 4-22 : FTIR spectrum of sample P9 II L or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 2000 cm^-1 as Wavenumbers.

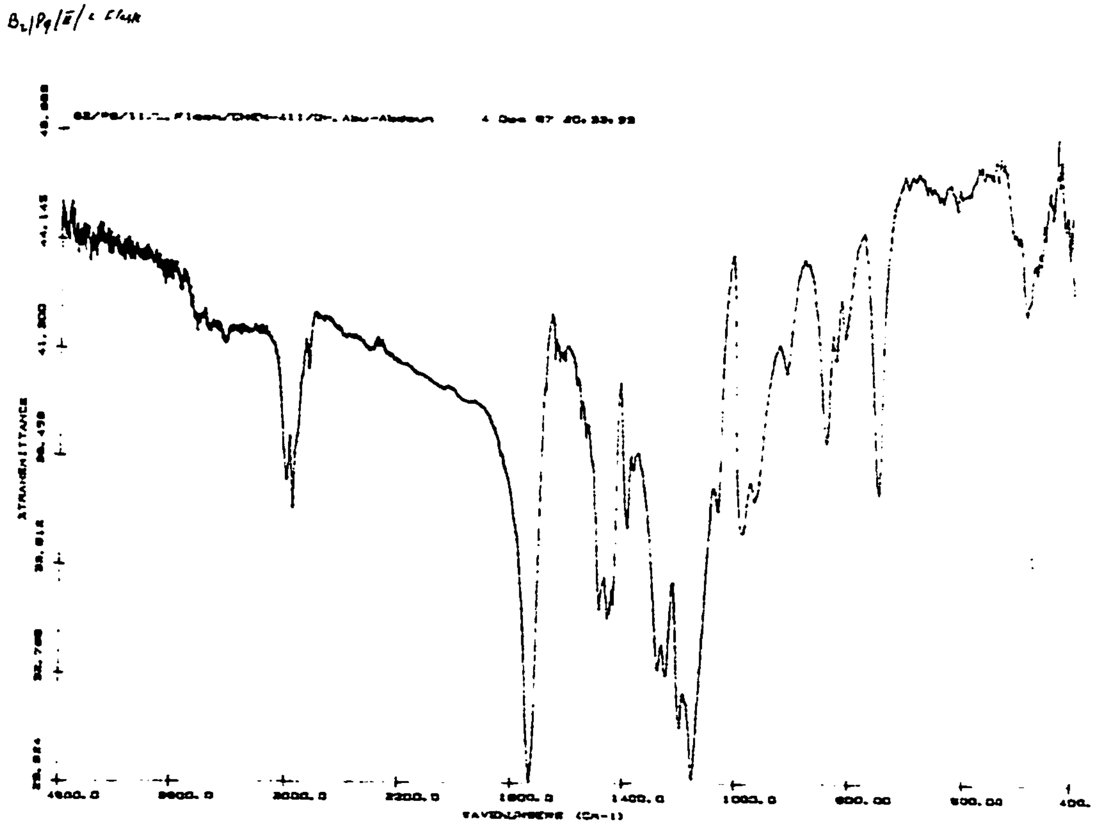


Figure 4-23 : FTIR spectrum of sample P9 II L or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 4600 cm^-1 as Wavenumbers.

