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Quarterly Technical
Progress Report
for

Responsive Copolymers for Enhanced Petroleum Recovery

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by

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I. Summary of Technical Progress

A. Task - Advanced Copolymer Synthesis

AM/AMBA/BPAM TERPOLYMERS

Synthetic efforts have included synthesis of hydrophobically modified terpolymers based on acrylamide (AM) and one of three anionic monomers: Acrylic acid (AA), 2-Acrylamido-2-methyl-propanesulfonic acid (AMPS) or 3-Acrylamido-3-methylbutanoic acid (AMBA). N-(4-butyl)phenylacrylamide was used as the hydrophobic monomer; it possess both the hydrophobic character desired, plus a chromophore which allows the use of UV spectroscopy for accurate determination of hydrophobic monomer content in the terpolymers.

Polymer Synthesis

Monomers used in polymer synthesis are depicted in Figure 1. The micellar polymerization of Turner, et. al.[1] was used for all polymerizations. This aqueous polymerization method utilizes a surfactant, sodium dodecyl sulfate (SDS) to solubilize the hydrophobic BPAM monomer. A total monomer concentration of 0.44 M was used with monomer feeds of 0.5 mole% BPAM and 5 or 25 mole% AA, AMBA, or AMPS; the remaining balance of the feed was acrylamide. The acidic monomers were neutralized just prior to polymerization. Potassium persulfate, $K_2S_2O_8$ was used as a free radical initiator ([monomer]/[$K_2S_2O_8$] = 3000). Polymerizations were conducted at 50°C for 4-6 hrs, followed by precipitation into acetone. The terpolymers were dried under vacuum, crushed and redissolved in water, followed by dialysis against deionized to remove residual surfactant and monomers. The terpolymers were then lyopholized to a constant weight.

NaAMPS/AMPTAC COPOLYMERS and AM/NaAMPS/AMPTAC TERPOLYMERS

Synthetic efforts have centered on the synthesis of ionically modified polymers which possess both anionic and cationic functionalities pendant from the polymer backbone. Prior research in our labratories has demonstrated that solution behavior of polymers containing both anionic and cationic functionalities is strongly dependent on the ratio of the anionic to cationic charged groups.[4,5,6] This behavior allows selective synthesis of polymers operative over a wide range of conditions. This section describes the synthesis and solution behavior of copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate(NaAMPS) and (2-(acrylamido)-2-methylpropyl)trimethylammonium chloride (AMPTAC), the ATAS series, as well as terpolymers of acrylamide (AM), NaAMPS, and AMPTAC, the ATASAM series. Monomers used in the ATAS and ATASAM polymer series are shown in Figure 3.

Monomer and Polymer Synthesis

The AMPTAC monomer was prepared by reacting 2-acrylamido-2-methylpropanedimethylamine[7] with methyl iodide to afford (2-(acrylamido)-2-methylpropyl)trimethylammonium iodide (AMPTAI). The iodide ion was then ion-exchanged using Dowex Cl^- resin to obtain the desired AMPTAC. Acrylamide (AM) and 2-(acrylamido)-2-methylpropanesulfonic acid(AMPS), which was neutralized to NaAMPS prior to polymerization, were obtained from Aldrich. The copolymers and terpolymers were prepared by free radical polymerization in a 0.5M NaCl aqueous solution under nitrogen at 30°C using 0.1 mol% potassium persulfate as the initiator. The feed ratio of NaAMPS/AMPTAC copolymers was varied from 90:10 to30:70 mol% while the feed ratio of AM/NaAMPS/AMPTAC terpolymers was varied from 99:0.5:0.5 to 70:15:15 mol%. Total monomer concentration was held constant at 0.45M for all polymerizations. All polymers were dialyzed against deionized water to remove residual monomers and salts and isolated by lyophilization.

AM/APS Copolymers

Photophysical studies were conducted on copolymers of acrylamide containing less than 0.5 mol. % 2-(1-pyrenylsulfonamido) ethyl acrylamide in order to relate the aqueous solution behavior to the molecular structure. The copolymer prepared by a surfactant technique was shown to possess some inherent blockiness or short runs of the pyrenesulfonamide label in dilute solution. Intermolecular associations were observed above a critical concentration of polymer. I_E/I_M values paralleled the rheological response as a function of concentration. The copolymer prepared by solution polymerization showed random incorporation of the pyrenesulfonamide comonomer and no intermolecular association tendency over the concentration range studied. Associative thickening behavior observed in the surfactant-polymerized copolymer is consistent with microphase organization of hydrophobic pyrenesulfonamide aggregates above a critical concentration.

