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Surfactant-induced phase separation and network formation of surface-active graft copolymers

Dualeh, Abdulkadir Jibril, Ph.D.

City University of New York, 1990

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SURFACTANT-INDUCED PHASE SEPARATION AND NETWORK FORMATION OF SURFACE-ACTIVE GRAFT COPOLYMERS

BY

ABDULKADIR J. DUALEH

A dissertation submitted to the Graduate Faculty in Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1990

This manuscript has been read and acceptd for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Executive Officer

Charles Maldarelli
Roberto mauri
Nan-Lo yang
Supervisory Committee

The City University of New York

ABSTRACT

SURFACTANT-INDUCED PHASE SEPARATION AND NETWORK FORMATION OF SURFACE-ACTIVE GRAFT COPOLYMERS

by

ABDULKADIR DUALEH

Adviser: Professor Carol Steiner

An extensive experimental investigation of the behavior of a particular class of surface active graft copolymer in aqueous surfactant solution is presented. The experiments performed include fluorescence spectroscopy and rheology.

The specific copolymer used in this study is hydrophobically modified hydroxyethyl cellulose (HMHEC) and is shown in appendix 2. It is a surface active copolymer composed of a hydrophilic cellulose backbone grafted with linear hydrophobic side chains (C_{12} alkyl hydrocarbons). The properties of this copolymer in aqueous sodium dodecyl sulfate solution are presented.

Strong site-specific adsorption of surfactant occurs on the hydrophobic side chains of water-insoluble HMHEC. The resulting interactions give rise to a network composed of hydrophobic microdomains dispersed throughout an aqueous polymer solution or gel, depending on the composition of the system.

The hydrogel phase which forms from HMHEC below the cmc of the surfactant appears to be an important new material. It is clear, flexible, viscoelastic, and homogeneous. It is composed of hydrophobic microdomains, which can solubilize a water-insoluble probe, dispersed throughout a water-swollen gel. The size as well as compositions of the microdomains can be varied. These characteristics, coupled with the mechanical stability of the gels, makes these new materials interesting candidates for such applications as chromatography or controlled drug release.

This study is intended to contribute towards our understanding of the bulk and microscopic properties of amphiphilic copolymers in surfactant solutions. We have identified the physico-chemical interactions between the polymer and surfactant that give rise to these bulk properties. We present evidence showing that the properties observed in this system are due to comicellization among the alkyl grafts from the polymer and the free surfactant molecules.

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INTRODUCTION

Numerous authors investigating the properties of amphiphilic copolymers in solvents of different polarities have reported that spontaneous microphase separation of the copolymer segments occurs. This phenomenon is similar to that encountered in surfactant/water solutions where the hydrophobic tails of the surfactant molecules cause the molecules to aggregate into micelles that stay dispersed in the bulk solvent. This self aggregation is not unique to polymeric solutions but is also very common in bulk copolymers as well polymer blends. Aggregation of nonpolar side groups also determines the conformations as well as the reactions of most proteins. In general, the association of different segments of copolymers gives rise to profound changes in the rheological properties of polymers. Among the physical property changes are increased viscosity and elastic moduli of polymer solutions and the formation of materials with dispersed microdomains.

The viscosification property of copolymers is a very attractive way of controlling the rheological properties of polymer solutions. The reason is that the effective hydrodynamic radius and hence the viscosity of low molecular weight polymer molecules can be increased through intermolecular associations without increasing the MW of the polymer. These associations are disrupted under shear and quickly reform, but the polymer chains are not permanently shear degraded. As a result, the flow properties of displacement fluids in enhanced oil recovery can be efficiently controlled. Also, excellent rheological properties can be achieved in many other important industrial processes such as cosmetics, coating, laundry aids and pharmaceuticals where self aggregating polymers are used as thickeners.

Materials which have dispersed microdomains in the bulk are also useful for a variety of other applications. For example, hydrophilic membranes with hydrophobic regions can be used to sequester lipophilic solutes and release them at a constant rate. However, the formation of materials with this characteristic and the selection of the conditions required for the optimal aggregation of the nonpolar segments of the polymer require a fundamental understanding of the factors governing the microphase separation of the different segments of the polymer.

I present a basic study of the structure and properties of a class of surface active graft copolymers in aqueous surfactant solutions. The specific copolymer we used in this study is hydrophobically modified hydroxyethyl cellulose (HMHEC). This has a nonionic water-soluble backbone derived from cellulose. Addition of low levels of linear alkyl grafts on the backbone results in diminished solubility of the polymer in water due to the insolubility of hydrocarbons in aqueous solutions. Beyond a certain level of hydrophobic grafting the copolymer will not stay in an aqueous solution. We focus on the behavior of HMHEC in dilute aqueous solution of sodium dodecyl sulfate.

The objective of this study is to determine the conditions that induce microphase separation of the alkyl grafts and the backbone of the copolymer. Various surfactants have been tested for their ability to solubilize the alkyl grafts. We have learned that the structure of the surfactant, specifically the charge of the head group and the structure and length of the nonpolar tail all determine whether the alkyl grafts are clustered together or not. Work already done by Steiner has shown that at high hydrophobe content (>0.8% by weight), HMHEC is insoluble in water. We postulate that in this condition the hydrophobes are unable to form aggregates that successfully shield them from unfavorable interactions with water. As a result, intramolecular associations among the hydrophobes give rise to coiled polymer chains that precipitate out of the solution without any interesting properties. In the presence of sodium dodeccyl sulfate (SDS), on the other hand, the polymer forms clear viscoelastic hydrogels. It is postulated that the alkyl grafts from various chains are bridged by surfactant molecules.

The work presented here is divided into different chapters. Chapter 1 is a literature review and mainly deals with the underlying phenomena of hydrophobic bonding of nonpolar hydrocarbons in aqueous solutions. This serves as a background to explain intermolecular association of hydrophobes in polar solvents. It also contains a brief summary of results from representative studies involving surfactant/polymer solutions. Chapter 2 deals with the experimental techniques and procedures that are employed in the investigation. The results of these experiments and their discussions are presented in chapters 3, 4 and 5. Chapter 6 presents conclusions and recommendations for future work.

Chapter 1

LITERATURE REVIEW

The association of polymers with surfactants is a well known phenomenon that has been exploited in industry for a long period of time. The details of the interactions that give rise to such associations have, however, been regarded as too complex to study given the little information that is known about the behavior of surfactants and polymers in solution. Recently, many investigators have undertaken various experimental studies on polymers in surfactant solutions in an attempt to shed some light on the physico chemical properties of these solutions (1-12). It has been shown that the extent of polymer surfactant associations is dictated by the degree to which the polymer can participate in hydrogen bonding, hydrophobic and coulombic interactions with the surfactant. However, strong interactions of this type between the polymer and the surfactant will not by themselves result in strong polymer surfactant complex formation. In general, such associations are a result of a competition among the interactions between the various molecules in the solution including the solvent. Strong solvation of the polymer by the solvent molecules as well as the ability of the surfactant molecules to form energetically favorable structures like micelles might, for example, preclude the formation of polymer surfactant complexes. In these cases, hydrophobic interactions between a hydrophobic polymer segment and the hydrocarbonous surfactant tails which might have been favorable are eliminated once surfactant micelles form and their hydrocarbon tails are buried in the micelle interior. Similarly, micelle formation might encourage strong favorable coulombic interactions between the charged headgroups of an ionic surfactant and the segments of a polyelectrolyte of opposite charge. Naturally, a clear starting point for understanding this complex phenomenon is to study polymers and surfactants whose interactions with the solvent as well as with themselves are well characterized.

All the work done so far in polymer/surfactant interactions falls into one of three categories depending upon the original objectives. The first is concerned with establishing the existence of polymer/surfactant association in a particular system. The second category is an attempt to elucidate the structure of any polymer/surfactant complexes that may be formed in the solution. The objective is to determine whether the surfactant molecules bind to the polymer individually at random sites or cooperatively at specific sites. If they bind cooperatively, what is the size, geometry and the degree of ionization of the bound surfactant aggregates relative to surfactant micelles that form in the absence of polymer? The third category is an investigation of the anomalous rheological properties of polymers in surfactant solutions. Among other factors, increase in polymer chain dimensions which may account for the viscosity enhancements are investigated in this category.

1.1 Polyethylene oxide in sodium dodecyl sulfate

The most extensively studied polymer-surfactant system to date is the aqueous solution containing sodium dodecyl sulfate (SDS) and polyethylene oxide (PEO) (1-4). Various experimental techniques including NMR (1) and neutron scattering (2) have been employed in these investigations. The NMR spectra of the various nuclei of SDS and PEO atoms are used to trace interactions between the surfactant and the polymer. Results of these studies indicated that below the critical micelle concentration (CMC) of the surfactant, some of the monomers of the polymer adsorb on the hydrocarbon/water interface of surfactant aggregates while the rest of the polymer is in contact with only water molecules. This suggested the existence of PEO-SDS complexes in this system. The picture that has emerged out of this study is a polymer/surfactant complex that is composed of a polymer molecule wrapped around small surfactant aggregates. In a similar study, the same authors (1,2) analyzed the intensity of neutrons scattered from samples of PEO-SDS solutions and drew the following conclusions: The surfactant aggregates are attached to the polymer backbone at approximately 8 nm intervals. There is a certain stoichiometric relationship that is followed in the adsorption process and thus, when the solution composition differs from the stoichiometry due to, for example, the presence of excess surfactant, free surfactant micelles exist in equilibrium with the polymer/surfactant complexes. The number of surfactant aggregates that are bound to an individual polymer chain varies with the molecular weight of the polymer as well as the total amount of surfactant in solution. It is estimated that at low surfactant concentration the change in free energy of the aggregates as result of binding is about 10-20 kT but that as the number of bound aggregates increases the change in free energy decreases due to coulombic repulsion among bound aggregates. Nevertheless, binding is favored as long as the binding has associated with it a change in free energy of atleast 1 kT. Beyond that, free micellar aggregates are favored.

Structural information about the bound aggregates, specifically the sizes and the geometries of the polymer bound aggregates have also been obtained using fluorescence probe techniques (3,4) . Fluorescence probes whose emission spectra are sensitive to their environments and which are preferentially solubilized in hydrophobic regions are added to the solutions. Their emission is then monitored to detect the presence of any hydrophobic aggregates in the solutions. These studies used poly vinyl pyrrolidone (PVP) and PEO with SDS. The results from these studies confirmed those mentioned earlier and lead to the conclusion that SDS micelles cooperatively bind to the polymers. However, the fluorescence method also provided information about the interior of the aggregates since the site of solubilization of the probe is inside the aggregate. It has been shown that the fluorescence probe is in a more polar environment when there is a polymer present in the solution than in the case with surfactant alone. This has been interpreted to mean that the size of the polymer-bound micelle is smaller than SDS micelles in the absence of the polymer. Indeed, measured aggregation numbers of the polymer bound micelles (4) led to values that are 30-50% smaller than those for SDS micelles in the absence of the polymer, i.e 25-45 molecules per aggregate vs 60-70 molecules per aggregate. This difference has been attributed to the adsorption of PEO chain in the micelle water interface and an increase in ionization of the micelles.

1.2 Poly(vinyl pyrrolidone in SDS

Dye solubilization, dialysis, and electrical conductivity have also been used to investigate the properties of polymer/surfactant solutions (9-12). These investigations were focused on determining the effect of the polymer on the solubilization power (detergency) of surfactant, the specific amount of surfactant that is bound to the polymer at equilibrium, and the degree of ionization of the polymer bound surfactant aggregates relative to the degree of counterion dissociation of surfactant micelles in the absence of polymer. Most of these studies used poly(vinyl pyrrolidone) (PVP) and sodium alkyl sulfates of varying degree of alkyl length as their polymer and surfactant respectively (11).

These studies (9-12) demonstrated that adsorption of surfactant onto PVP starts abruptly at a concentration which is about 40% lower than the respective critical micelle concentrations of the various surfactants in the absence of polymer. These polymer bound aggregates are called premicelles. The adsorption continues until the formation of free micelles becomes favored. The surfactant concentration at which this transition occurs depends on the concentration of PVP. The weight ratio of PVP to SDS consumed for the complete adsorption is found to be constant 1:2.3 regardless of the amount of PVP in solution. Further, it was shown that the free energy of transfer of methylene from the aqueous phase to the premicelles is 1.1 kT which is the same as that observed in transferring a surfactant methylene group from the aqueous phase to the free micelles. Thus, it appears that upon adsorption onto PVP surfactant molecules contact each other and are not uniformly distributed on the PVP molecules.

1.3 Effect of surfactant adsorption on rheology of polymer solutions

Significant changes in the rheology of polymer solutions in the presence of surfactant are attributed to the adsorption of the surfactants onto the polymer (9,10). This conclusion is a result of studies done employing electrical conductivity and viscosity measurements. These studies did not yield anything quantitative such as variations in chain dimensions, but were informative insofar as they gave a qualitative picture of changes in polymer dimensions as result of surfactant binding. A steep expansion of the polymer coil with increasing surfactant concentration was found in the region between the onset of adsorption and the formation of free micelles. This effect was shown to be analogous to the expansion, due to segment repulsion, observed in polyelectrolytes with increasing degree of dissociation of the ionizable groups. Further but less rapid expansion of the polymer chain was also observed when adsorption stops and free micelles form. This was attributed mainly to a repulsion among the bound aggregates and the free micelles. However, the rheological changes were not large enough in this particular experiment, nor was any other independent confirmation found in the literature. These studies point to the possibility of variations in the polymer chain dimensions in the presence of surfactant compared to polymers in pure solvent, but so far there is no systematic study of these effects available in the literature. Indeed, the viscosification properties of many industrially used polymers may be a result of the increased chain dimensions of these polymers in the presence of surfactant.

1.4 Other surfactants and polymers

Surfactants other than SDS and polymers other than PVP and PEO have also been used (5,6,25) to study polymer/surfactant interactions. Studies on charged polymers like polymer JR (6), as well as nonionic polymers like poly(ethylene glycol), poly(vinyl alcohol), poly(vinyl acetate), etc in ionic, nonionic, and cationic surfactants have also been carried out (25). Results from these investigations show that interactions between the surfactants and the polymer strongly depend on the chemical composition of the surfactant and polymer. For example, PEO and PVP show strong interactions with sodium tetradecyl sulfate but hardly interact with tetradecyl trimethyl ammonium bromide. This indicates that the polymer/surfactant interactions are caused by specific interactions between the surfactant ionic head group and the segments of the polymer and, therefore, do not involve the surfactant alkyl chain in these cases. Many cases where polymers and surfactants do not interact are known and are apparently due to the absence of such favorable interactions between the surfactant headgroup and the polymer segments. However, there is as of yet no way of predicting a priori whether there will be any interaction between a polymer and a surfactant given the structure of the surfactant head group and the chemical composition of the polymer. It seems that factors other than the chemical nature of the surfactant and the polymer also play a role in the ultimate properties of polymers in aqueous surfactant solutions.

Polyethylene oxide with flexible backbone and dextran with a rigid backbone have been examined in solutions of ionic, cationic and nonionic surfactants. It was found that no polymer/surfactant association occurs in the case of dextran. For polyethylene oxide, the extent of polymer/surfactant association is large for anionic surfactants and small for cationic surfactants. It decreases with increases in the bulkiness of the surfactant head group. Thus, it is concluded that the rigidity of the polymer chain as well as the shear size of the surfactant head group also play a role in the extent of polymer/surfactant association

For the cases when the polymer and surfactants interact, the behavior is fairly general and similar to the PEO/SDS system mentioned earlier, i.e in the absence of polymer, the surfactant forms well defined micelles at concentrations higher than a critical concentration (critical micelle concentration, cmc). When a polymer is added in a surfactant solution, there is no association between the polymer and the surfactant until surfactant concentration x_1 is reached. Above x_1 (which is lower than the cmc), the polymer/surfactant association starts abruptly and then saturates abruptly at a concentration x_2 (higher than the cmc). Between x_1 and x_2, the surfactant binds onto the polymer cooperatively and form what is called " pre-micelles". These premicelles have lower aggregation numbers than the pure surfactant micelles. Above x_2, free surfactant micelles similar to those that form in the absence of the polymer begin to appear. The surfactant concentration x_1 is generally considered as the cmc of the surfactant in the presence of polymer. Thus, it is generally accepted that the presence of the polymer reduces cmc and aggregation number and increases the degree of ionization of the micelles. In the cases when there is no interaction the polymer has no effect on the properties of the surfactant.

All the cases of polymer/surfactant complexes that have been observed can be classified in to the following types:

1) No surfactant is bound to the polymer and the latter remains as free polymer in solution.

2) Single surfactant molecules are bound linearly along the length of the polymer molecule.

3) A single surfactant molecule binds at more than one binding site of a single polymer molecule, giving rise to intramolecular bridging. Alternatively a single surfactant molecule binds to more than one polymer molecule giving rise to intermolecular bridging.

4) The polymer molecule along with a layer of surfactant molecules bound on it is solubilized in the interior of surfactant micelle.

5) Clusters of polymer segments and surfactant molecules associate to form pseudo-micelles such that the hydrocarbonous regions of the polymer segments and of the surfactant are shielded from having contact with with water.

6) Pure surfactant micelles associate with the polymer molecule in such away that the polymer segments

partially penetrate and wrap around the polar head group region of the surfactant micelles. A single polymer molecule can associate in this manner with one or more surfactant micelles depending on the polymer and micellar properties.

1.5 Thermodynamics of polymer/surfactant interactions

The variations in the degree of interactions between polymers and surfactants have been explained. It has been suggested that these differences are due to an ability of some polymer segments to penetrate the head group region of the micelle and therefore diminish electrostatic repulsion among surfactant headgroups. Thus, the polymer surfactant interaction can be treated as an adsorption/desorption process with different energies. A theoretical model based on this concept has been attempted (26). The basic idea is to quantify the competitive equilibria of micellization and polymer-micelle complexes in aqueous solutions. The model assumes that the presence of polymer decreases the positive free energy of formation of the micelle-water interface on the one hand, while increasing the positive free energy change arising from the steric repulsions due the presence of polymer at the micellar surface on the other. The relative degree importance of the above two effects is assumed to determine the occurrence of polymer-micelle complexes. This formulation ignores the physico-chemical properties of the polymer in solution but provides an empirical way of quantifying the various factors that have been experimentally found to contribute to or oppose polymer/surfactant association. The polymer is treated simply as an agent that merely disrupts or enhances the formation of surfactant micelles and the free energies of micelle formation are thus modified to account for the presence of the polymer. For instance, the surface area of contact between water and hydrocarbonous part of the surfactant micelle is assumed to be reduced a certain amount due to the effect of the polymer shielding water/hydrocarbon contact. As a result, the free energy associated with the formation of hydrocarbon/water interface in micellar solution is modified.

The heats of micellization for an ionic surfactant is represented by the equation

$$\Delta H_{mic} = RT\ln(cmc)$$

(12) where R is the gas constant, T absolute temperature. The heats of formation of free micelles and polymer bound aggregates were found by comparing the cmc's of the surfactant with and without the polymer over a range of temperatures. These results have shown that the heat of complex formation between

the surfactant and polymer is less exothermic than the heat of micellization. It was argued that the difference is a result of higher counterion dissociation of the bound surfactant molecules compared to free micelles. This gives rise to a higher surface charge density per aggregate for the polymer bound premicelles relative to free micelles. Electrical conductivity results, which are a more direct way of observing this effect, confirmed this hypothesis and also showed that increasing polymer concentration at constant surfactant concentration increases the degree of counterion dissociation. Thus, PVP and PEO act as a nucleating agents for surfactant molecules and stabilize surfactant aggregates which are smaller than free micelles.

1.6 Polymeric micelles

A slightly different class of problem that has received some attention in the literature (13-23) is the behavior of charged amphiphilic polymers in aqueous solutions without surfactant. These polymers have monomer units with an ionizable group and a linear alkyl segment. It has been observed that under certain pH conditions the alkyl groups from one or more polymer molecules aggregate in a manner similar to that of monomeric surfactants. These aggregates, which have been called polymeric micelles, have characteristic geometries (cylindrical, ellipsoidal,etc) and aggregation numbers (number of alkyl chains per aggregate) which depend upon the length of the alkyl monomers of the polymer. They also have solubilizing power similar to that of surfactants with the same hydrocarbon chain length. The formation of these aggregates is driven by the decrease in free energy of the system which occurs when the contact of the hydrophobes with the water molecules is replaced by contact among themselves.

In all the solutions considered so far, the incompatibility of the hydrophobic segments of amphiphilic molecules and polar solvent molecules is the sole reason for the formation of organized assemblies, such as micelles. Thus in the next section, I will try to shed some light on the origin of this incompatibility.

1.7 Origins of the hydrophobic effect

Organic molecules in an aqueous solution modify the ability of the water molecules to form hydrogen bonds thereby changing the water structure. The water molecules order themselves around the nonpolar molecule and hydrogen bonding formation is enhanced. The large entropy loss that accompanies this effect makes the presence of hydrophobic molecules in a water environment unfavorable. As a result there is a great tendency of the organic molecules to associate due to the more favorable van der Waals interactions among themselves. When two or more nonpolar groups come into contact in an aqueous environment and as a result decrease the extent of interaction with the surrounding water, a hydrophobic bond is said to be formed between them. The presence of these hydrophobic bonds is found to be responsible for the various conformations that are observed, for example, in proteins with varying degrees of hydrocarbon content in aqueous solutions. It has been shown that hydrophobic bonds achieve a high degree of importance only in aqueous environments.