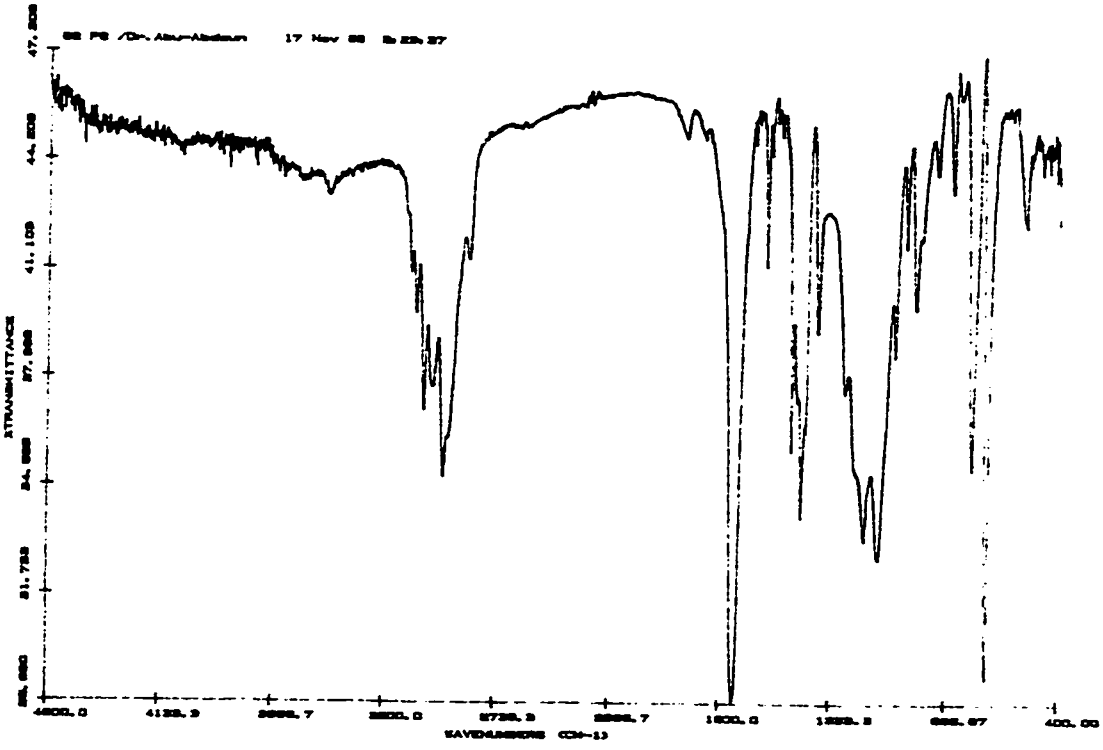
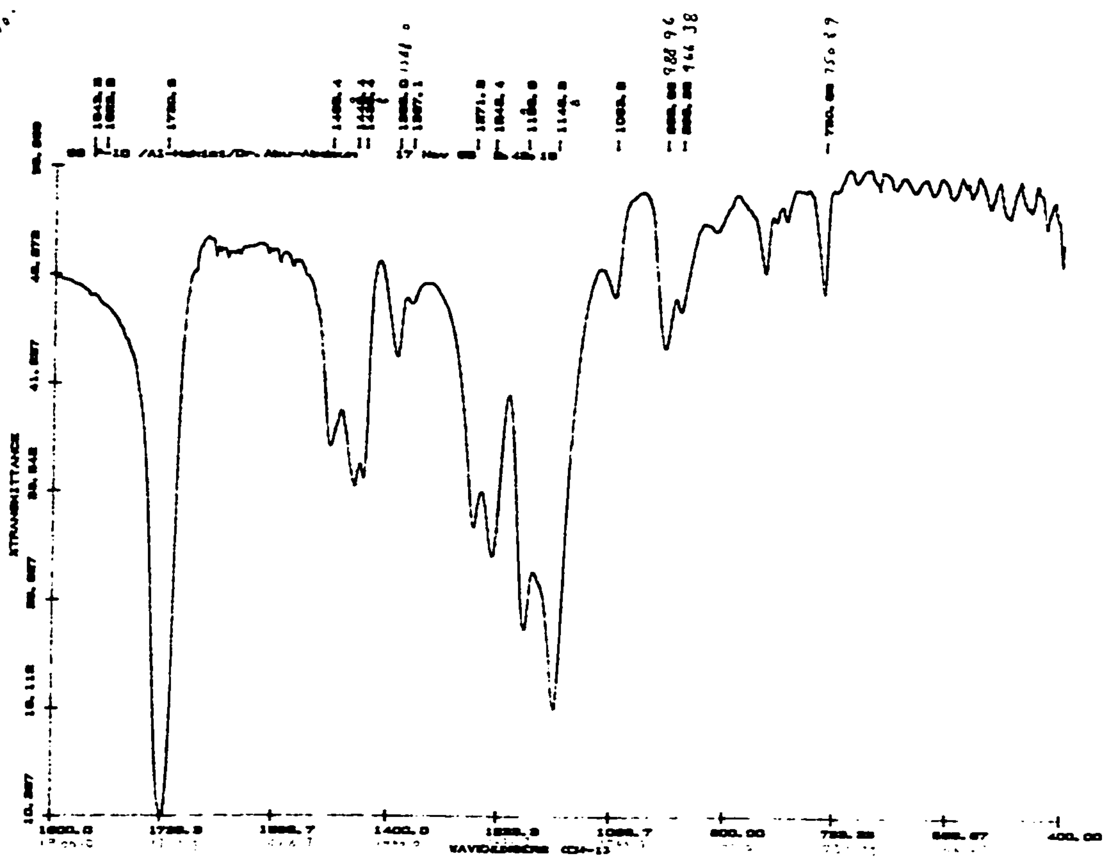


Figure 4-24 : FTIR spectrum of sample P8' or poly(MMA-b-ST) using Perkin-Elmer Spectrometer from 400 cm^-1 to 4600 cm^-1 as Wavenumbers.