In other strongly polar solvents, the driving force for the formation of hydrophobic bonds mainly arises from enthalpically favorable interactions among the hydrophobes rather than strong entropic tendencies as in water. In addition, it has been observed that hydrophobic bonding is nonspecific. For example, this bonding can occur between a hydrophobic segment of the solvent molecules and nonpolar side chains from a macromolecule. Thus, for an amphiphilic macromolecule in a mixed solvent composed of water and a relatively nonpolar solvent such as a short chain alcohol, the nonpolar segments of the macromolecule do not necessarily aggregate among themselves but participate in hydrophobic bonding with the nonpolar solvent molecules.

Furthermore, it is required that the various segments that form a hydrophobic bond must literally contact each other (27) . This is because the water molecules whose structure is affected by the presence of the organic molecule are those in contact with the hydrophobe and the van der Waals forces that bring the hydrophobes and water molecules together fall off rapidly with separation. As a result, if the hydrophobic segments on a given long chain macromolecule are sparsely distributed along the backbone and are therefore not able to overlap, or if there are any other steric or conformational factors that hinder contact among the hydrophobes, the polymer will not be able to form stable hydrophobic bonds and may become insoluble in water. However, the polymer may once again be soluble in water at high concentrations where intermolecular hydrophobic bonds can be formed.

1.8 This work

In this study, we will investigate properties of solutions containing HMHEC and surfactants. This polymer differs from those investigated by others in that at even relatively low hydrophobe substitution it is insoluble in water. However, the presence of surfactant modifies the solubility of the polymer in solution. In all other studies, water is a good solvent for the polymer and therefore, the interactions between the polymer and water dominate the properties of the solution. In our case, the behavior of the polymer in solution will be a direct result of specific interactions between polymer and surfactant.

We have found in the HMHEC/SDS system the presence of different regions of behavior corresponding to different surfactant and polymer concentrations (chapter 3). Surfactant binding to the polymer starts abruptly at a surfactant concentration that varies with the amount of polymer in the system. In addition, hydrogels whose strengths depend on the solution composition form in the HMHEC/SDS system.

We present the investigation of the bulk and structural properties of the hydrogels as function of composition of the starting solution. We used rheology, fluorescence spectroscopy, viscometry and conductivity to characterize these materials.

The long-term objectives of this work are: To develop understanding of phase separation behavior. Develop and characterize new phase separating material. Explore possible applications for these material

Chapter 2

Experimental program

The experimental techniques to be used in characterizing the solutions and gels in our system are neutron scattering, rheology, fluorescence spectroscopy, viscometry and conductivity. The principles of and specific properties measured by each of these techniques will be explained inturn.

2.1 Linear viscoelastic properties of the gel and the solutions

The response of polymer solutions and gels to externally applied deformations is a manifestation of the dynamic processes which the polymer chains are undergoing at the molecular level. In general, a polymer chain subjected to a small deforming outside force attempts to dissipate the external energy through a combination of bond rotations and stretching of the overall chain from its equilibrium end to end length. Large outside forces require bulk movement of the sample since the small internal rearrangements are not sufficient to dissipate all the energy. After the cessation of the outside force, the polymer relaxes to its equilibrium configuration and most of the stretching energy and some of the rotational energy are released. The time required to bring two successive bonds back to their original spatial relationship is alot faster than that required to relax long range conformational rearrangement of the whole chain. As a result, any dynamic outside stress with frequency higher than the relaxtion frequency of the polymer dynamics will work against an already stretched polymer chains. Consequently, the rigidity of the polymer depends on the frequency of the applied stress.

The dependence of stress on the time derivative of strain or frequency of strain in polymers is characterized by a pattern of certain regions on the rigidity vs frequency plots. For most polymers there is the terminal region, the plateau region, and the glassy region. These regions can be associated qualitatively with different kinds of molecular responses, and appear with different degrees of prominence depending on the polymer properties such as the influence of chain mobility by the presence of the other chains and the rotational felixibility of the bonds connecting successive monomer units.

Dynamic Mechanical Measurements

Viscoelastic materials subjected to an oscillatory shearing flow are characterized quantitatively by a complex viscosity and complex modulus. In a typical experiment, the sample is placed in space between a cone with a small angle and plate. The cone is then caused to oscillate sinusoidally. For a perfectly elastic sample the stress and the strain are related through Hooke's law and therefore the stress developed within the sample by the oscillating strain will also be sinusoidal and in phase with the strain. On the other hand the sinusoidal rate of strain will lead the stress by 90 degrees in viscous (inelastic) Newtonian fluids. The behavior of viscoelastic fluids and gels is intermediate between that of the elastic solid and the viscous liquid and therefore the stress will lead the strain by an angle less than 90 degrees. It is usual to resolve this response into elastic and viscous components, that is, a component in phase with the imposed strain and a component 90 degrees in advance of the strain. The response can be described by a complex modulus G^*, which is the vector sum of the (in-phase) storage modulus G' and the (out-of-phase) loss modulus G'':

$$G^* = G' + i\,G''$$

In-phase stress component

where G′ = ------------------------

Strain amplitude

out-of-phase stress component

and G" = -------------------------

Strain amplitude

We have:

$$G^* = \tau^* / \gamma$$

We also define the complex dynamic viscosity,

$$\eta^* = \tau^* / \dot{\gamma}$$

for sinusoidal angular deflections at a radian frequency ω , with angular amplitude ϕ and shear strain amplitude γ .

Thus:

$$\eta^* = \frac{G^*}{i\omega}$$

$$= \frac{G'}{i\omega} + \frac{G''}{i\omega}$$

$$= \frac{G''}{\omega} - i\frac{G}{\omega}$$

$$= \eta' - i\frac{G'}{\omega}$$

where

$$\eta' = \text{dynamic viscosity}$$

For a cone and plate geometry:

$$\gamma = \frac{\phi r}{h}$$

$$= \frac{\phi}{d}$$

Thus
$$G^* = \tau^*/\gamma$$

$$G^* = \frac{12Ta}{\pi d^3 \phi}$$

where T is the measured torque, a is the cone angle and d is the plate diameter.

Hence by measuring the amplitude ratios of peak torque to peak angular deflection, and the phase angle between them, the modulus and complex viscosity can be determined.

Viscoelasatic properties such as the dependence of the bulk viscosity on the shear rate as well as viscometric functions such as storage and loss moduli are the quantities that are measured in a typical rheological experiment. These quantities are related to the molecular structure of the sample through various theories and models. The applicability of any of the available theories and models to a particular system depends on the physicochemical properties of that system. In the case of permanently cross linked polymers, for example, the highly elastic response of the sample to a deformation is attributed to the chemical cross links that physically tie different chains together. The theory of rubber elasticity (36) is, therefore, used to determine the structural properties of the polymer, such as the molecular weight between crosslinks, from measurements of the viscometric functions. The origin of the nonNewtonian behavior which is also observed for uncrosslinked bulk and concentrated polymer solutions is found to be due to entanglements of many polymer chains and the resulting constraint that an individual chain cannot cross the contour of another chain in response to a deforming force (37-42) . The theory of Doi and Edwards (42) is mostly used to investigate the structure of polymers solutions in this case. It says that entangled polymer solution respond to an external stress by diffusing in a snake-like fashion along their own contours. Individual polymers chains move from one large scale conformation to another with a relaxtion time t given as

$$t = \eta_0 / J_{0e}$$

where η_0 is the zero shear viscosity, the ratio of steady state shear stress to shear rate; and J_{0e} is the recoverable compliance, the ratio of total recoil strain to shear stress at steady state.

In our system, neither is the polymer concentration high enough to expect any entanglement of the polymer main chains nor are there any chemical crosslinks to physically hold chains together. However, due to the intermolecular aggregation of the alkyl grafts, we have observed viscoelasticity in our system (see Chap.3). No theory has been developed to deal with this kind of polymer interactions. Considering these intermolecular interactions as weak crosslinks between different polymer chains, the theory of rubber elasticity may be applicable up to shear rates that do not break up the aggregates. This will enable us to relate certain structural properties of our system, such as the molecular weight between aggregates, to visometric functions such as the plateau modulus in oscillatory shear experiments. The relationship that will be used is from rubber elasticity and is as follows:

$$M_e = \frac{\rho \upsilon R T}{G_n}$$

Where ρ is the density of dry polymer, ν is the volume fraction of polymer in the solution, R is the universal gas constant, M_e is the molecular weight between links and T is the absolute temperature of the sample. G_N is the so called plateau modulus and is the plateau value of G′, the storage modulus, measured experimentally from dynamic viscoelastic measurement.

2.2 Fluorescence spectroscopy

A. Detection of hydrophobic aggregates:

Fluorescence is the emission of photons by an excited molecule. The frequency of emission (nanoseconds) as well as the emission intensity of a particular fluorophore is influenced by anything that interacts with the fluorophore during its excited state period (43). Those interactions can be, e.g. dipole-dipole interactions between the solvent and the probe. The variation in the emission spectra of a probe as its environment changes is used to determine certain properties such as the dielectric constant and conformational changes of macromolecules in solution (43). We postulated that in our system a change in emission spectra of a fluorophore will occur if microdomains form in our solutions. To insure that the method was successful, a hydrophobic probe that is only sparingly soluble in water and hence prefers to associate with hydrophobic regions as they form was be used. This probe was introduced into solution and its spectrum monitored as described above under different conditions. Thus, we will be able to detect the presence or absence of hydrophobic aggregates.

Using fluorescence spectroscopy, we have shown the existence of hydrophobic microdomains dispersed in the hydrophilic polymer gel in our system. Results from that investigation, the principles involved and the detailed experimental procedure used are presented in chapter 3.

B. Determining the size of the aggregates:

We have also used fluorescence spectroscopy to determine the size of the hydrophobic domains. This size, as reflected by the aggregation number, which is defined as the number of alkyl grafts in any one aggregate, can be obtained using either steady state or time resolved fluorescence spectroscopy (44). In both time resolved and steady state, a fluorescence probe and an appropriate quencher are brought into close proximity within an aggregate(44,45,46). The degree of quenching, as measured by the associated decrease in the emission intensity, has been shown to be related to the size of the aggregate.

C. Relationship between fluorescence intensity and size of the aggregate:

Consider a solution containing a fluorescence probe and quencher. Consider also the case where they are both solubilized in a hydrophobic aggregate that is dispersed in the bulk solution. If light with a wavelength in the region where only the probe can absorb is now shone on the solution, the probe will fluoresce. The emitted light will, however, have a lower intensity than that absorbed due to quenching and other nonradiative processes,such as intersystem crossing, that occur during the lifetime of the probe. This decrease in intensity can modelled as follows:

$$P^* \xrightarrow{k_f} h\nu + P \quad \text{Fluorescence decay}$$

$$P^* \xrightarrow{k_{nr}} P \quad \text{Nonradiative decay}$$

$$[P^* \ldots M_i] \xrightarrow{ik_q} [P \ldots M_i] \quad \text{Quenching, } i=1,2\ldots$$

where P^* and P represent excited and ground state probes respectively, M_i represents the fraction of aggregates containing iQ quencher molecules, k_f and k_{nr} are the rate constants for the above decaying processes.

Deactivation due to quenching requires the contact of the probe and the quencher during the lifetime of the probe. The quenching constant, k_q, is a measure of the encounter frequency of the pair of molecules confined in the aggregate. It is, therefore, assumed that the rate of quenching in an aggregate containing i quenchers is i times that in an aggregate with just one quencher. It is further assumed that the overall quenching process is kinetically first order with a rate constant of k_q by analogy with intramolecular rate processes.

M_i represents the fraction of aggregates containing iq quencher molecules. The partitioning of hydrophobic molecules in hydrophobic regions dispersed within a hydrophilic environment is shown to follow a Poisson distribution. Thus, the distribution of quenchers among the aggregates is

$$[M_i]/[M] = n_q^i \, \mathrm{Exp}(-n_q)/i$$

where [M] is the total number of aggregates in the sample and n_q is the Poisson average number of quenchers in an aggregate.

The equation governing the above deactivation processes is, therefore:

$$d[P^*]/dt = n_q^i \, \mathrm{Exp}(-n_q)/i \; F(P) - (k_f + k_{nr} + ik_q)[P^*_i]$$

F(P) is the formation of P^* molecules and $[P^*_i]$ is the concentration at time t of probe molecules in an aggregate that contains iQ quencher molecules.

D. Steady state fluorescence:

The solution to the above equation at steady state is:

$$\ln (I_0/I) = n[Q]/([C])$$

where I_0 and I are the fluorescence intensity with and without quencher, respectively, n is the aggregation number, [Q] is the concentration of the quencher in mol/l, and [C] is the alkyl graft concentration in the system. Thus, a plot of the log of the intensity ratio vs. quencher concentration will give the aggregation number. The validity of this technique is based on the assumption that both the probe and the quencher are present only in the aggregates, that they distribute among the aggregates according to the same distribution function (usually assumed to be a Poisson distribution) (45,46), and the quenching rate is faster than the decay rate of the probe itself. We have used a probe/quencher pair which have been demonstrated to meet these requirements in other systems. We have also used this pair ourselves in another study involving surfactants (chapter 5). The structure of the probe and quencher and the relevant experimental parameters such as the excitation and emission wavelengths are in the appendix. The aggregation numbers obtained in this way are weight averaged and will therefore complement those obtained in neutron scattering experiments.

2.3 Conductivity

Sodium dodecyl sulfate is the only conducting species in our solutions. Any changes in the conductivity of SDS due to the presence of the polymer can be detected. If the surfactant molecules aggregate on to the polymer chains their specific conductance decreases. In this way polymer surfactant interactions can be detected. We have used this method in our investigation and the details are in the experimental section of chapter 3.

2.4 Viscometry

Viscosity of the solutions were measured using a Ubbelohde viscometer, in which the time for a liquid to flow through a cylindrical capillary under gravity is measured. The viscosity of the polymers relative to the solvent are obtained over a range of surfactant concentrations. Results were found that allowed us to locate the regions where surfactants and polymers interact (Chap.3).

2.5 Conclusion

From viscometry and conductivity, we were able to show that polymer/surfactant interactions occur. We have also shown, through fluorescence spectroscopy, the existence of hydrophobic aggregates in some solutions. We have synthesized hydrogels which are also characterized by hydrophobic domains that are dispersed in a swollen polymer matrix. The rheological experiments enabled us to relate the mechanical properties of the hydrogels with the composition of the hydrogels. In the proposed neutron scattering experiments, we plan to obtain the size and the geometry of these domains.

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Chapter 3.

HYDROPHOBIC MICROPHASE FORMATION IN SURFACTANT SOLUTIONS CONTAINING AN AMPHIPHILIC GRAFT COPOLYMER

This chapter contains the aqueous solution properties of HMHEC/SDS system. Of particular interest are the formation of either heterogenous two phase solutions and gels or a homogenous solution depending on the surfactant concentration. This is unlike the behavior observed in all other polymer/surfactant systems reported in the literature. Some of this work is published already in the macromolecules Journal.

3.1 ABSTRACT

Strong association between the hydrophobic side chains on water insoluble C_{12} grafted hydroxyethyl cellulose and sodium dodecylsulfate in aqueous solution is reported. This association gives rise to viscoelastic solutions and hydrogels with dispersed hydrophobic microdomains, indicating that intermolecular surfactant bridges are linking alkyl chains from more than one macromolecule. The solutions were characterized using conductivity, viscosity, and pyrene fluorescence measurements.

3.2 INTRODUCTION

Considerable effort has been devoted toward understanding the bulk and microscopic properties of aqueous solutions containing surfactants and water soluble polymers. This work has made use of a variety of experimental techniques including neutron scattering (1), nmr (2), fluorescence spectroscopy (3,4,5), dye solubilization (5,6), viscosity (6,7) esr spin probe techniques (8), and has focused on determining the types of structures that form as a result of interactions between the polymer segments and the surfactant molecules. Both polymer/surfactant interactions and self-aggregation of surface-active copolymers have been studied.

Results on water soluble homopolymers like poly(ethylene oxide) (1-4) and poly(vinylpyrrolidone) (3,9-12) in sodium dodecyl sulfate (SDS) indicate that initially surfactant molecules prefer to adsorb onto the polymer chain rather than aggregate into micelles. These interactions occur on uniform hydrophilic polymer backbones where there is no preferred site for adsorption. The adsorbed surfactant aggregates have aggregation numbers that are 30 - 50% lower than pure surfactant micelles (4). Beyond a certain concentration of the surfactant which is higher than the critical micelle concentration (cmc), the system favors aggregation of any additional surfactant molecules into free micelles. This transition occurs because coulombic repulsion among the adsorbed surfactant aggregates precludes any additional adsorption on the polymer (1).

With water soluble surface-active copolymers in pure water, self-aggregation has been observed which is reminiscent of the process of micellization in monomeric surfactants. The formation of these aggregates depends on the free energies of the hydrophilic and hydrophobic groups in water. Self-aggregation has been demonstrated using water soluble copolymers composed of long chain alkenes alternating with maleic anhydride (poly(1-alkene-co-(maleic anhydride))) (13-15). They form polymeric micelles with aggregation numbers comparable to those of surfactants with the same alkyl groups. These polymeric aggregates may form either inter- or intermolecularly depending on the length of the hydrophobic side chains and the flexibility of the polymer, as governed in this case by the charge density of its backbone. Also, the shape of the resulting aggregates has been shown to vary with side chain length (15).

The present study is an investigation of the properties of water insoluble surface-active copolymers in aqueous surfactant solutions. We have investigated the properties of a hydrophobically modified water soluble polymer to determine the effects of alkyl grafts on the association of the polymer with surfactant and with itself. The polymer used in this study is hydrophobically modified hydroxyethyl cellulose (HMHEC). Its hydroxyethyl cellulose (HEC) backbone is highly soluble in water and has been shown to interact only very weakly with SDS (6). However a small degree of alkyl substitution on the polymer main chain renders it insoluble in water. Other studies on less-substituted water soluble HMHECs have shown evidence of both polymer/surfactant association and self-aggregation of the polymer via intra- and intermolecular association of the hydrophobes (8,16). We will show that this self-aggregation also occurs in water insoluble HMHECs in the presence of surfactant. Moreover, beyond a critical surfactant concentration, the polymer separates into two distinct macroscopic phases - a water-rich solution and a polymer-rich hydrogel - both of which are characterized by dispersed hydrophobic microphases made up of surfactant molecules and polymer side chains. These dispersed-phase polymer networks are expected to retain permeants in proportion their hydrophobicity, and should therefore have applications in separations and controlled delivery technology.

3.3 EXPERIMENTAL

The polymer hydrophobically modified hydroxyethyl cellulose (HMHEC) was obtained from Aqualon Co., Wilmington, Delaware. Its main chain, hydroxyethyl cellulose (HEC), is composed of anhydroglucose units rendered water soluble by addition of ethylene oxide groups. The HEC polymer is then modified with C_{12} alkyl grafts. The degree of substitution of alkyl grafts in the HMHEC used here is ~0.8% (w/w), corresponding to about one alkyl group per 130 monomer units. The viscosity average molecular weight is 4×10^5. The surfactant sodium dodecyl sulfate (SDS) (Fluka, >99% pure) was used as received. Pyrene (Aldrich, 99% pure), was recrystallized twice from ethanol.

Any conducting material was removed from the both HEC and HMHEC by batch extraction in ethanol. The ethanol does not dissolve the polymer, but the conducting impurity was soluble in the ethanol as indicated by the specific conductivity of the extract. Thus, the polymer was repeatedly washed with fresh alcohol until the specific conductance of the washing solvent fell to 2×10^{-6} mho. The polymer was then dried in vacuum and used within 2 days of purification.

Conductivity measurements on the polymer solutions were performed in a conductance-resistance meter (Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio 45387) using a probe with a cell constant of 1.0 cm^{-1}. In the cases where the sample solutions were composed of two phases (see results below), only the conductivity of the supernatant solution was measured.

All solutions were made up by weight in distilled water saturated with pyrene (3 x 10^{-7} M pyrene) and stirred for an hour. Fluorescence spectra of the pyrene in the solutions were obtained on a Spex Fluorolog-2 Model 112A Fluorescence Spectrophotometer (Spex Industries, Inc., Edison NJ). All spectral characteristics of the pyrene remained constant for at least 24 h after solution preparation. For samples in which both a gel and a supernatant had formed, this indicated that the pyrene had equilibrated between the two phases.

Viscosity of the solutions was measured using a Ubbelohde viscometer, in which the time for a liquid to flow through a cylindrical capillary under gravity is measured. The procedure was repeated three times on each solution with an accuracy greater than +-0.5%.

3.4 RESULTS

We observed first of all that on addition of 0.15% (w/w) HMHEC to pure water without any surfactant present, the polymer precipitates in the form of individual swollen globules. Up to 1 x 10^{-3} M SDS, some of the polymer forms a macroscopic layer on the surface, with the rest precipitating out as before. At higher SDS concentrations, two distinct homogeneous phases are formed. The supernatant phase is a clear solution which was found to contain most of the surfactant and a small amount of polymer. The polymer-rich phase is a one-piece flexible hydrogel which takes the shape of its container and does not swell further or disperse in pure water. The gel phase disappears, with all of the polymer becoming solubilized in the supernatant, as the surfactant level is increased above the cmc (~8 x 10^{-3} M). In the region just above the cmc, the solution exhibits recoil on pouring and cannot pass through ordinary filter paper. The solution remains clear on further addition of SDS, but ceases to exhibit recoil and may be poured easily through a filter. These different regions of solution and gel behavior were investigated individually to determine the nature of the polymer/surfactant interactions in each case.

Figure 1 shows plots of the specific conductance of SDS solutions with and without polymer as a function of surfactant concentration. A break in the specific conductance of pure SDS solutions appears at 8.1 x 10^{-3} M, the cmc of the surfactant. This occurs because the total number of ions in the solution is reduced due to aggregation of the surfactant and the high degree of counterion binding to micelles (17). The specific conductance of solutions containing HEC (the control polymer) and SDS coincides with that of pure SDS solutions. The presence of HMHEC, however, decreases the specific conductance of the solutions relative to controls, beginning at 4 x 10^{-3} M SDS. The only conducting species in the solutions are the surfactant amphiphiles and sodium counterions. Thus it is clear that the surfactant amphiphiles form aggregates in the presence of HMHEC, even blow the cmc. We conclude that within the sensitivity of these measurements the surfactant associates with HMHEC but not with HEC, as expected (6). Note that there is also a sharp break similar to that observed for pure surfactant solutions at 9 x 10^{-3} M surfactant. Thus micelles still form, but at a slightly higher SDS concentration in the presence of HMHEC. Similar increases in the apparent cmc of surfactants in polymer solutions have been observed elsewhere (3), and were attributed to the fact that initially surfactant prefers interacting with the polymer, and only forms micelles when the former interactions become unfavorable.

Figure 2 shows the viscosities of the various solutions as a function of SDS concentration. For pure surfactant, the viscosity is approximately that of water and is independent of surfactant concentration even beyond the cmc. Addition of 0.15% (w/w) control polymer raises the viscosity of both the water and SDS solutions by a factor of ~3, but once again the viscosity does not vary with surfactant. For surfactant solutions containing 0.15% HMHEC the behavior is quite different. Note that HMHEC viscosity data below the cmc (where two phases formed) are for the supernatant solution only. At 4 x 10^{-3} M SDS, the viscosity of the solution begins to rise slowly. This is the point where conductivity results indicated the onset of association between HMHEC and the surfactant. This transition point was reproduced on 3 separate solutions. The observed increase in viscosity above 4 x 10^{-3} M is evidence that polymer has begun to enter the supernatant from the gel. However, this alone does not explain the high viscosity, since all the polymer remains in solution above the cmc where the viscosity drops off, finally levelling off close to the value for HEC in surfactant. We conclude that below the cmc, where the solutions appeared viscoelastic, polymer networks composed of surfactant-mediated hydrophobic interactions are present. These networks break down above the cmc, where the hydrophobes may be solubilized individually by surfactant micelles, making the polymer behave much like the unmodified control material. The similarity in behavior between HMHEC and HEC of the same backbone MW at high surfactant concentration is reasonable in light of the findings of Cabane and Duplessix (1). Their work shows that the minimum intermicellar distance over which adsorbed SDS micelles do not interact either electrostatically or sterically corresponds to 60 PEO monomer units, which is equivalent to approximately 23 HEC units. The HMHEC used here has an average distribution of 1 alkyl side chain per 130 monomer units, so SDS micelles adsorbed on the side chains will be separated enough not to affect the dimensions of the polymer and hence the viscosity of polymer solutions.

The relative intensities of the vibrionic bands of pyrene fluorescence spectra are closely related to the polarity of the pyrene's environment. The spectra are characterized by 5 distinct peaks; the ratio of the intensities of peaks 3 and 1 (I3/I1) has been shown (18) to be direct function of the hydrophobicity of the pyrene's environment. We used this property to probe the microscopic structure of the aggregates that gave rise to the bulk properties described above. Pyrene is only sparingly soluble ($\tilde{}3 \times 10^{-7}$ M) in water, and will partition into any non-polar regions in a solution or dispersion.

Typical pyrene spectra in HMHEC/surfactant solutions are shown in Figure 3. Figure 4 gives values for the ratio I3/I1 for aqueous SDS/polymer solutions containing pyrene as a function of SDS concentration. For SDS in water, I3/I1 assumes two different values above and below the cmc, as expected. Below the cmc, the pyrene resides in the bulk (aqueous) solution, with I3/I1 = 0.58 ($I3/I1_{water}$ = 0.55 (3)); above the cmc the pyrene partitions into micelles, and the value of I3/I1 goes to 0.83, reflecting a more hydrophobic environment. Solutions containing 0.15 % (w/w) HEC produced similar results, with I3/I1 values depending only on whether or not surfactant micelles are present. The slightly higher hydrophobicity of the solutions below the cmc of SDS may be attributed to the presence of the polymer. With HMHEC, on the other hand, the environment of the pyrene in the supernatant solution becomes increasingly hydrophobic on addition of SDS, leveling off at the cmc of pure surfactant. Recall that in these solutions the total HMHEC concentration in the supernatant phase goes up with increasing SDS. However, here again the observed increase in hydrophobicity of the solution with SDS cannot be due to the increase in polymer concentration alone, as discussed below. Thus we have evidence that hydrophobic regions have begun to form in the supernatant phase of HMHEC/SDS solutions even below the cmc. Results on the gel phase are even more dramatic. Here we see that regardless of either surfactant or polymer concentration, hydrophobic regions are present and their average polarity remains constant until all of the polymer leaves the gel to dissolve in the supernatant. Thus the microscopic composition of the gel is independent of its bulk composition.

3.5 DISCUSSION

HMHEC/surfactant solutions will be characterized by interactions between surfactant molecules and the polymer backbones, surfactant and polymer side chains, and among several side chains. The first of these will also be present in HEC/surfactant solutions; thus any unusual behavior observed with HMHEC may be attributed directly to the presence of the hydrophobes on the polymer.

The possible types of interactions involving the hydrophobes are as follows:

1. Intramolecular associations of alkyl grafts from the same polymer chain, giving rise to polymer chains with a relatively coiled configuration. Intramolecular micelles of this type must be characterized by an aggregation number similar to that of monomeric surfactant micelles with the same hydrophobe chain length (15). This packing density is required in order to exclude water completely and provide maximum contact among the hydrophobes in the aggregates. In our polymer, the total side chain content per polymer molecule is too low to satisfy this requirement; hence the polymer precipitates in water.

2. Intermolecular associations among hydrophobic grafts from several polymer chains. Intermolecular interactions in polymer solutions give rise to non-Newtonian behavior and a high bulk viscosity. Such interactions have been observed in water soluble poly(1-alkene-co-(maleic anhydride)) (13-15), maleic anhydride-hexyl vinyl ether copolymer (19), and in water soluble HMHEC both with (7,8,16) and without surfactant (7,20). They have been described as polymeric micelles with relatively bulky "head groups" made up of the main chains of the polymer. However, they did not form spontaneously with our water insoluble HMHEC, but required the intervention of surfactant.

3. Alkyl grafts solubilized by SDS. When the surfactant concentration has reached a high enough level, there is enough surfactant present to solubilize most or all of the polymer side chains individually. Thus intermolecular interactions disappear, leading to a decrease in the bulk viscosity of the solution. This explanation is supported by the fact that the surfactant concentration at which the interactions begin to break down is a linear function of the total HMHEC concentration in the solution (16).

Thus the following picture of HMHEC/surfactant interactions emerges. In the presence of some small but finite amount of surfactant, surfactant molecules begin to adsorb onto the polymer chain from the bulk phase. This can be seen from the decrease in the specific conductance of the solution with polymer (Figure 1). It is known (1-4, 9-12) that in aqueous solutions of PEO and PVP, for example, surfactant molecules adsorb on the polymer backbone even below the cmc. However, in these cases as with our control polymer the adsorption process is not site-specific and the viscosity did not vary with surfactant concentration as it does with HMHEC. With HMHEC the side chains provide a nucleus for surfactant adsorption. The resulting side chain/surfactant complexes are hydrophobic and micelle-like in nature, and can solubilize pyrene readily. Note that when all of the HMHEC is solubilized (0.15% w/w), the total moles of C_{12} contributed by the polymer is 7.1×10^{-5} mol/l. This is over an order of magnitude less than the starting C_{12} concentration from the surfactant, which we have seen has almost no effect on the pyrene fluorescence signal until micelles begin to form. Thus the presence of the additional hydrophobe from the polymer cannot by itself be responsible for the observed higher hydrophobicity in the supernatant phase.

As the surfactant concentration is increased, surfactant molecules replace polymer side chains in the aggregates. A relatively high ratio of surfactant molecules to polymer side chains in these aggregates is favored because it permits denser packing of the hydrophobes. Once the intermolecular associations are disrupted, the HMHEC in solution resembles HEC, the backbone polymer, with the hydrophobes completely shielded from the water phase and therefore not contributing at all to the bulk solution properties. This can be seen from Figures 2 and 4.

3.6 CONCLUSIONS

Strong site-specific adsorption of surfactant occurs on the hydrophobic side chains of water-insoluble HMHEC. The resulting interactions give rise to a network composed of hydrophobic microdomains dispersed throughout an aqueous polymer solution or gel, depending on the composition of the system.

The hydrogel phase which forms from HMHEC below the cmc of the surfactant appears to be an important new material which bears further investigation. It is clear, flexible, viscoelastic, and homogeneous and contains hydrophobic regions in an aqueous network. This material may have numerous applications in separations technology and controlled release, and a detailed investigation of their structure and composition is presented in chapter 4.

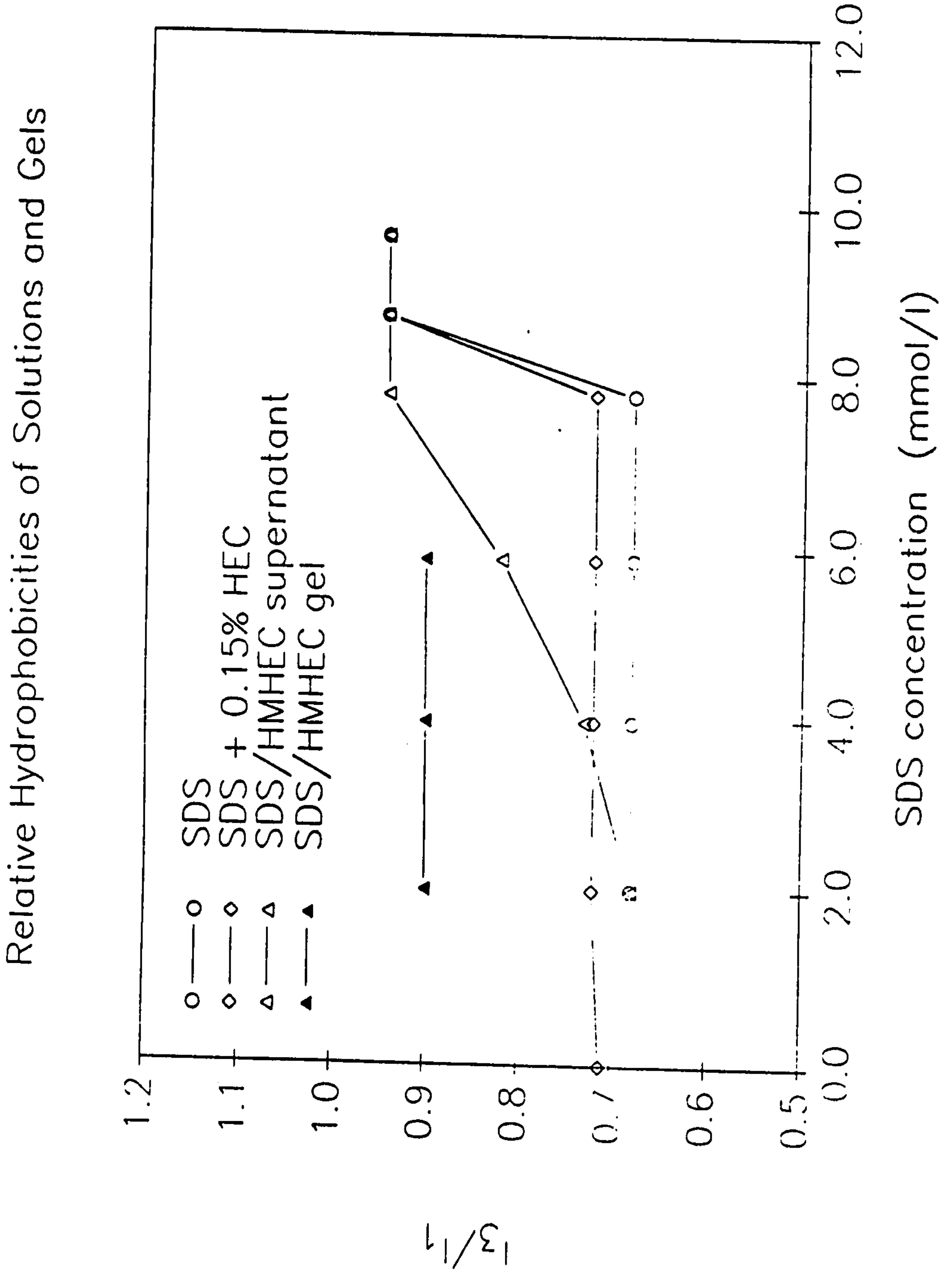
Relative Hydrophobicities of Solutions and Gels
○——○ SDS
◇——◇ SDS + 0.15% HEC
△——△ SDS/HMHEC supernatant
▲——▲ SDS/HMHEC gel
I3/I1
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.0
2.0
4.0
6.0
8.0
10.0
12.0
SDS concentration (mmol/l)

FIG. 4

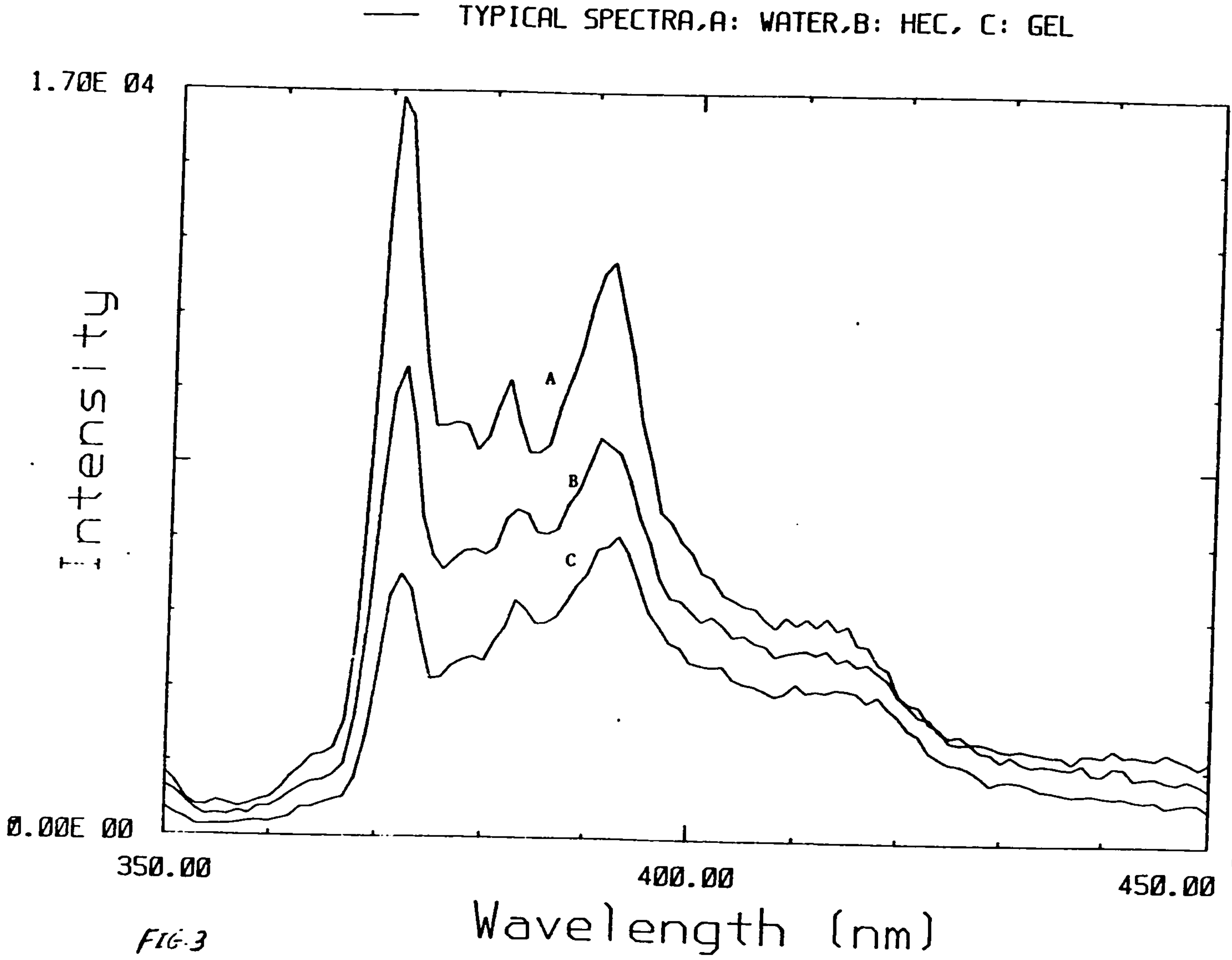
TYPICAL SPECTRA,A: WATER,B: HEC, C: GEL
1.70E 04
0.00E 00
Intensity
350.00
400.00
450.00
Wavelength (nm)
A
B
C

FIG-3

Effect of SDS Concentration on Polymer Solution Viscosity

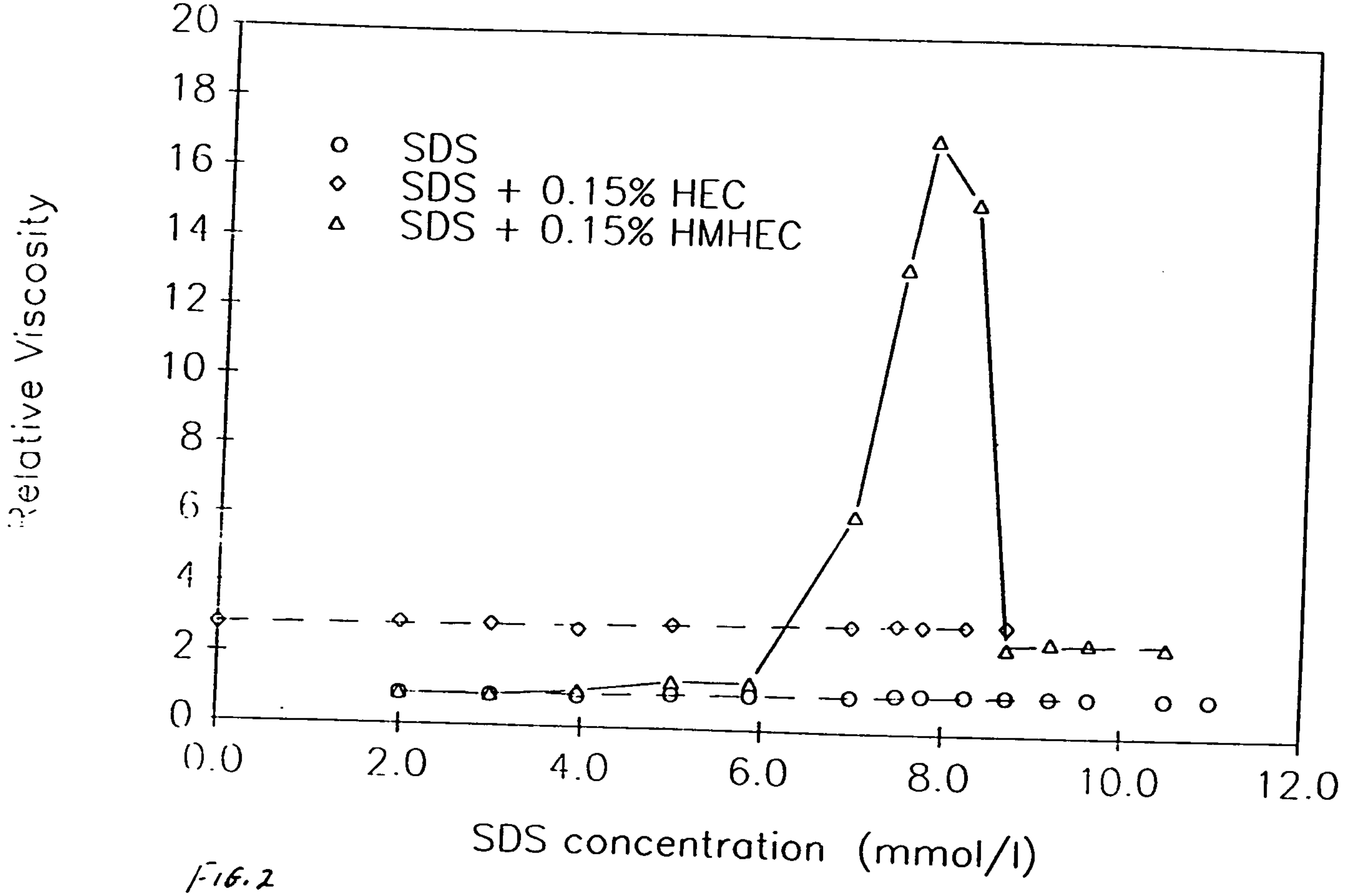

FIG. 2

Specific Conductance of SDS/Polymer Solutions

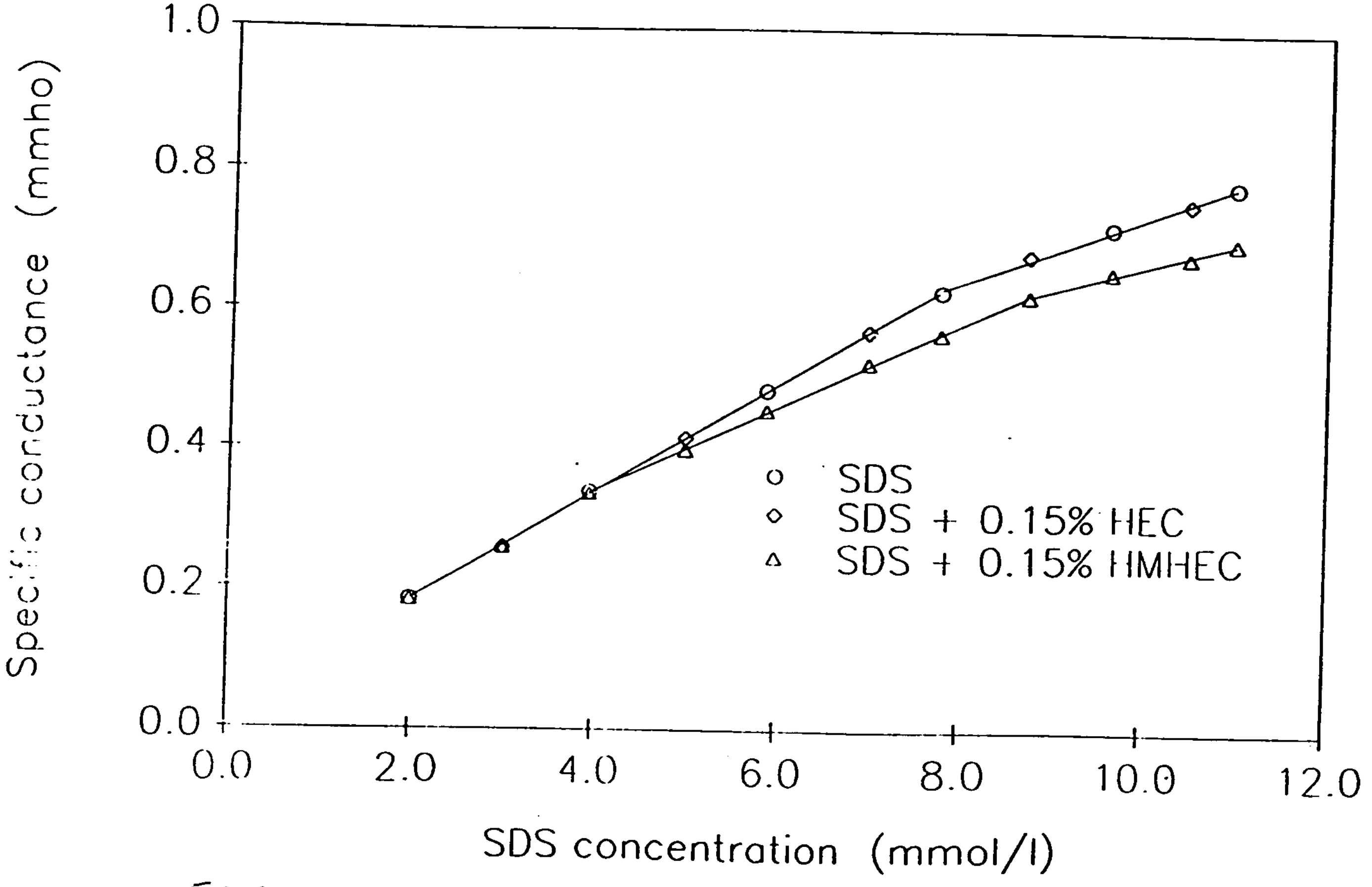

FIG. 1

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Chapter 4.