B2 P10



b2 P10 p(MMA-b-AN)

Figure 4-25 : FTIR spectrum of sample P10' or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 1900 cm^-1 as Wavenumbers.

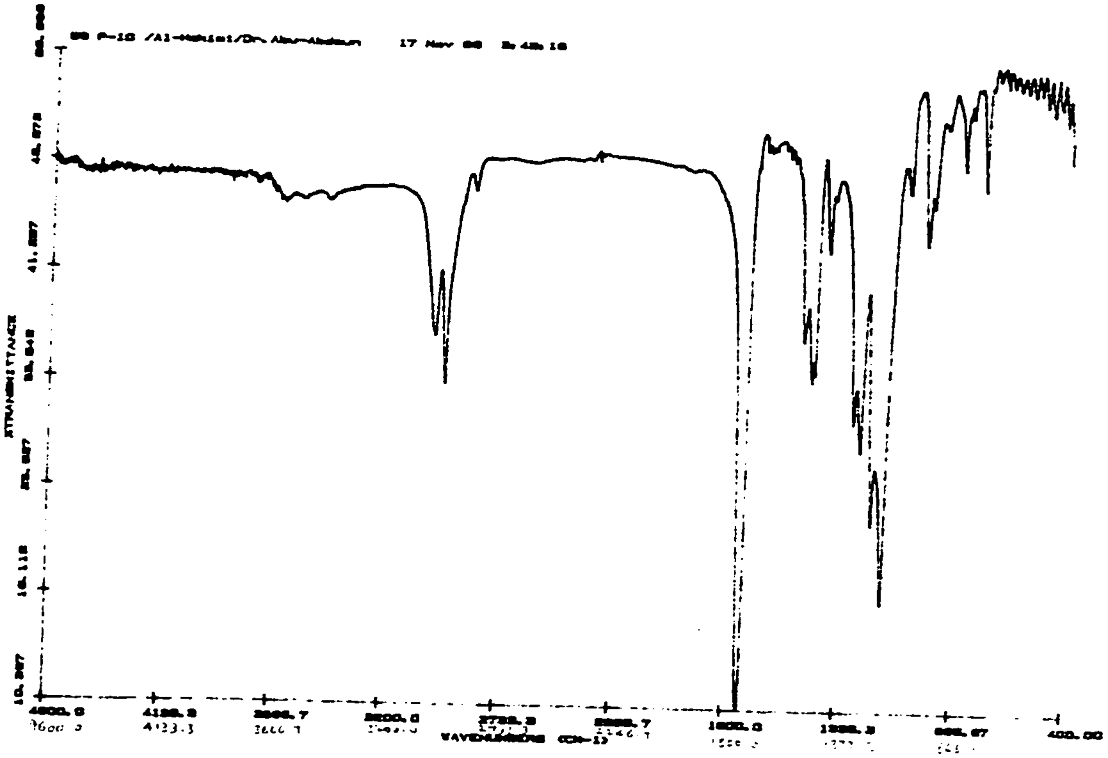


Figure 4-26 : FTIR spectrum of sample P10' or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 4600 cm^-1 as Wavenumbers.