Bulk and Microscopic Properties of Surfactant-Bridged Hydrogels Made from an Amphiphilic Graft Copolymer

This Chapter contains the text of a manuscript currently in review. I present a summary of results pertaining to the properties of the hydrogels. I also present all of the rheological spectra and fluoresence data not included in the manuscript for publication. All the figures refered to in this chapter are in the end of the chapter.

4.1 ABSTRACT

Water-swollen hydrogels characterized by hydrophobic microdomains within an aqueous polymer network have been investigated. The microdomains consist of comicelles of sodium dodecyl sulfate (SDS) and alkyl grafts from a hydrophobically modified water-soluble polymer, and form at concentrations below the critical micelle concentration of the surfactant alone. These aggregates behave like pseudo-crosslinks, bridging together many polymer molecules to form a viscoelastic network. The comicelles have the ability to solubilize water-insoluble dyes, hence these materials may be of use in separations and controlled release processes.

4.2 Introduction

In chapter 3 (1), we reported the formation of hydrogels from a nonionic graft copolymer in the presence of unmicellized sodium dodecyl sulfate (SDS). The gels are characterized by dispersed micelle-like hydrophobic aggregates. These aggregates bridge several copolymer chains, acting as crosslinks. At concentrations higher than the critical micelle concentration of pure SDS, the gels disperse. In this work we explore the composition and properties of the aggregates themselves with an eye toward exploiting the unique structure of these new materials in numerous applications.

Micelles consisting of insoluble side chains from graft copolymers have been shown to form in aqueous solutions of alternating copolymers with both ionizable and hydrophobic monomer units (2-6). The existence and aggregation number of these micelles, as well as whether they are comprised of units from one or more polymer chains, depend on such factors as the flexibility of the backbone (as governed by the pH of the solution) and the length of the hydrophobic group. Under conditions where micelle formation is unfavorable, these copolymers are insoluble in water because of their relatively high hydrophobicity.

The polymer used in the present study, hydrophobically modified hydroxyethyl cellulose (HMHEC), is insoluble in water but soluble in high concentrations of surfactants, due to association of the hydrophobic polymer side chains with the surfactant (7-11). The resulting aggregates are analogous to mixed micelles which form in solutions containing surfactant and free monomeric amphiphiles which may or may not form aggregates on their own (12-15). The size and composition of these mixed micelles vary with the molar ratio of surfactant to the monomeric amphiphiles in the bulk. Mixed micelles among surfactant molecules and alkyl grafts from an alternating copolymer are also known to occur (6).

The composition of the aggregates in our nonionic polymer hydrogels will determine their ability to solubilize small molecules permeating the gel. The more hydrophobic the aggregate, the more likely hydrophobic solutes will be to partition into and remain within its interior. Thus gels with these immobilized "micelles" may be useful in chromatography or controlled release applications.

In this paper we present an analysis of the composition of the dispersed hydrophobic aggregates which form under various conditions in nonionic dispersed-phase hydrogels. We used steady state fluorescence measurements to determine the size and composition of the aggregates (13,16-18). We also examine the effect of aggregate composition on the dynamic rheological properties of the gels.

4.3 Experimental

Materials:

Hydrophobically modified hydroxyethylcellulose (HMHEC) (commercial name Natrosol Plus^R), MW ~10^6, with 3.7% molar substitution of ethylene oxide per anhydroglucose unit and 1.33% by weight $C_{12}H_{25}$ alkyl hydrophobe substitution, was a gift from Aqualon Corp., Wilmington, De. Sodium dodecyl sulphate (SDS), 99% pure, was obtained from Fluka and used as received. The critical micelle concentration (cmc) was found by conductivity to be 8e-3.

The fluorescence probe used was Tris(2-2 bipyridine) ruthenium (II) chloride ($Ru^{2+}Cl^-$) (AESAR, 892 Lafayette Road, P.O. Box 1087, Seabrook, NH 03874-1087), emission wavelength maximum in SDS of 628nm (excitation at 453nm). The quencher was 9-methyl anthracene. This probe/quencher pair was selected because it satisfies all of the requirements for use with this technique as discussed elsewhere (16) and has been used successfully to characterize SDS/water solutions.

Sample preparation and methods:

From a fixed stock surfactant solution (8e-2 M), a series of solutions ranging from 1e-3 to 7.2e-3 M surfactant and 100 to 600 ml in volume were prepared. A fixed amount (0.4g) of polymer was stirred into the vortex of each solution, giving a ratio of surfactant to alkyl graft concentrations (C_s/C_a) of between 15:1 and 150:1. Microliter amounts of the probe and quencher were introduced into the solutions from stock probe and quencher solutions in ethanol. The solutions were then allowed to equilibrate for two hours, leading to the formation of a gel phase and supernatant solution. By injecting the probe and the quencher during mixing, we were able to insure the solubilization of all the quencher in the gel phase, as indicated by the lack of any fluorescence of 9-methyl anthracene in the supernatant. A small but reproducible (^{t}o +0.5%) amount of probe always remained in the supernatant. If the probe and quencher were introduced after the gel had formed, they remained in the supernatant.

Dynamic mechanical measurements of the gels were performed using a cone and plate Instron 3250 Rotary Rheometer operating in an oscillating mode. The torque and phase angle were measured with a Solartron frequency response analyzer and the storage and loss moduli of the gels were obtained.

Steady state fluorescence measurements were performed on a Spex Model 112A Fluorolog-2 Fluorescence Spectrometer.

4.4 Results

Below the critical micelle concentration (cmc) of the surfactant, the mixtures of polymer and surfactant always form a polymer rich gel phase and a supernatant phase composed primarily of surfactant and water. Only mixtures giving a supernatant with viscosity <1.5 cp were used, allowing us to neglect the presence of polymer in the supernatant for the purposes of our analysis. Thus all of the gels described here are assumed to have an identical polymer content equal to 0.4 g. It will be seen, however, that the volume of the gels containing this constant amount of polymer ranges from 37 to 88 ml depending on the composition of the initial solution.

The volume of the gel increases with increasing surfactant concentration as shown in Figure 1. On the other hand, for a fixed concentration of surfactant, the gel density rises with increasing total polymer concentration in the initial solution. It is also apparent that the molar ratio of surfactant to polymer, and hence surfactant to alkyl graft (C_s/C_a) in the initial solution does not uniquely determine the final gel volume. For example, note that solutions containing 4.8e-3 M with 0.0133g polymer/ml and 7.2e-3 M surfactant with 0.02g polymer/ml, with the same C_s/C_a (45 molecules of SDS per alkyl graft), give rise to gel volumes of 38 and 63 ml, respectively.

Typical rheological spectra of the gels are shown in Figures 2-9, showing the storage (G′) and loss (G″) moduli. The plateau value of the storage modulus (G_n) is inversely proportional to the molecular weight between crosslinks (M_e) or entanglements in network polymers (19). G_n was obtained from our data by averaging the 6 values of G′ spanning the frequency 30 rad/sec, which was near the middle of the plateau for every gel. The plateau modulus decreases with increasing surfactant concentration as shown in Figure 10; thus the molecular weight between entanglement points, M_e, is rising. For a fixed surfactant concentration, M_e also rises with C_s/C_a. This is consistent with the increase in volume observed with increasing C_s/C_a. Results are summarized in Table 1.

Steady state fluorescence quenching is used to determine the aggregation number of surfactant micelles. We have adopted this method to investigate the microstructure of our gels. A fluorescence probe and quencher which are only sparingly soluble or completely insoluble in water will partition into hydrophobic regions in an aqueous system. The resulting fluorescence spectra provide a measure of the size, or aggregation number, of these regions, if they exist, according to the following relation (16):

$$\mathrm{Ln}(I_o/I) = [Q]/[M] \qquad (1)$$

where I_o and I are the fluorescence emission intensity of the probe without and with quencher, respectively, [Q] is the quencher concentration and [M] is the concentration of aggregates in the sample. The slope of this plot is thus the reciprocal of the molar concentration of aggregates. Thus the aggregation number is given by [M] divided by the total moles of aggregated species.

Figures 11-18 shows the effect of quencher concentration on the fluorescence emission intensity of $Ru^{2+}Cl^-$ probe solubilized in a typical gel with and without quencher. The slopes for various gels along with the corresponding compositions are presented in Table 1. From the slope, the number of surfactant molecules (N_s) and the number of alkyl grafts (N_a) in an aggregate can be calculated as follows:

$$N_s = ([\mathrm{surf}]_o - [\mathrm{surf}]_{free})/[M] \qquad (2)$$

$$N_a = ([\mathrm{alkyl}]_o - [\mathrm{alkyl}]_{free})/[M] \qquad (3)$$

where $[\text{surf}]_o$ and $[\text{alkyl}]_o$ are the total surfactant and alkyl graft concentrations in the gel, respectively, and $[\text{surf}]_{\text{free}}$ and $[\text{alkyl}]_{\text{free}}$ are, respectively, the surfactant and alkyl concentrations in the gel that are not part of an aggregate.

The total and free concentrations of the various species in the gel phase were estimated as follows. The conductivity of the supernatant, which is a measure of the concentration of charge carrying species, is approximately equal to the surfactant solution conductivity in the absence of polymer. For lack of a better calibration, we assume this to mean that the total surfactant concentration in both the supernatant and the gel is the same and equal to the surfactant concentration in the starting solution, which is of order e-3. The free surfactant and alkyl concentrations in the gel may be estimated from the cmc of mixtures of SDS and polyoxyethylene (POE) lauryl ether, which form mixed micelles at concentrations far below the cmc of SDS alone (12) in the mole fraction range corresponding to the value of C_s/C_a in our gels. We use values of 5e-5 M and 3e-4 M for the concentrations of free side chain and SDS, respectively, based on studies with mixed micelles of SDS and POE lauryl ethers having 6 and 8 ethoxy groups.

It is clear from these values that N_s and N_a are not very sensitive to errors in the estimation of the free species. Note that the alkyl HMHEC side chains which appear to be combining with SDS in our gels have only 1 or 2 ethoxy groups, so these values represent only a best guess. The calculated values of N_s and N_a for each gel are given in Table 1. The total aggregation number, $N_{tot} = N^s + N_a$, of the SDS/alkyl group comicelles increases with increasing overall surfactant concentration, from 57 to 84 in the range studied (Table 1). The aggregation number of pure SDS near the cmc is 57 (20). It may be that larger assemblies are necessary to accommodate the bulky polymer "head group" from the cosurfactant in an assembly dense enough to exclude water from the interior. Figure 19 presents a summary of the aggregation number results on Table 1, showing that as the SDS concentration increases, the proportion of SDS in the aggregates increases as well. Thus SDS molecules displace the side chains.

4.5 DISCUSSION

Under the same conditions where we observed the formation of both a gel and supernatant phase with HMHEC, HEC formed a homogeneous solution. Thus clearly the gel structure must arise due to interactions involving the hydrophobic side chains. All of the evidence points to the formation of comicelles composed of SDS and alkyl polymer side chains. When these comicelles contain alkyl groups from more than one polymer chain, they act as pseudo-crosslinks, and a polymer network results.

The rheological spectra indicate that high gel volumes correspond to a high Me, as expected. At the same time, the gel volume changes with the structure of the crosslinks, as indicated by the fluorescence results. Several factors contribute to these effects. First, the composition of the aggregates is fixed by the concentrations of the individual species in the initial solution. As the ratio of surfactant to polymer increases in the bulk, this proportion changes in the aggregates as well, as shown in Figure 19. With fewer side chains per aggregate, we expect more bound aggregates on each polymer chain, i.e. a higher Me. At the same time, this increased number of aggregates gives rise to a higher static charge density on the polymer, which is also associated with a higher swollen gel volume (21). Another effect which is important here is the fact that as the surfactant concentration of the bulk solution increases, the solution becomes more hydrophobic and the polymer becomes more compatible with the solvent. This is in accordance with our earlier results showing that at very high surfactant concentration a homogeneous solution is formed (1). It also follows from the fact that for mixed micelles of SDS and POE, the cmc increases above that of pure POE as the SDS mole fraction is increased, showing that POE becomes more soluble in the presence of SDS. Thus at high surfactant concentrations there may be a significant number of free (unmicellized) side chains in the gel, which would also give rise to a high Me. It is not possible to determine which of these factors is the most significant in governing gel volume; however, they all would contribute in the same manner to the effects seen here.

By analogy with crosslinked polyelectrolyte gels, another parameter which contributes to the final swollen gel volume is the mobile ion concentration gradient between the gel and the supernatant. This is a very complex function in the case of these gels. The dissociation constant of bound surfactant molecules depends on the area available per head group in the aggregate. This area will be profoundly affected by the presence of cosurfactant, and hence by the ratio of polymer side chains to surfactant molecules in the aggregates. There is polymer-bound surfactant in both the gel and supernatant phase in our system, with different ratios of the two species in the aggregates in each phase. There is also free dissociated surfactant present in both phases. Thus although the total mobile ion concentration goes up with surfactant concentration, the mobile ion concentration gradient cannot readily be evaluated.

4.6 CONCLUSIONS

The results presented here demonstrate the tendency of $C_{12}H_{25}(EO)_2$ molecule grafted to a cellulose polymer to form comicelles with sodium dodecyl sulfate. This is not unexpected in light of the huge literature showing the formation of comicelles among SDS molecules and cosurfactants (12) or long chain alcohols (13-15) at concentration below the cmc of pure SDS. When the cosurfactant is attached to a polymer, it is apparent from this study that the cmc of SDS is lowered and that mixed micelles still form. In this case, however, a stable polymer network of infinite molecular weight forms spontaneously as a separate phase. These networks behave much like cross-linked polyelectrolytes despite the absence of covalent bonds. This presents a new method of forming hydrogels with many of the desirable characteristics of cross-linked gels but without requiring additional reaction steps in the process.

The networks described in this work are composed of hydrophobic microdomains, which can solubilize a water-insoluble probe, dispersed throughout a water-swollen gel. These characteristics, coupled with the mechanical stability of the gels, makes these new materials interesting candidates for such applications as chromatography or controlled drug release.

Table 1

Summary of Gel and Microdomain Properties

alkyl graft concentration (mM)	SDS conc. (mM)	gel volume (cc)	M_e (g/mol)	1/[M] $(mol/l)^{-1}$	N_s	N_a	N_{tot}
0.105	4.8	39	5.3e4	10820	48.7	8.3	57
	5.6	46.3	7.4e4	10990	58.3	6.9	65.2
	6.4	55.1	1.3e5	11214	68.4	5.8	74
0.157	7.2	63	2.9e5	10556	73	4.7	78
0.32	4.8	38	3.9e4	11259	50.7	8.8	59.5
	5.6	40	4.6e4	10900	57.8	8.1	65.8
	6.4	44.6	8.3e4	10703	65.3	7	72.3
	7.2	46.4	9.4e4	11166	77	7	84

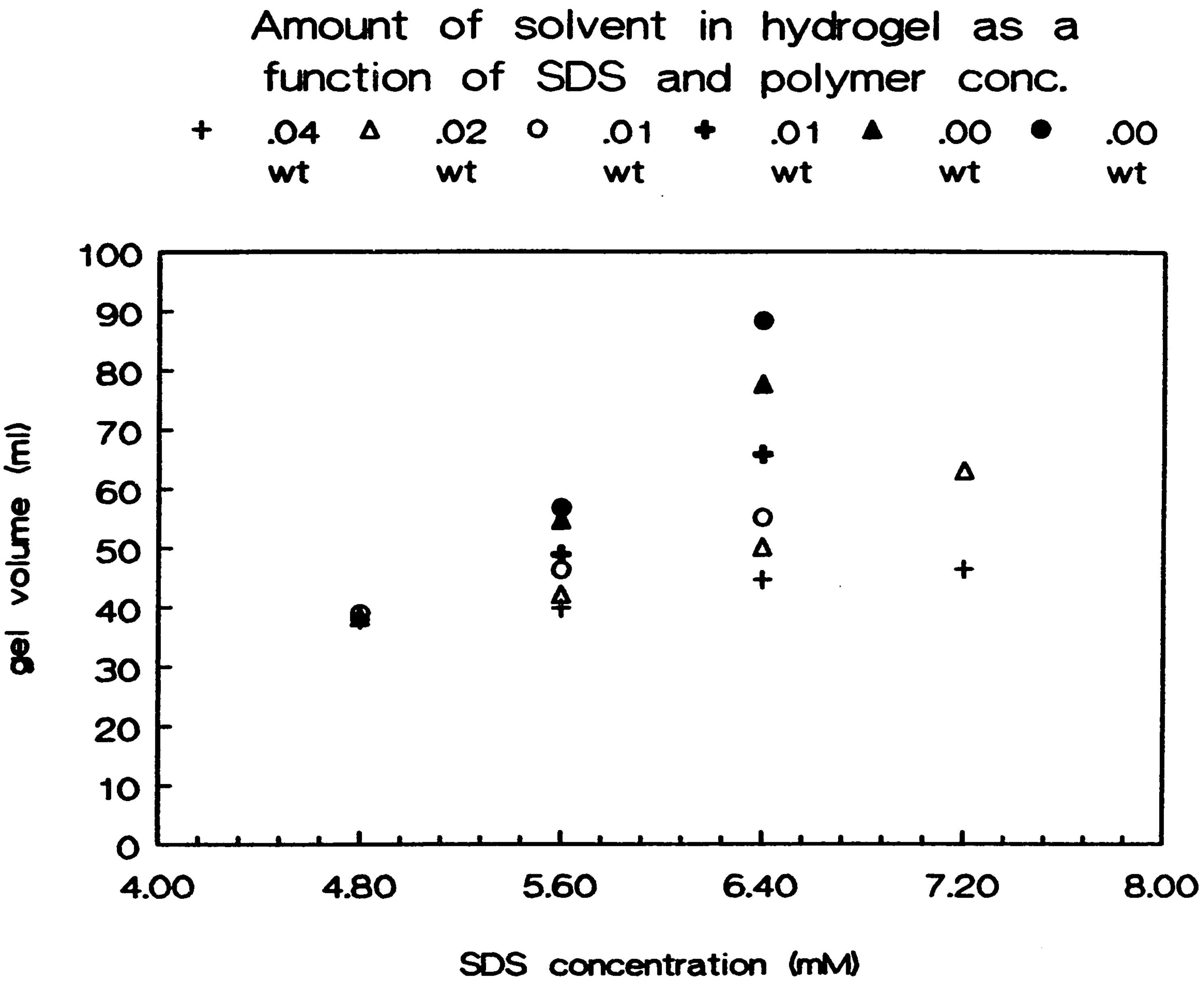

Amount of solvent in hydrogel as a function of SDS and polymer conc.
+ .04 wt
Δ .02 wt
o .01 wt
✚ .01 wt
▲ .00 wt
● .00 wt
gel volume (ml)
100
90
80
70
60
50
40
30
20
10
0
4.00
4.80
5.60
6.40
7.20
8.00
SDS concentration (mM)

FIG 1

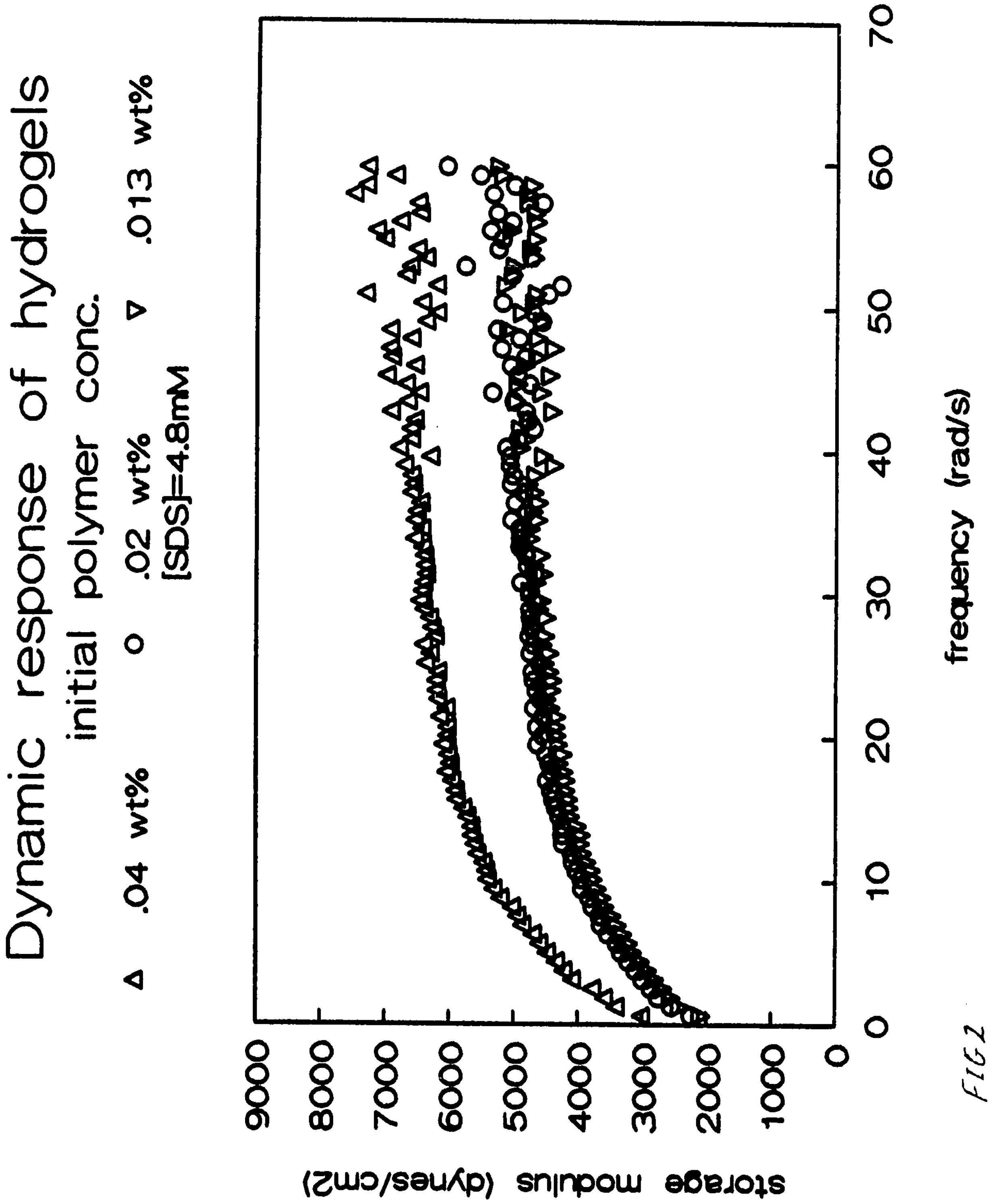

Dynamic response of hydrogels
initial polymer conc.
◁ .04 wt%
○ .02 wt%
▷ .013 wt%
[SDS]=4.8mM
storage modulus (dynes/cm2)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
frequency (rad/s)
0
10
20
30
40
50
60
70

FIG 2

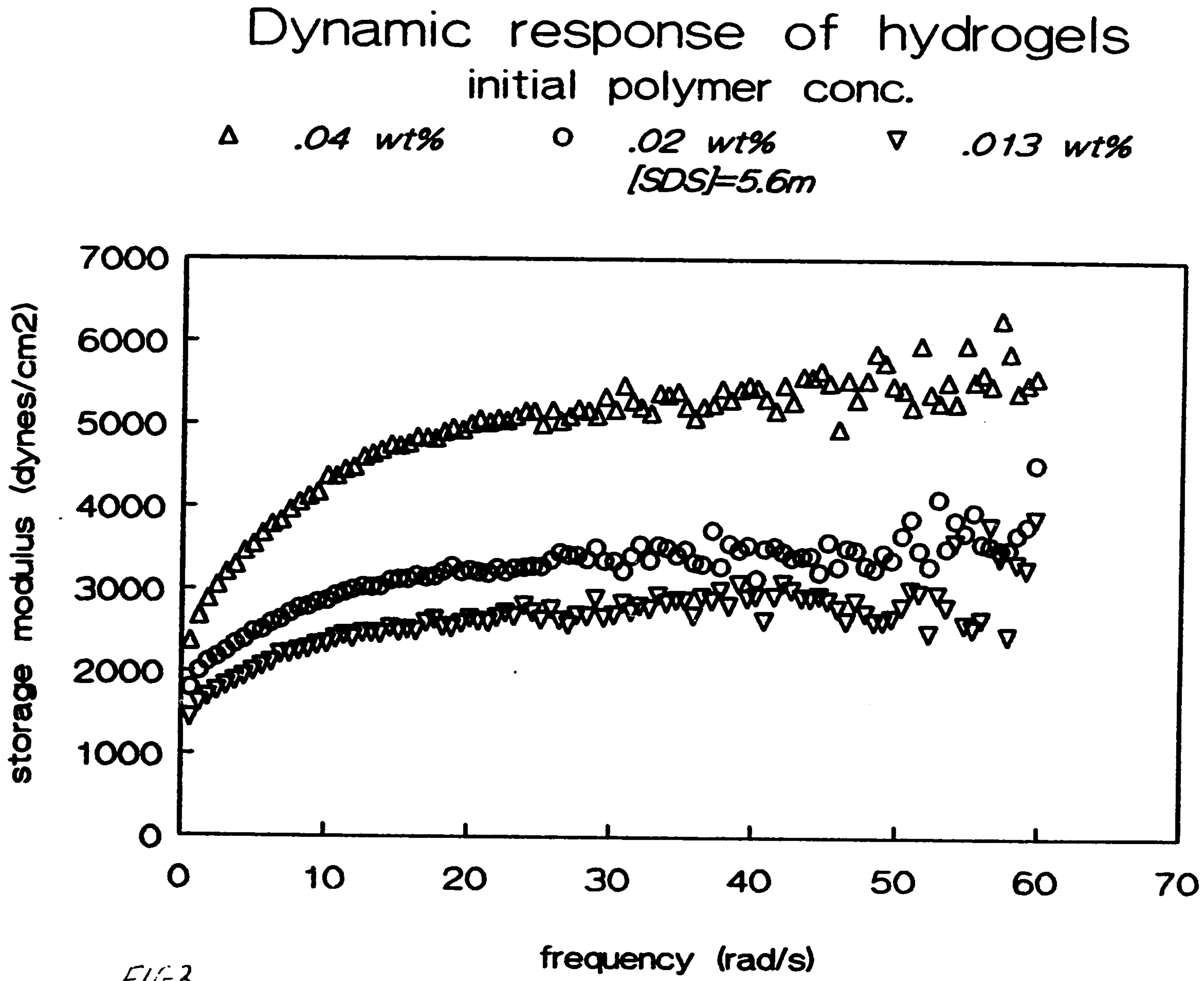

Dynamic response of hydrogels
initial polymer conc.
△ .04 wt%
○ .02 wt%
▽ .013 wt%
[SDS]=5.6m
storage modulus (dynes/cm2)
0
1000
2000
3000
4000
5000
6000
7000
0
10
20
30
40
50
60
70
frequency (rad/s)

FIG-3

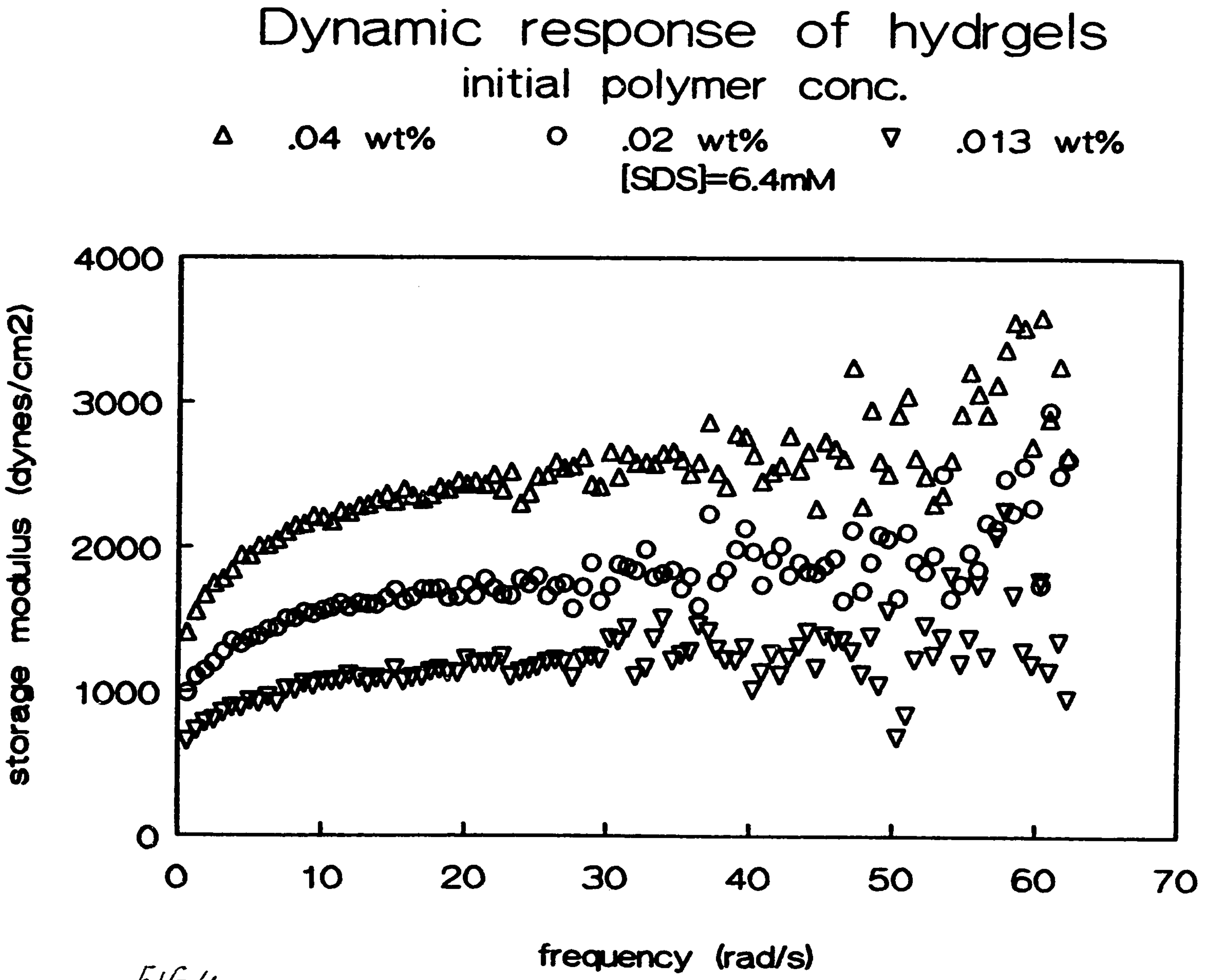

Dynamic response of hydrgels
initial polymer conc.
△ .04 wt%
○ .02 wt%
▽ .013 wt%
[SDS]=6.4mM
storage modulus (dynes/cm2)
0
1000
2000
3000
4000
0
10
20
30
40
50
60
70
frequency (rad/s)

FIG 4

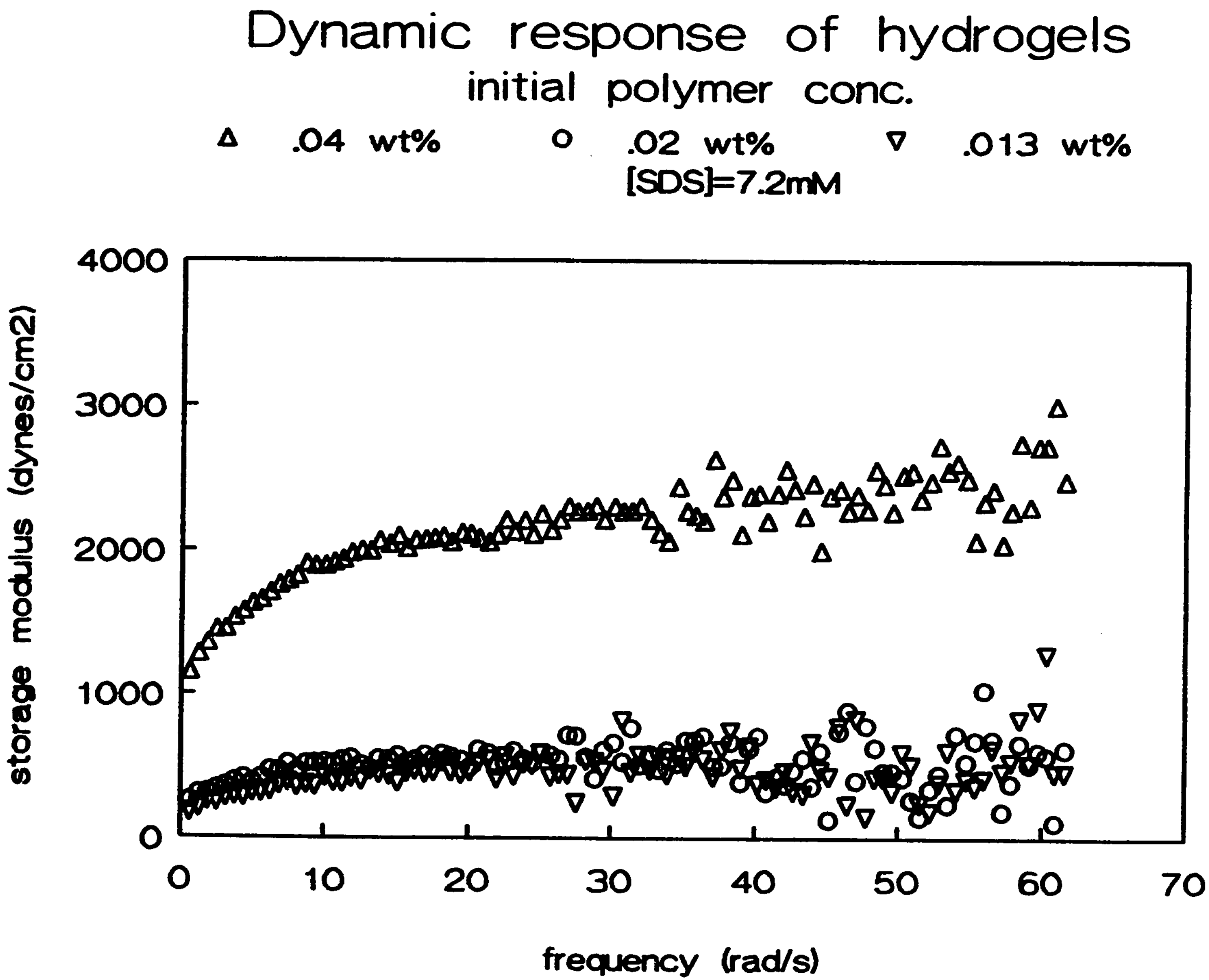

Dynamic response of hydrogels
initial polymer conc.
△ .04 wt%
○ .02 wt%
▽ .013 wt%
[SDS]=7.2mM
storage modulus (dynes/cm2)
4000
3000
2000
1000
0
0
10
20
30
40
50
60
70
frequency (rad/s)

FIG 5

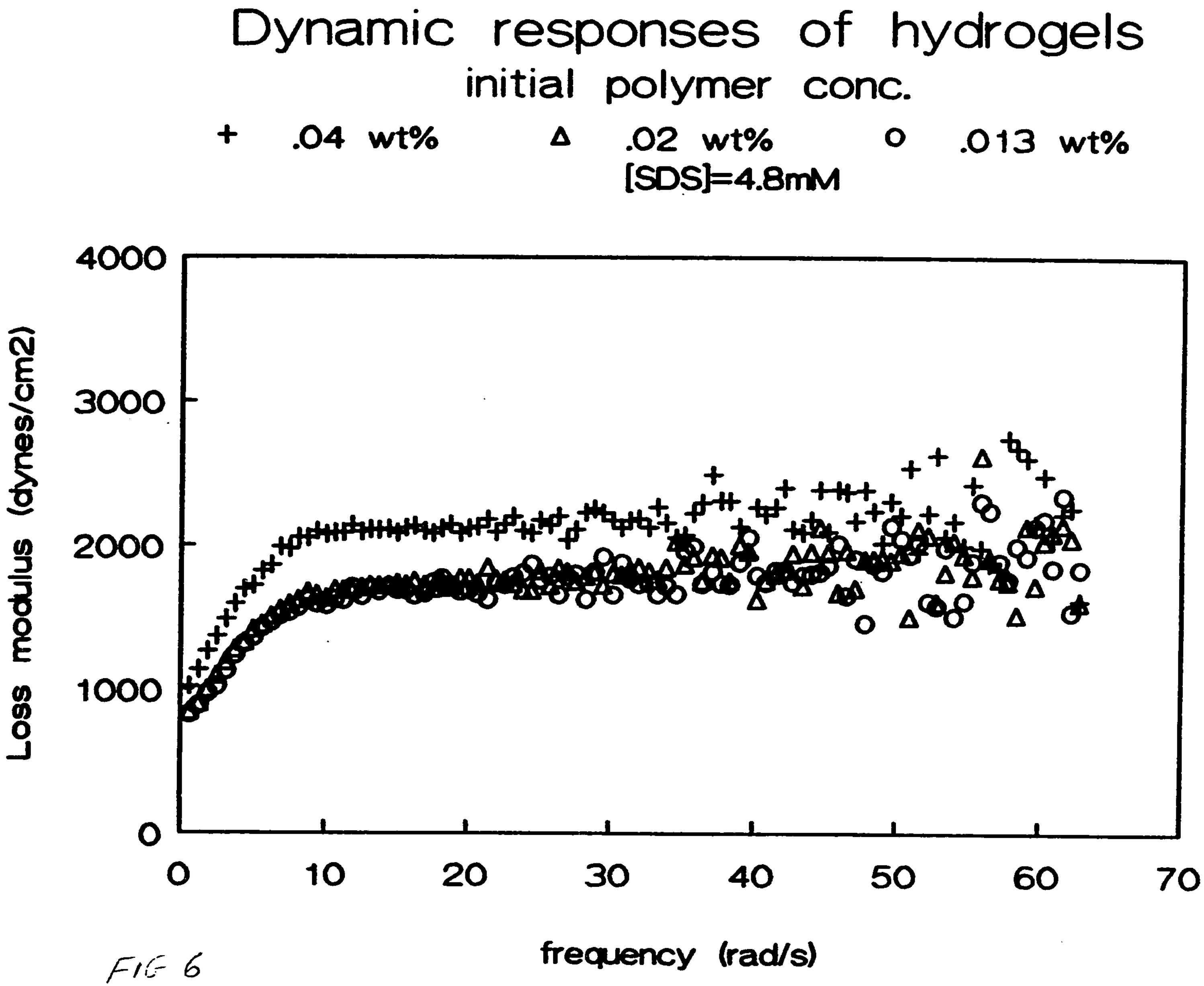

Dynamic responses of hydrogels
initial polymer conc.
+ .04 wt%
Δ .02 wt%
o .013 wt%
[SDS]=4.8mM
Loss modulus (dynes/cm2)
4000
3000
2000
1000
0
0
10
20
30
40
50
60
70
frequency (rad/s)