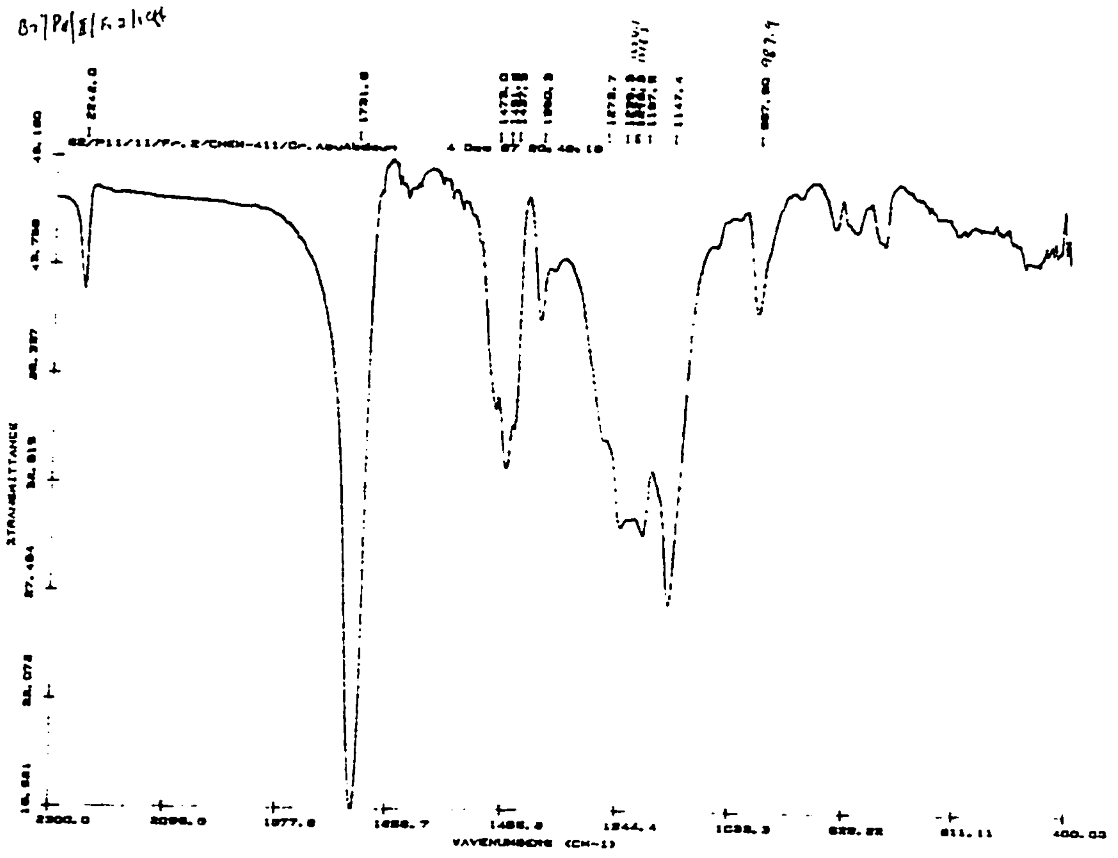


Figure 4-27 : FTIR spectrum of sample P11/II/F2 or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 2300 cm^-1 as Wavenumbers.