FIG 6

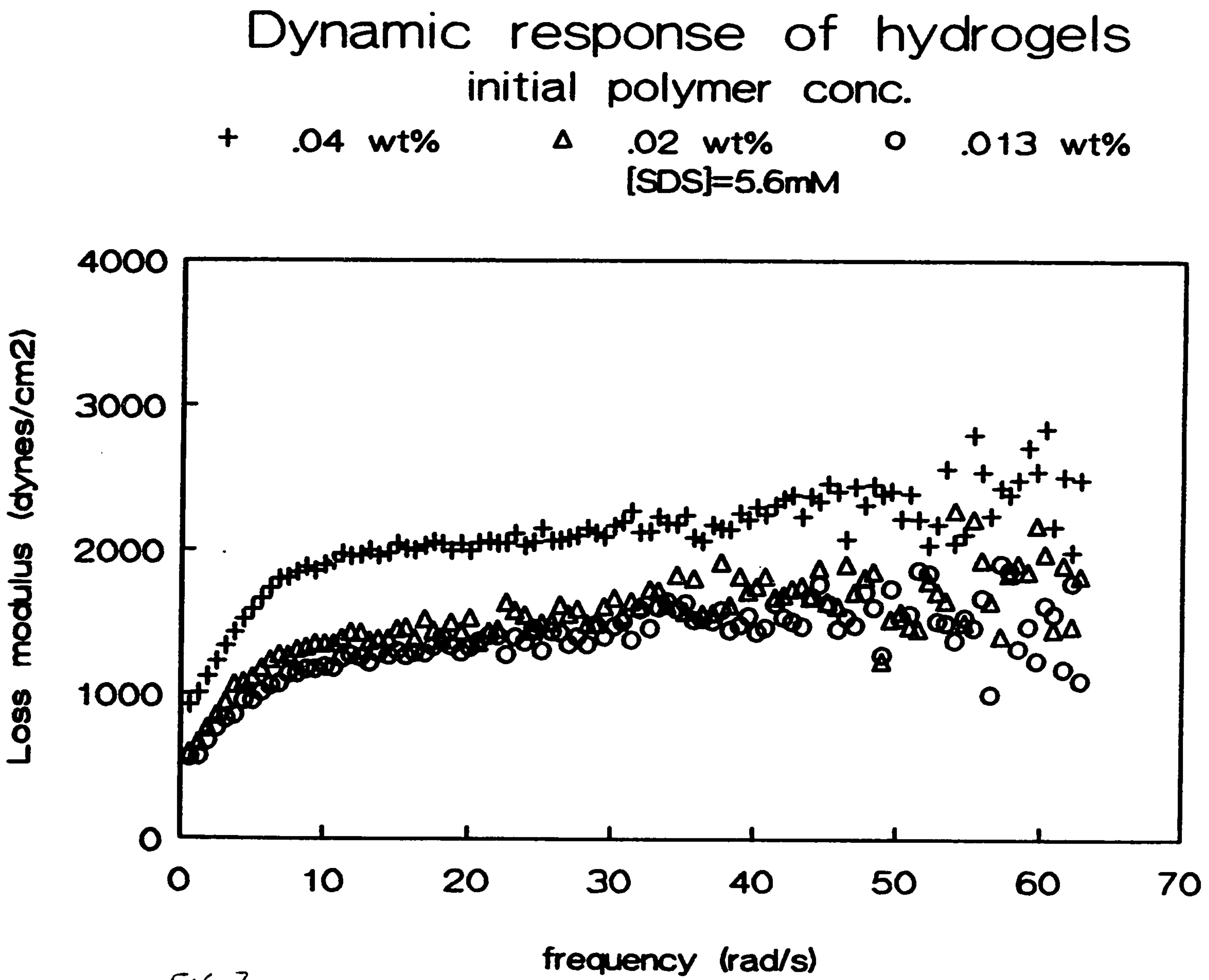
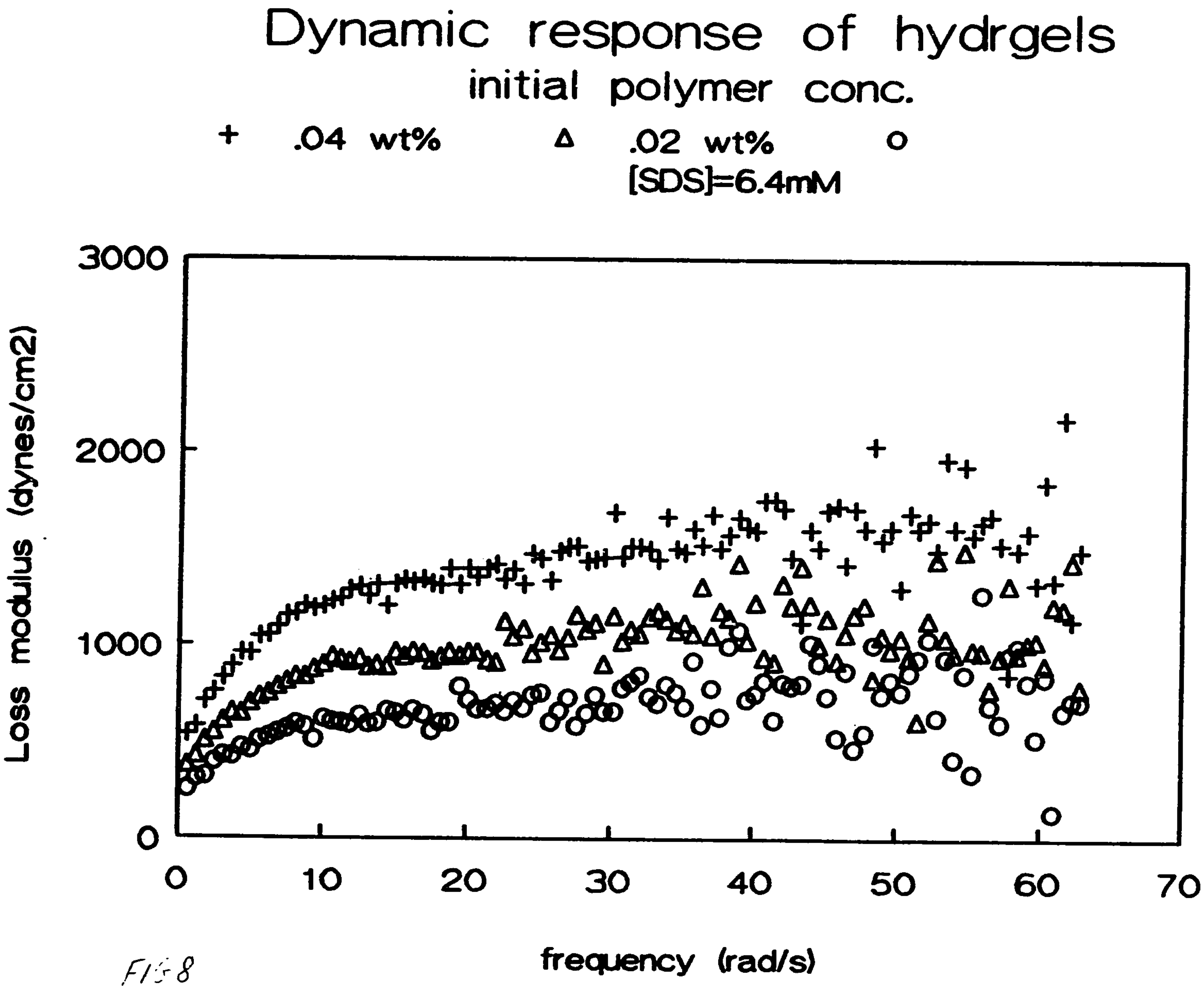

Dynamic response of hydrogels
initial polymer conc.
+ .04 wt%
Δ .02 wt%
o .013 wt%
[SDS]=5.6mM
Loss modulus (dynes/cm2)
4000
3000
2000
1000
0
0
10
20
30
40
50
60
70
frequency (rad/s)

FIG 7


Dynamic response of hydrgels
initial polymer conc.
+ .04 wt%
Δ .02 wt%
o
[SDS]=6.4mM
Loss modulus (dynes/cm2)
3000
2000
1000
0
0
10
20
30
40
50
60
70
frequency (rad/s)

F1G 8

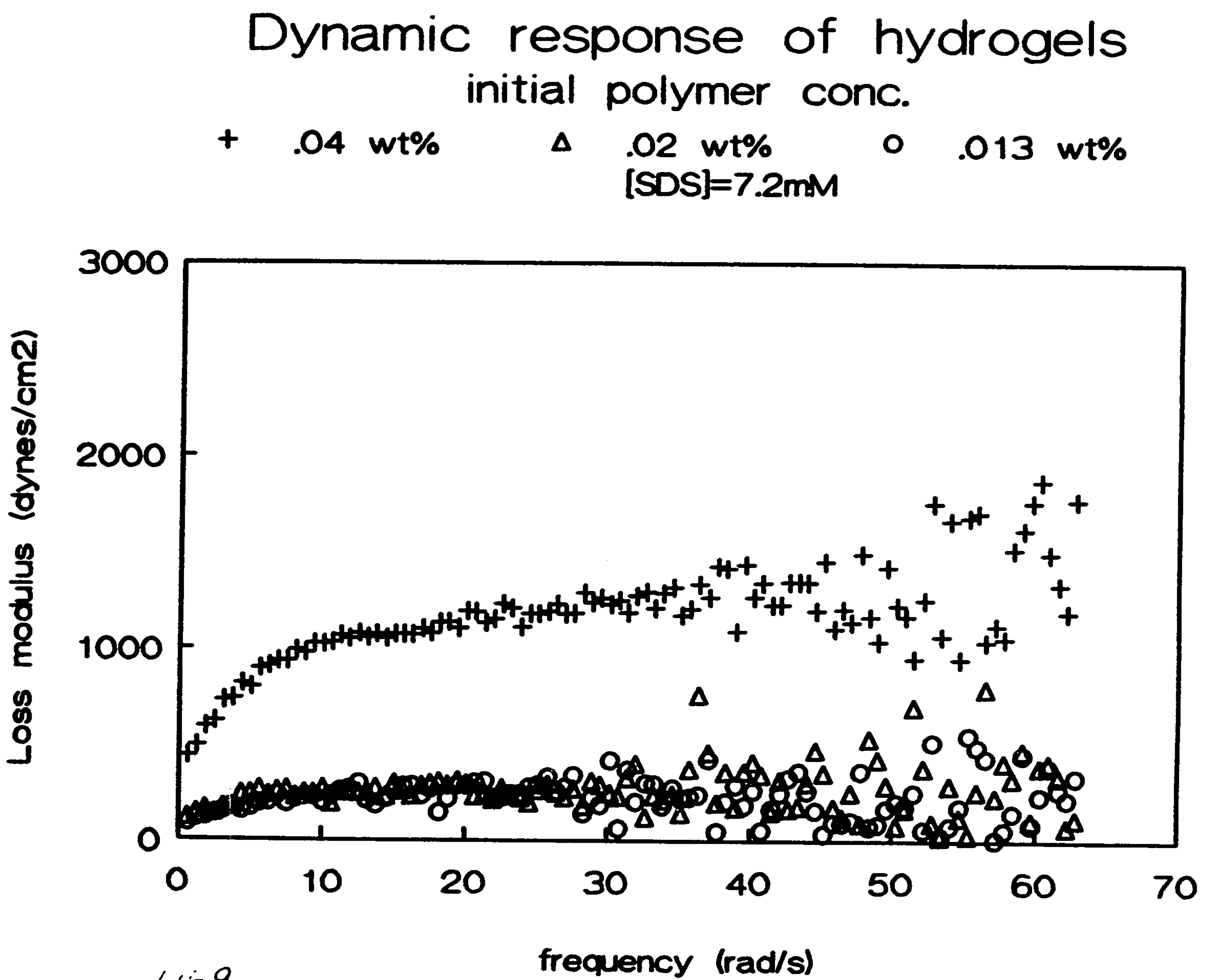

Dynamic response of hydrogels
initial polymer conc.
+ .04 wt%
Δ .02 wt%
○ .013 wt%
[SDS]=7.2mM
Loss modulus (dynes/cm2)
3000
2000
1000
0
frequency (rad/s)
0
10
20
30
40
50
60
70

Fig 9

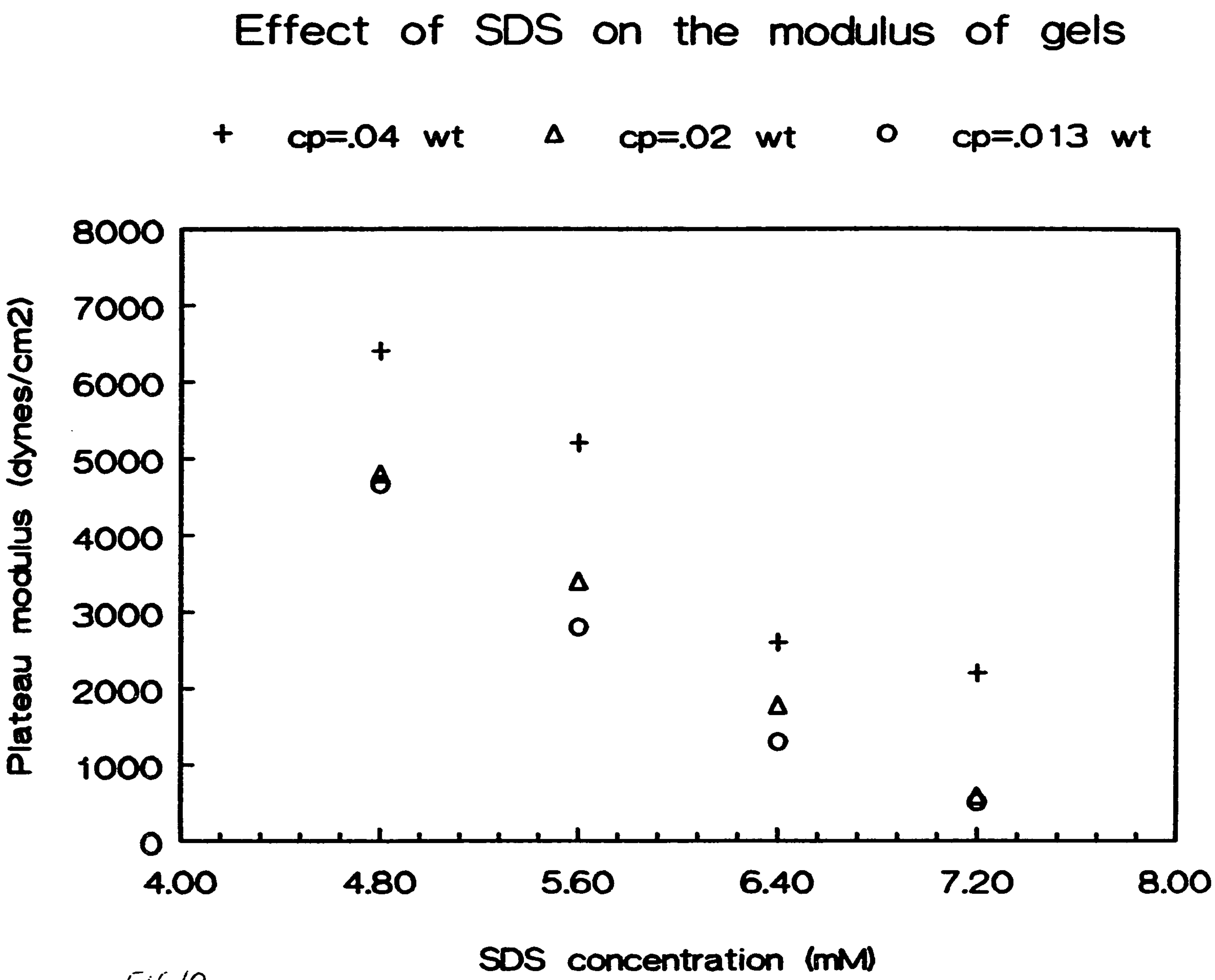

Effect of SDS on the modulus of gels
+ cp=.04 wt
Δ cp=.02 wt
o cp=.013 wt
Plateau modulus (dynes/cm2)
8000
7000
6000
5000
4000
3000
2000
1000
0
4.00
4.80
5.60
6.40
7.20
8.00
SDS concentration (mM)

FIG-10

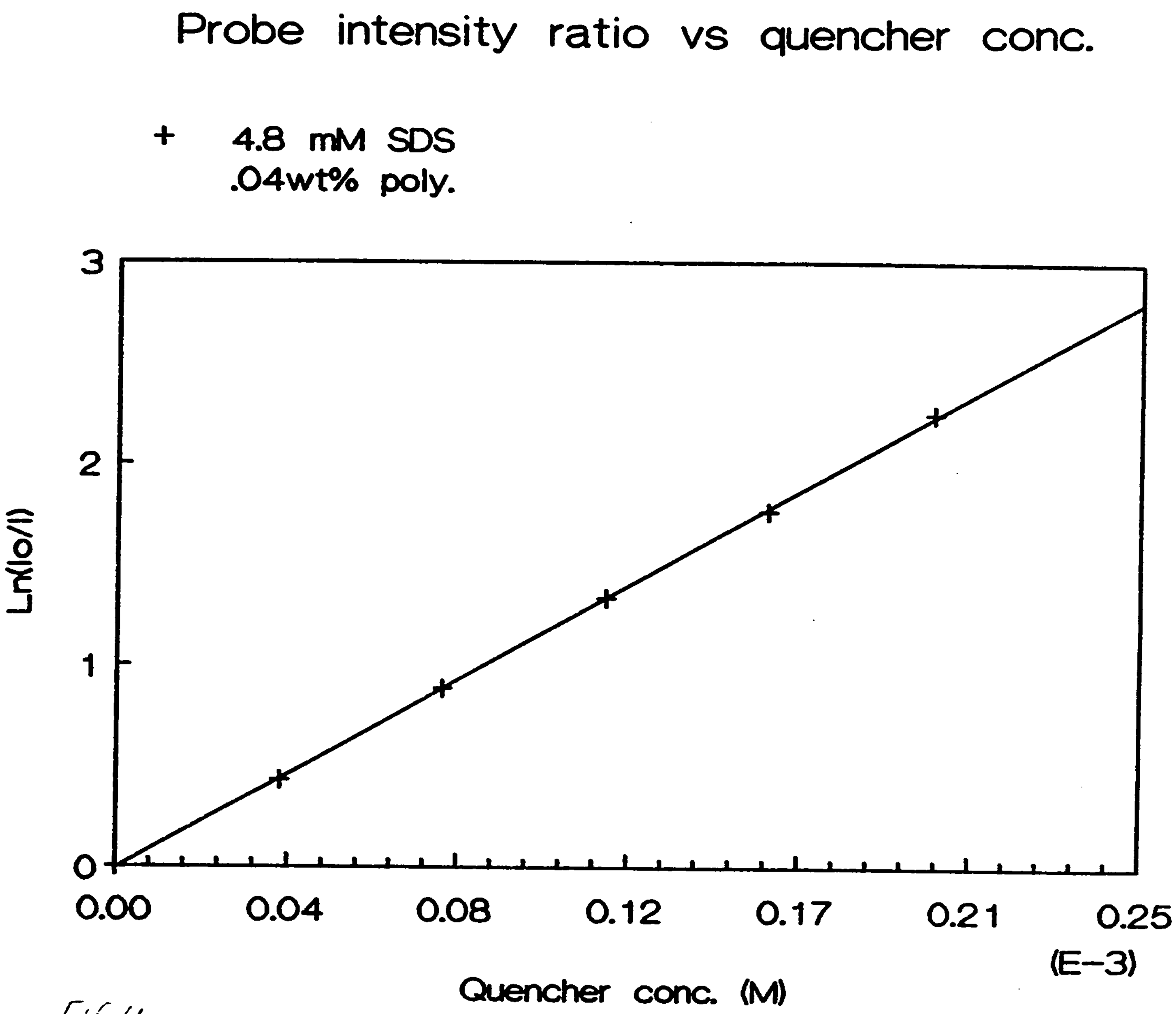

Probe intensity ratio vs quencher conc.
+ 4.8 mM SDS
.04wt% poly.
Ln(Io/I)
3
2
1
0
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E-3)
Quencher conc. (M)

FIG 11

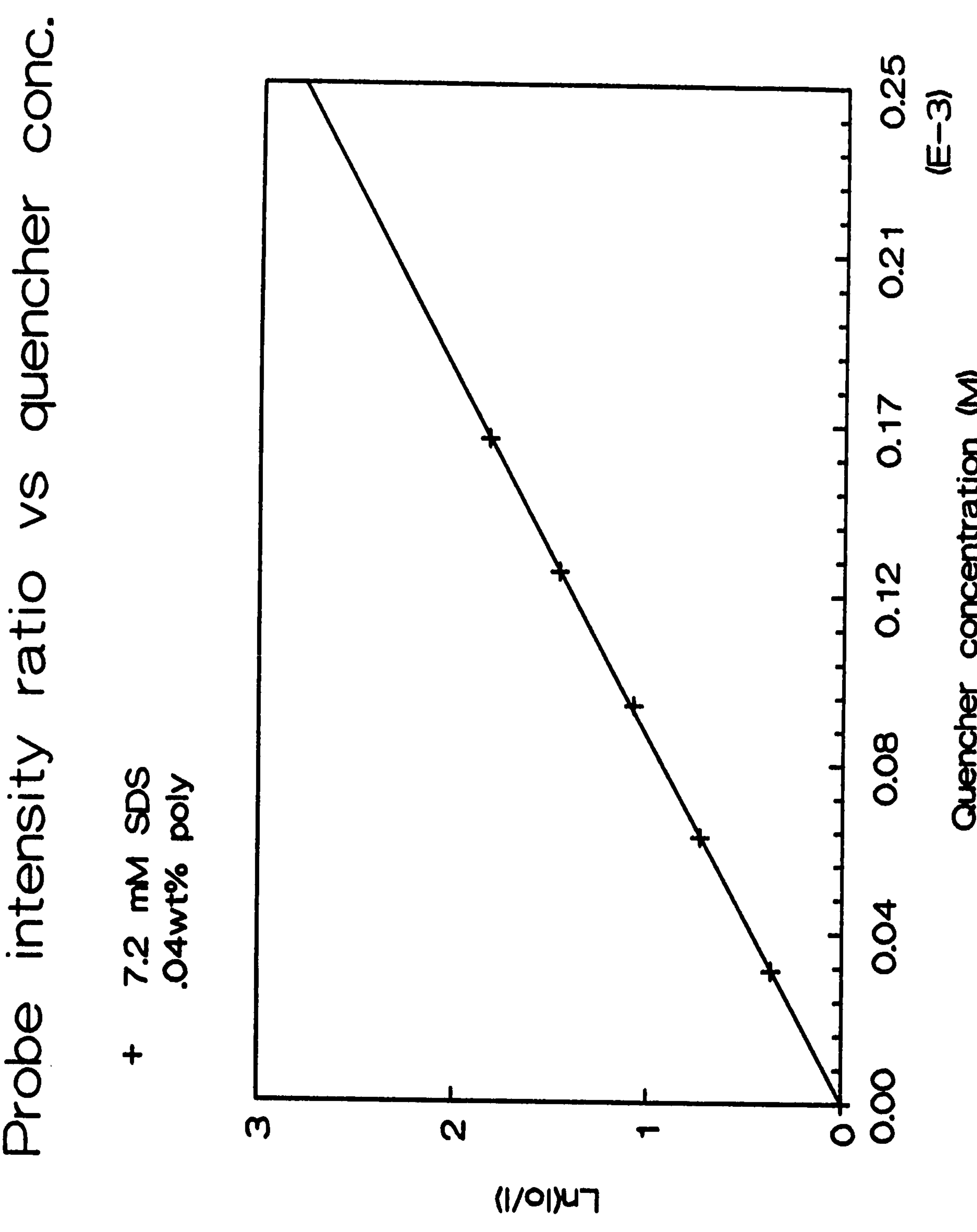

Probe intensity ratio vs quencher conc.
+ 7.2 mM SDS
.04wt% poly
Ln(Io/I)
3
2
1
0
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E-3)
Quencher concentration (M)

FIG 14

Probe intensity ratio vs quencher conc.