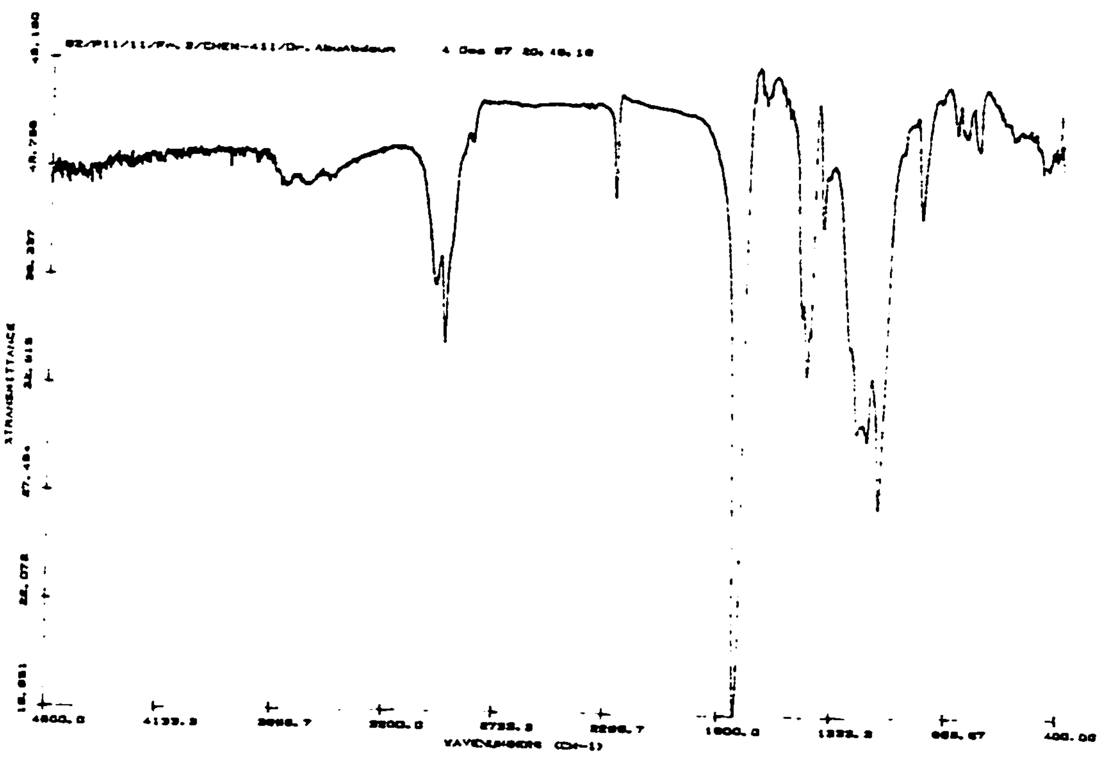


Figure 4-28 : FTIR spectrum of sample P11/II/F2 or poly(MMA-b-AN) using Perkin-Elmer Spectrometer from 400 cm^-1 to 4800 cm^-1 as Wavenumbers.

NOMENCLATURE

List of Notations:

A_{co}	Solvent Attraction Between Surfactant and Oil.
A_{cw}	Solvent Attraction Between Surfactant and Water.
C12	1-Deodecene
C*	Characteristic (overlap) concentration
x, y	Repeat Units
ΔP	Pressure Drop Across the Interface of Water and Oil.
F	Measured Force
F_{ef}	The Correction factor which accounts for the weight of the liquid lifted, while the Ring is removed
I_b	Wetted length (m)
K_w	Effective Water or Displacing Fluid Permeability of the Reservoir Rock, in the Zone Occupied by the Fluid.
K_o	Oil Permeability of the Reservoir Rock, in the Zone Occupied by the Oil.
K_{max}	Maximum Force (nM)
K	Measured Force (nM)
k	Porosity of the petroleum reservoir (Eq. 2.1)
k_w, k_o	Permeability to each phase (Eq. 2.3)
L	Wetted Length of Ring or Plate
m_w, m_o	Mobility to each phase (Eq. 2.3)
M	Water-Oil Mobility Ratio.
N, M	Repeat units
0	Angle of Wetting
N_c	Capillary Number
q	Flow rate per unit cross-sectional area of water.
r	The radius of the porous media.
R	The R ratio
-N=N-	Azo group

List of Abbreviations:

IFT	Interfacial tension
CMC	Critical micelle concentration
CTAB	Hexadecyl-triethyl-ammonium-bromide
AIBN	Azo-bis-isobutylenitrile initiator
Cps	Centi poise
CED	Cohesive energy density
OOIP	Original oil in place
RPM	Revolution per minute
SPF	Surfactant Polymer Flooding
SDS	Sodium dodecyl sulfate initiator
EOR	Enhanced Oil Recovery
PAM	Polyacrylamide
HPAM	Hydrolized polyacrylamide
HDV	Hydrodynamic volume
pH.	Ionic Strength
HAP	Hydrophobically associating polymers
MW	Molecular weight
ST	Styrene
AN	Acrylonitrile
MMA	Methylmethacrylate
NaCl	Sodium chloride
UV	Ultra-Violet
FTIR	Fourier transform infra-red spectroscopy
BP 1	Di-tert-butyl-4,4'-azo-bis-(4-cyanoperoxyvalerate)
ACV	4,4'-azo-bis-(4-cyanovaleric acid)
BP 7	Styrene polymeric initiator
VI	Vinylimadazole
HDx	Hydrolized polymer

Greek Symbols:

σ	Surface or Interfacial tension (mN/m)
$\Upsilon_{O/w}$	Interfacial tension Between Oil and Water.
μ_o	Viscosity of Oil
μ_w	Viscosity of Water or Displacing Fluid.
η_w	Aqueous solution viscosity
η_o	Oil viscosity
$[\eta]$	Intrinsic viscosity
τ	Shear stress
γ	Shear rate (Eq. 2.5)
ρ	Density

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VITA

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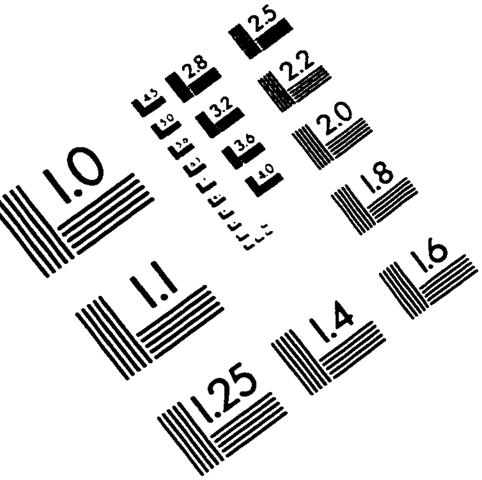
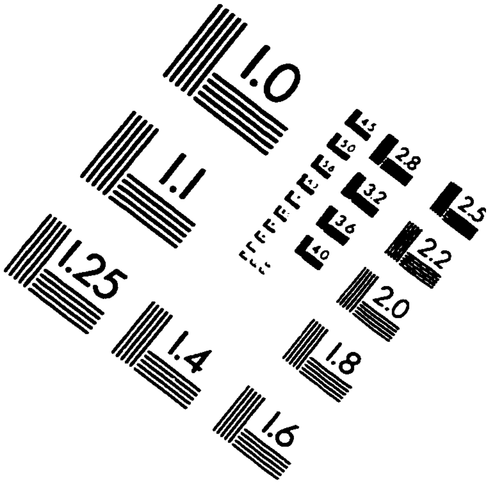
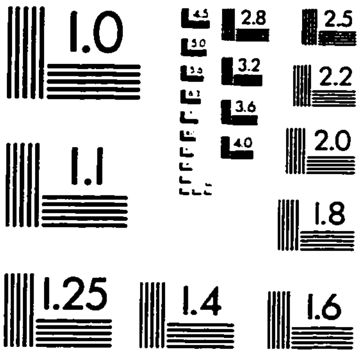
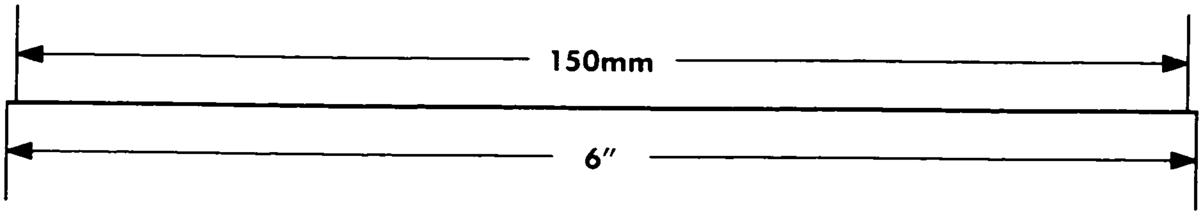
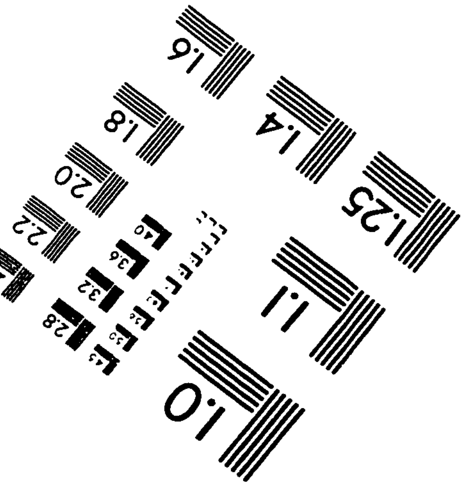
IMAGE EVALUATION
TEST TARGET (QA-3)

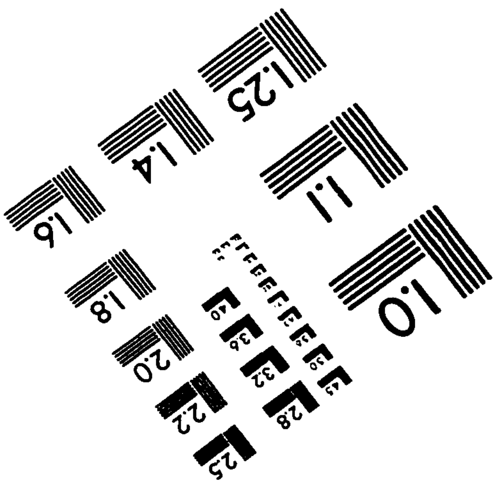












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