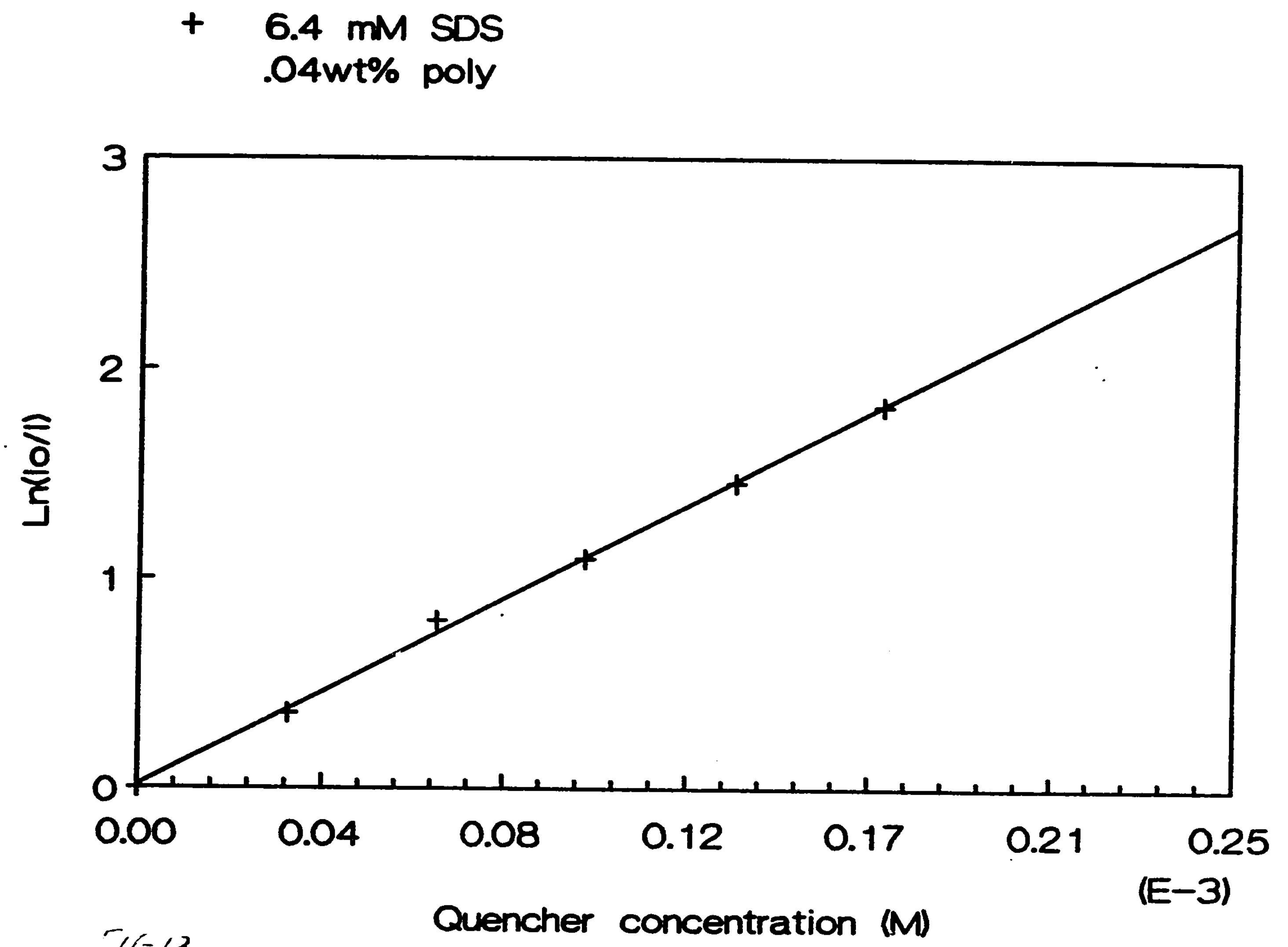


FIG-13

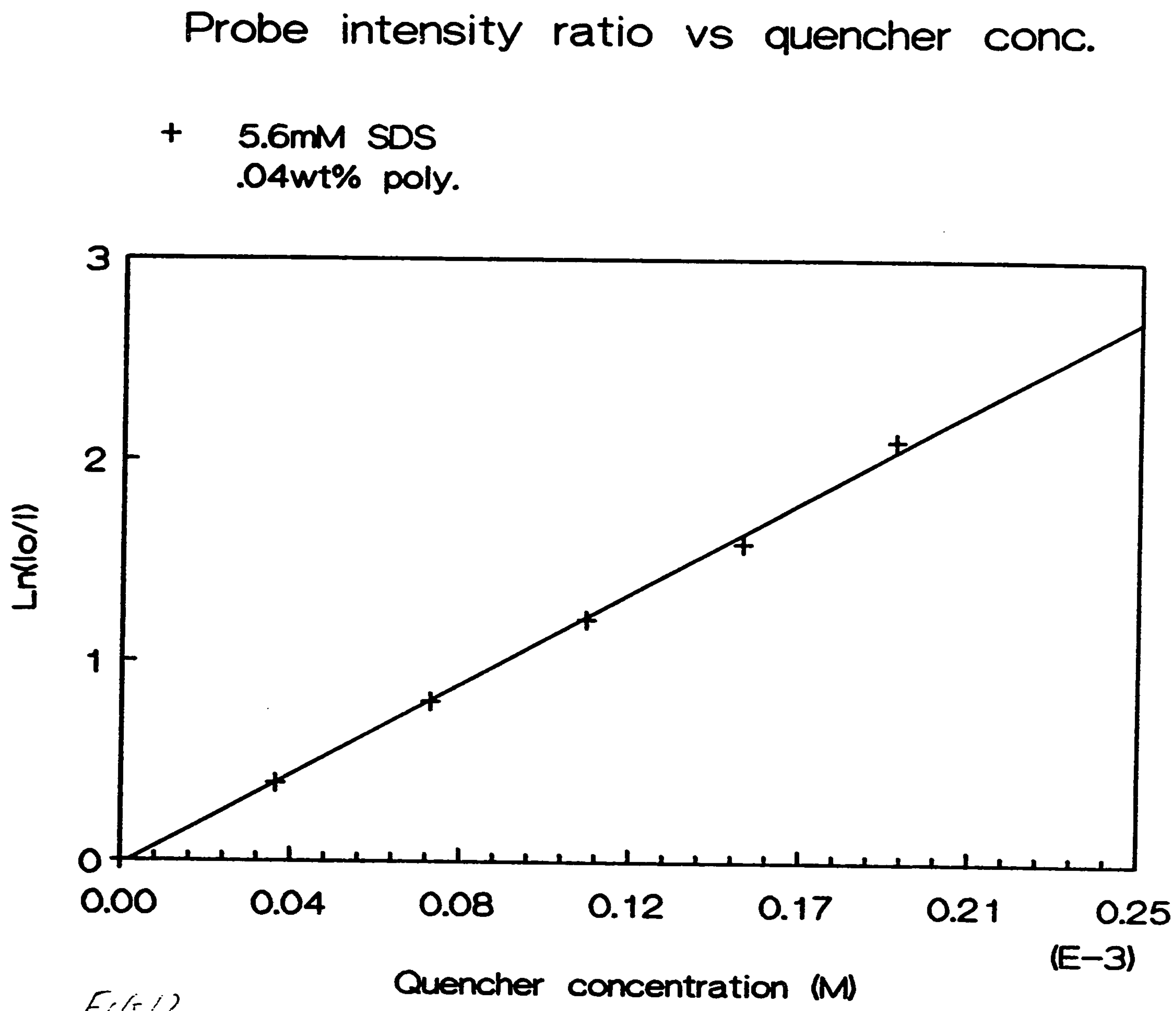

Probe intensity ratio vs quencher conc.
+ 5.6mM SDS
.04wt% poly.
Ln(Io/I)
3
2
1
0
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E−3)
Quencher concentration (M)

FIG 12

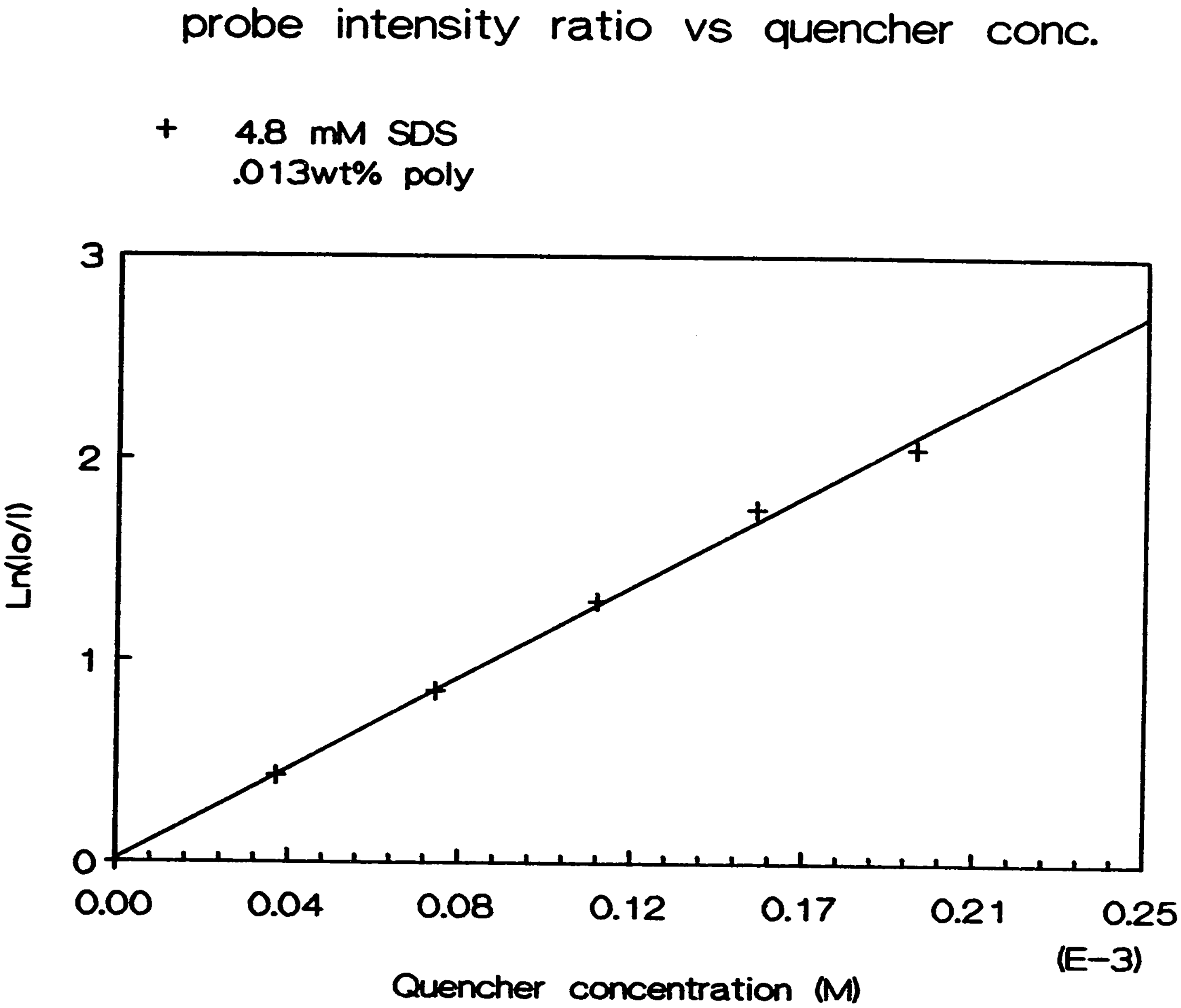

probe intensity ratio vs quencher conc.
+ 4.8 mM SDS
.013wt% poly
Ln(Io/I)
0
1
2
3
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E-3)
Quencher concentration (M)

FIG 15

Probe intensity ratio vs quencher conc.

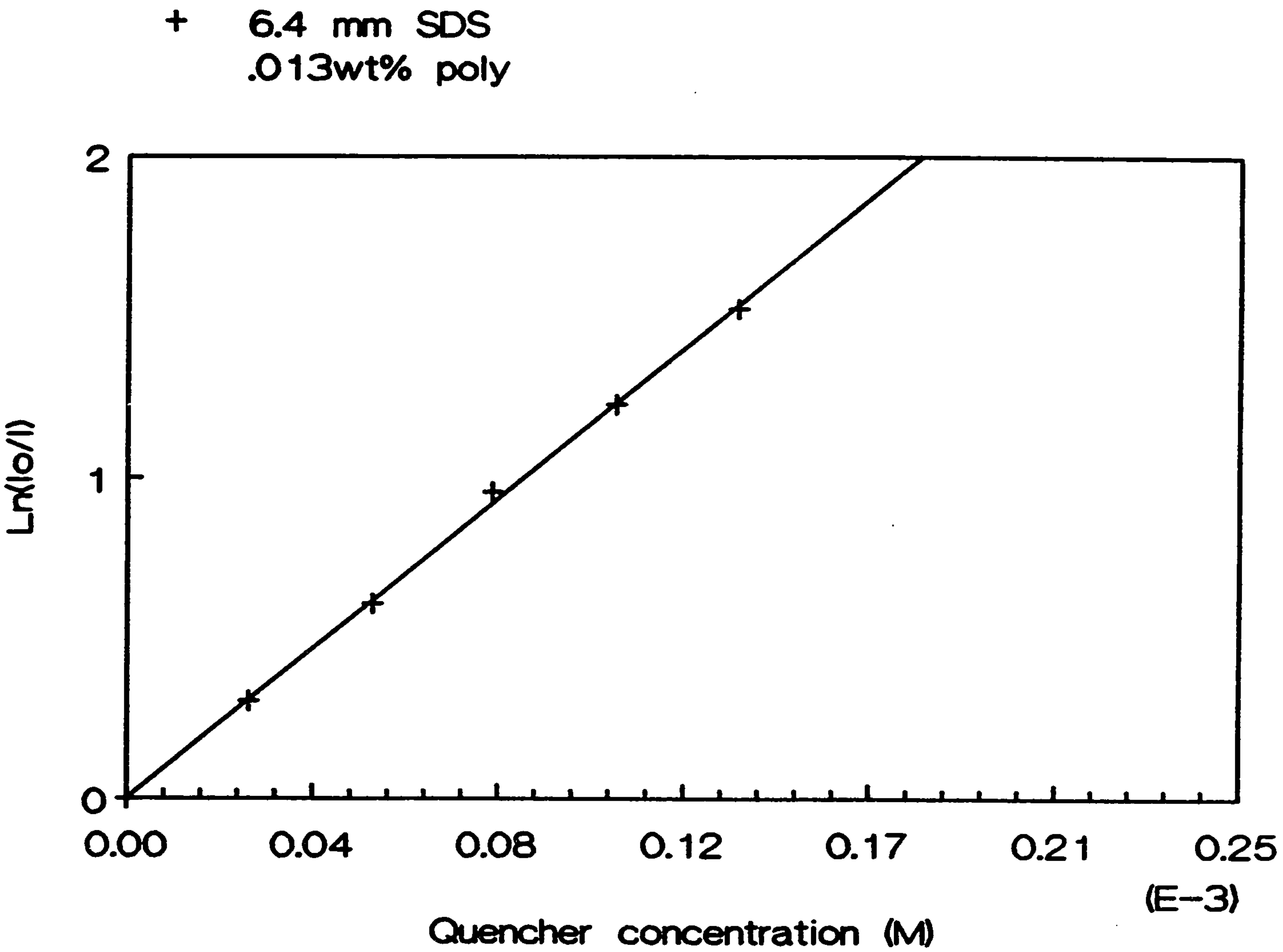


FIG 17

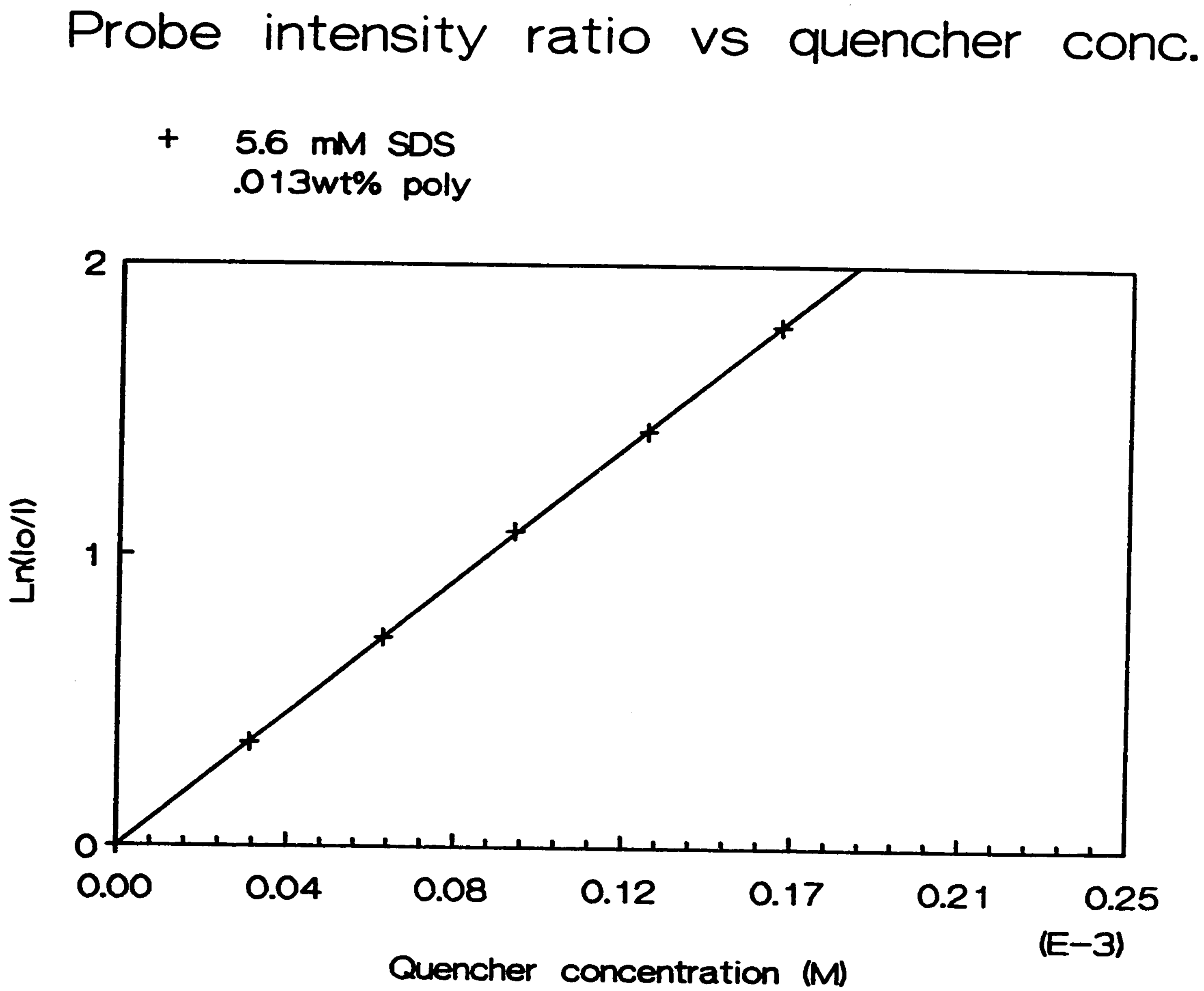

Probe intensity ratio vs quencher conc.
+ 5.6 mM SDS
.013wt% poly
Ln(Io/I)
2
1
0
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E−3)
Quencher concentration (M)

FIG 16

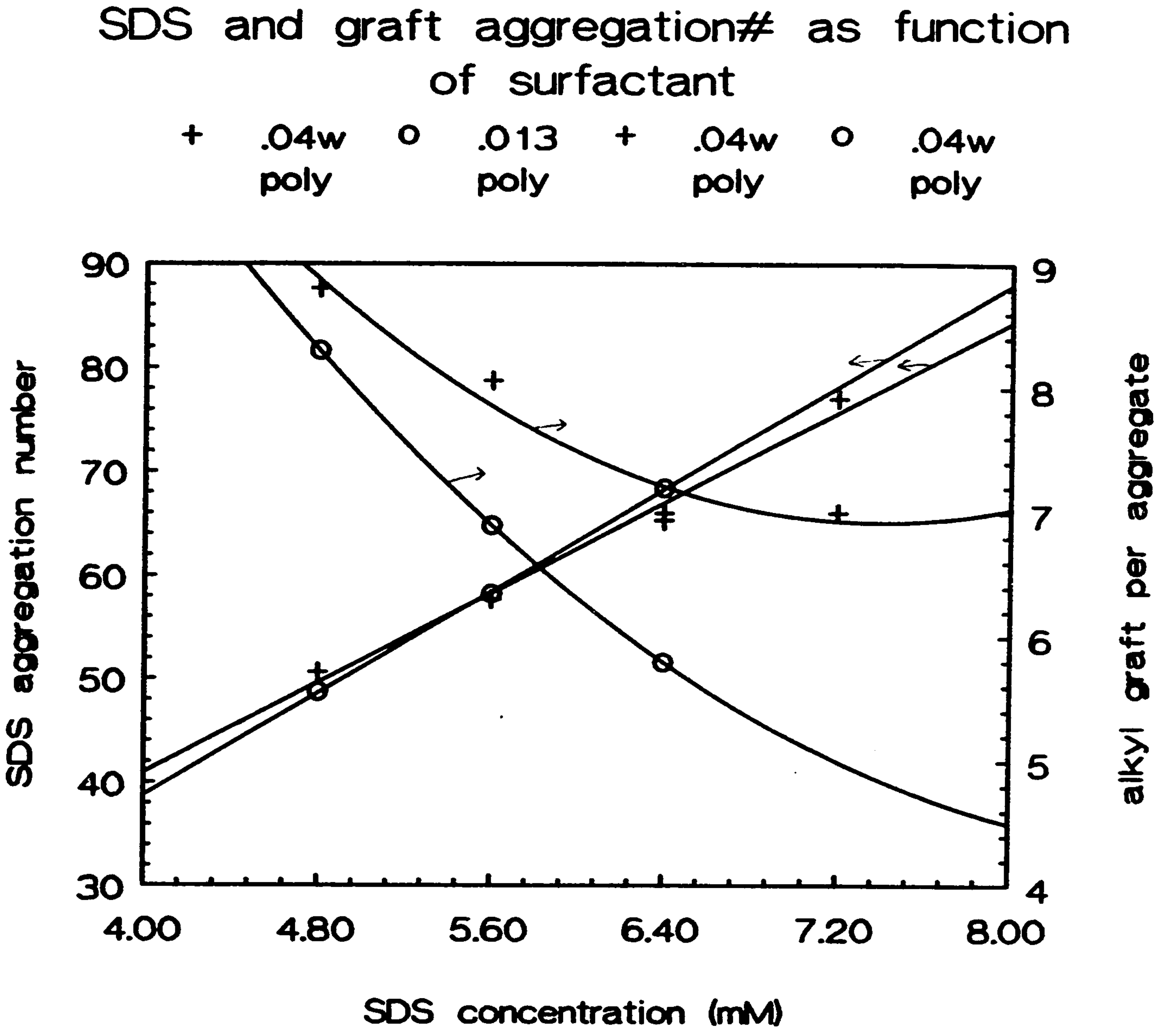

SDS and graft aggregation# as function of surfactant
+ .04w poly
o .013 poly
+ .04w poly
o .04w poly
SDS aggregation number
90
80
70
60
50
40
30
alkyl graft per aggregate
9
8
7
6
5
4
4.00
4.80
5.60
6.40
7.20
8.00
SDS concentration (mM)

FIG 19

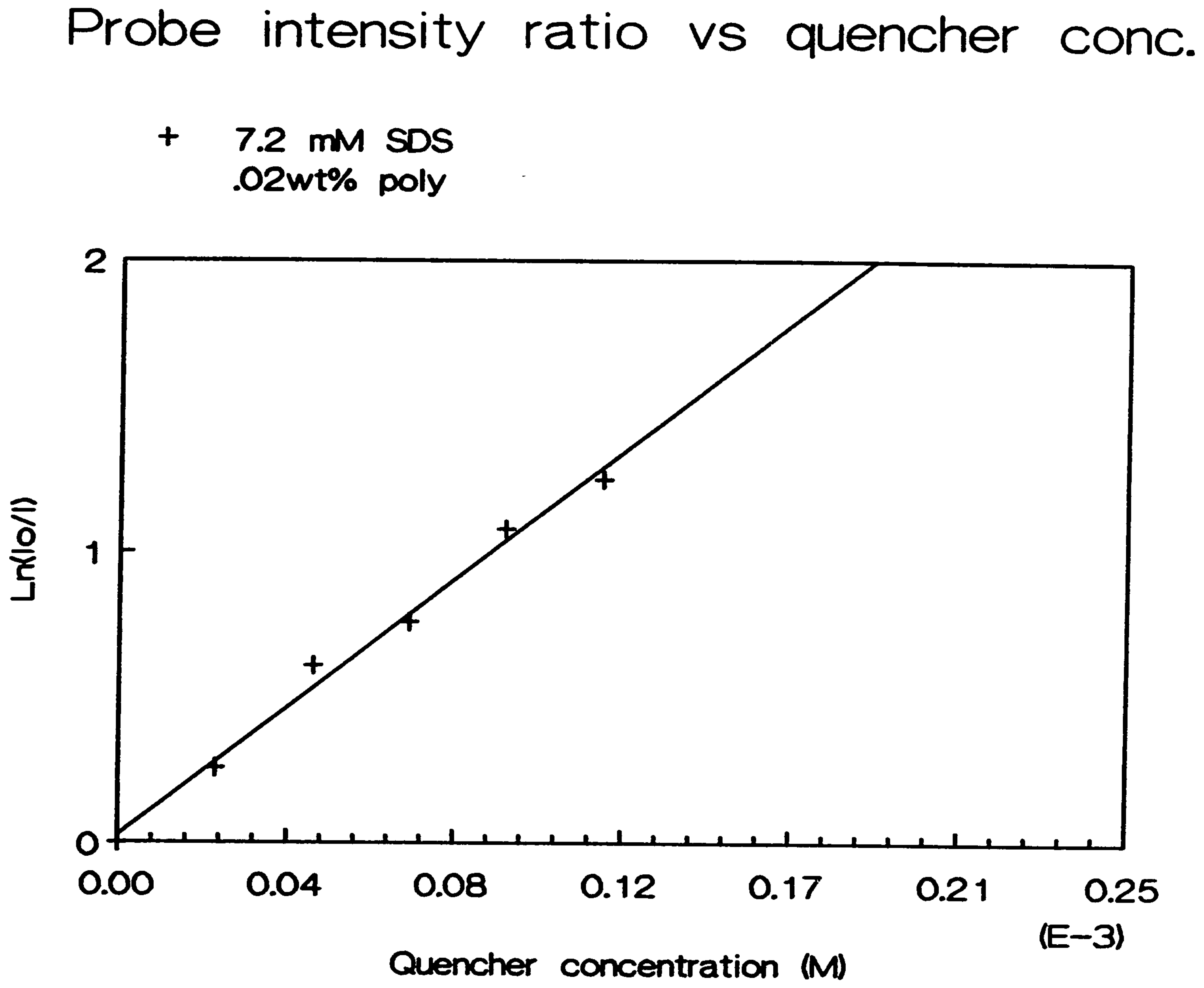

Probe intensity ratio vs quencher conc.
+ 7.2 mM SDS
.02wt% poly
Ln(Io/I)
2
1
0
0.00
0.04
0.08
0.12
0.17
0.21
0.25
(E-3)
Quencher concentration (M)

FIG 18

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Chapter5:

Future Work:

The work presented here can viewed upon as a basis for the design of a useful and practical device for drug delivery and separation of chemical species based on their chemical properties. For that to be successful however, future work must be along lines that will lead to the development of a quantitative methods of predicting the final properties of the gels that have been synthesized in this work. As a starting point, the gels can be treated as crosslinked swollen polyelectrolyte networks and thus Flory,s charged network thermodynamics applied.

Appendix 1

Neutron Scattering

Neutron scattering spectroscopy is used for, among other things, the determination of the sizes, geometries and conformations of particles dissolved in a solvent (21,22,28-33). This is possible because the angular distribution and the normalized intensities of neutrons scattered from a sample are related to both the chemical nature and the spatial correlation (structure) of all the scattering atomic nuclei. Different nuclei interact with incident neutron waves differently and even isotopes of the same element, such as ^1H and ^2D, give rise to different degrees of scattering. The amplitude of the scattered radiation from a given nucleus is characterized by the scattering length, b, or by the scattering length density , b , defined as

$$\rho = \frac{b_{total}}{v}$$

where b_{total} is the sum of the the scattering lengths of the scattering molecule and v is the atomic volume. The total intensity of scattered neutrons has two components, $I_{coherent}$ and $I_{incoherent}$. The first refers to waves which interfere to give scattering pattern from which structural information (geometry, MW, etc) can be derived and the second refers to interference which give rise to a flat background.

The coherent intensity is proportional to the square of the difference in scattering densities between the solvent (ρ_s) and the solute (ρ) molecules (28,29).

$$I_{coherent} \propto (\rho - \rho_s)^2$$

For multicomponent solutions, therefore, the components whose scattering length densities match that of the solvent will not contribute to the measured intensities. As a result, the intensity of individual components can be analyzed separately and their sizes, shape and weight determined. This is the basis for the contrast matching technique in neutron scattering which enables one to obtain the scattering due to the individual solutes by simply finding a solvent whose scattering density matches each of the solutes, except the one whose scattering is to be observed. Deuterated and protonated water have very different sacttering densities (table 2). Contrast matching in aqueous solutions is, therefore, easily achieved by using different mixtures of protonated and deuterated water to eliminate scattering due to all solutes except one. In the case of HMHEC gels, the different solutes to be observed separately are the hydrophobic aggregates and the polymer backbones.

To determine the molecular weight of the hydrophobic aggregates dispersed within the polymer gel we follow a method by Jacrot (28). We will first match the scattering length density of the polymer backbone with a mixture of hydrogenous and deuterated water so that only the hydrophobes scatter the neutrons to give a detectable signal. We will measure the scattered intensity as function of the scattering vector (Q) given as: $Q = 4\pi/\lambda \sin\theta/2$. Where λ is the neutron wavelength and θ is the angle of the scatter. We will then use the expression derived in ref 25:

$$I(0) = BM_w(\rho - \rho_s)^2$$

where I(0) is the coherent intensity scattered at zero angle, ρ and ρ_s are the scattering length densities of the aggregates and the solvent respectively, B is an experimental factor which takes into account the incoherent scattering and the transmission of the sample. I(0) is usually obtained by measuring the scattered intensity as a function of Q for a sample and then extrapolating the plot of I(Q) vs Q to zero Q. The scattering length densities are calculated from the known scattering lengths (b) of the various nuclei of the molecule (table 2). Molecular weight of tthe scattering particle is then obtained.

The shape of the aggregate can be determined from the dependence of the intensity of the scattered neutrons on the scattering vector, Q, with the condition that only the aggregates scatter (21,22) . Differential scattering cross section σ is defined as the ratio of the number of neutrons scattered per second to the incident neutron flux. The change in scattering cross section per unit solid angle is related to the spatial correlation of the scattering molecules as follows:

$$\frac{d\sigma}{d\Omega}=\frac{1}{v}\left\langle\left|\sum_{i=1}^{n_p}\exp(iQ\cdot R)\sum_{j=1}^{n_p}b_{ij}\exp(iQ\cdot x_j)\right|^2\right\rangle$$

where V is the sample volume, N_p is the number of scattering particles, R_i is the position vector of the center of mass of the i_{th} particle, X_j is the position vector of the j_{th} atom in the i_{th} particle relative to the center of mass of the particle, b_{ij} is the scattering length of the j_{th} atom in the it_h particle. Equation 1 can be rewritten as:

$$\frac{d\sigma}{d\Omega}=n_pP(Q)S(Q)$$

$$P(Q)=|F(Q)|^2=\left|\sum_{i=1}^{n_p}b_{ij}\exp(iQ\cdot x_j)\right|^2$$

$$S(Q)=\frac{1}{n_p}\left\langle\sum_{i=1}^{n_p}\sum_{j=1}^{n_p}\exp[iQ\cdot(R_i-R_j)]\right\rangle$$

where P(Q) and S(Q) are the so called the geometrical form factor and the structure factor of scattering particles respectively. n_p is the number of scattering particles per unit volume. The structure factor represents the fraction of the scattered intensity due to interparticle interactions; the form factor is the fraction due to the geometry of individual scattering particles, intramolecular interaction. It has been shown that scattering particles with different geometries give rise to different form factors. In a dilute solution or one with only weakly interacting particles, the interparticle structure factor is unity and the shape of the particle can be determined by fitting the scattered intensity to a theoretical form factor. There are various functions which represent different scattering geometries tabulated in (21,22,29,35). For the case of monodisperse spherical particles the form factor is given as

$$F(Q) = v(\rho - \rho_s)[3J_1(QR)/QR]$$

where $J_1(QR)$ is the first order spherical Bessel function

$$J_1(QR) = [\sin(QR) - QR\cos(QR)]/Q^2R^2$$

The intensity of scattered neutrons at a given angle Q is related to the scattering cross section as follows:

$$I(Q) = DI(0)\left(\frac{d\sigma}{d\Omega}\right)$$

Where D is an experimental factor which includes the efficiency of the detectors, temperature, etc. The radius of the spherical particle can then be obtained by fitting the experimentally measured intensity vs Q with the theoretical function. Particles with geometries other than spherical can also be analyzed in a similar way.

The relevant molecular parameters required for these experiments such as the molecular volumes of the alkyl grafts and the polymer backbone as well theoretical contrast lengths of the backbone and the grafts are given in table 2. Small angle neutron scattering will be carried out at the high flux beam reactor (HFBR) facility of Brookhaven national laboratory (BNL) in cooperation with Dr. Dieter Schneider of the BNL dept. of Biology.

TABLE 2

Neutron scattering parameters

Species	Molecular volume (nm^3)	b_{coh} (fm)	Scattering length density
CH_3	.0543	-4.574	-84
CH_2	.0269	-.8334	-31
SO_4^{2-}	.0579	26.07	450
Na^+	.0039	3.63	931
H_2O	.0299	-1.677	-56
D_2O	.0302	19.153	634
CRU	1.725	49.71	28.8

CRU: Cellulose repeat unit (2 anhydroglucose units)

TABLE 3

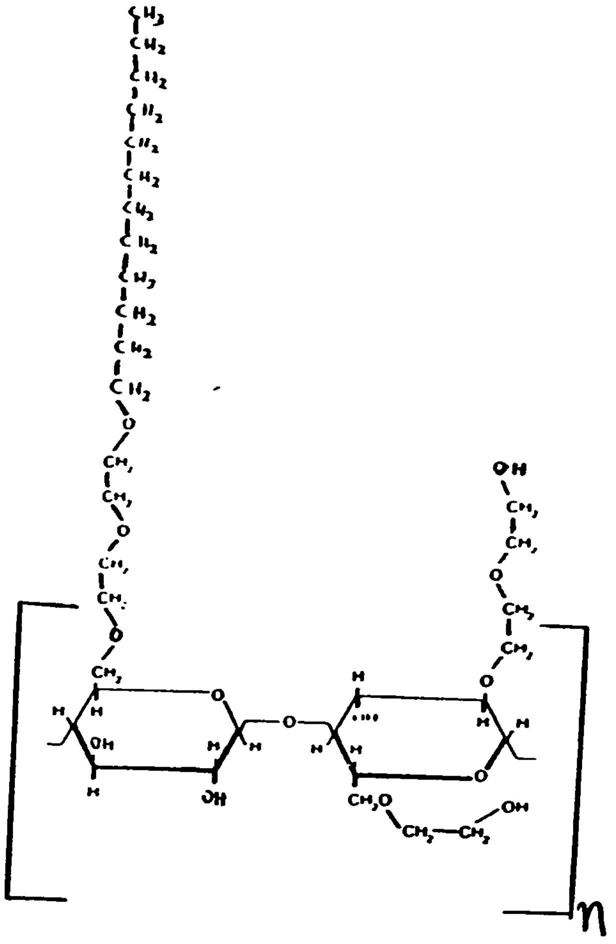
Polymer samples available

Hydrophobe type	Wt.% Hydrophobe	HEMS[a]
C_8	2.10	3.60
C_{12}	1.89	3.48
C_{16}	.90	3.97
C_{16}	1.44	4.04

Structure Of Hydrophobically Modified Hydroxyethyl Cellulose (HMHEC)

HC = 13%
MS = 3.7

SDS
CMC ≈ 8 x 10⁻³ M
AN = 60



Trade name Natrosol Plus
Agualon co., Wilmington, DE

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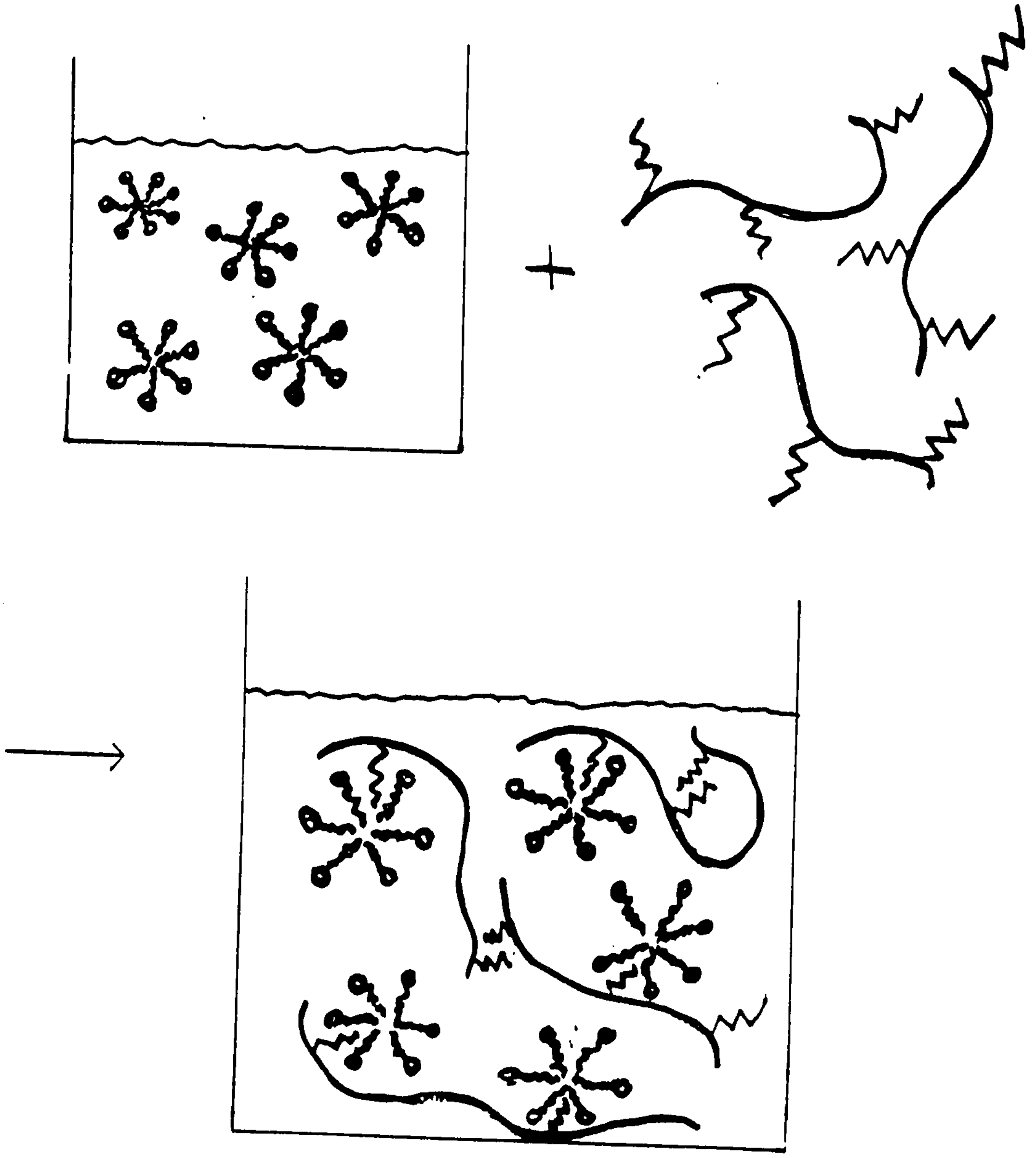
Nomenclature

G'	Storage modulus
G''	Loss modulus
G_N	Plateau modulus
γ	Strain
ν	volume fraction of polymer in solution
$\mathring{\gamma}$	strain rate
η	steady state shear viscosity
η^*	complex viscosity
η_0	Zero shear viscosity
ω	Angular frequency
b	Scattering length of the nuclei
V	Molecular volume
ρ	Scattering density
S	Structure factor
F	Form factor
g	Pair correlation function
Q	Scattering wave vector
	wavelength in nm
I_1, I_2	Intensities of the first and third peak of pyrene
$[C_m]$	Concentration of alkyl grafts in solution
I(0),I(Q)	Scattering intensities

B	Scattering experimental factor
M_w	Molecular weight
M_e	molecular weight between cross links
[Q]	Quencher concentration

SCHEMATIC OF POLYMER-SURFACTANT SOLUTION



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