Monomer and Polymer Synthesis

The synthesis of pyrenesulfonamide labeled copolymers **1** and **2** (Figure 6) have previously been described[8]. Labeled copolymer **1** was prepared via a surfactant copolymerization technique and contains 0.25 mol. % pyrenesulfonamide label. Copolymer **2** was synthesized via a solution copolymerization technique and contains 0.35 mol. % pyrenesulfonamide label. Copolymer compositions were determined by ultraviolet spectroscopic analysis in water of the pyrenesulfonamide chromophore at 351 nm ($\varepsilon = 24{,}120\ M^{-1}cm^{-1}$).

B. Task 2 - Characterization of Molecular Structure

AM/AMBA/BPAM TERPOLYMERS

Polymerization conversions were estimated gravimetrically. Polymer compositions were determined by a combination of UV spectroscopy and elemental analysis . The method of Valint, et. al.[2], was used to determine the percentage of BPAM incorporation into the terpolymers. The BPAM model compound, BPAP (Figure 1) was used to establish a calibration curve in water which was used in subsequent determinations of BPAM incorporation. Incorporation of BPAM was consistent with the feed level for polymerizations using 5 mole % of the anionic monomers. However, incorporation of BPAM was retarded in the polymerizations employing greater amounts of the anionic monomers, likely due ionic interferences between the anionic SDS micelles and the growing macro-radicals. Elemental analysis was used to determined the content of the anionic monomers in the terpolymers as reported previously[3]. Incorporation of the anionic monomers was slightly higher than the feed ratios in all cases.

Characterization of Polymer Associative Behavior

Associative behavior of these terpolymers was determined by low shear viscometry in salt solutions. These studies were performed as a function of terpolymer concentration as well as salt concentration. Three dimensional plots best demonstrate the viscometric behavior of these systems. An example is shown in Figure 2 for BPAM/NaAMB-5, containing approximately 0.5 mole% BPAM and 6 mole% NaAMB (the neutralized for of AMBA). As demonstrated by Figure 2, the BPAM/NaAMB-5 polymer exhibits a rapid increase in viscosity as a function of terpolymer concentration due to interpolymer hydrophobic associations through the BPAM moieties. The onset of these associations occur at very dilute concentration (below 0.1 g/dL), well below the critival overlap concentration of polyacrylamide. Also these associations persist at NaCl concentrations approaching 0.5M, indicating that these hydrophobically-modified polyelectrolytes show promise as salt-resistant thickening agents. More detailed studies of the viscometric properties of these terpolymer systems will be discussed in a forthcoming report.

NaAMPS/AMPTAC COPOLYMERS and AM/NaAMPS/AMPTAC TERPOLYMERS

Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were conducted by M-H-W Laboratories of Phoenix, AZ on the low conversion copolymer samples. Copolymer compositions were confirmed using ^{13}C NMR by integration of the amide carbonyl peaks. Molecular weight studies were performed on a Chromatix KMX-6 Low Angle Laser Light Scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 Laser Differential Refractometer. For quasielastic light scattering, a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25°C in 1M NaCl. Polymer stock solutions were made by dissolving a specified amount of polymer in solvent and allowing to age for two to three weeks before analyzing with a Contraves LS-30 rheometer.

Polymer Solution Behavior

The effects of sodium chloride on the intrinsic viscosities of the ATAS copolymers and ATAS-0 and ATAS-100 were determined at a shear rate of 5.96 sec^{-1} at 25°C (Figure 4). ATAS-0, the anionic homopolymer of NaAMPS, shows the greatest decrease in viscosity as the NaCl concentration increases. As more AMPTAC is incorporated into the copolymer this effect becomes less pronounced due to the transition from polyelectrolyte to polyampholyte character. ATAS-40 lies near the polyampholyte composition region but still possesses a net charge. This leads to a small change in viscosity for ATAS-40 with increasing ionic strength. At equal molar concentrations of each monomer, (ATAS-50) there is an increase in the viscosity. The copolymer ATAS-70 lies on the edge of the polyelectrolyte/polyampholyte transition and thus shows a small decrease in intrinsic viscosity.The effects of sodium chloride on the intrinsic viscosities of the ATASAM terpolymers are shown in Figure 5. ATASAM 5-5 displays a dramatic increase in viscosity with the addition of a small amount of sodium chloride. This is indicative of the elimination of intramolecular interactions and the resulting coil expansion. ATASAM 10-10 and ATASAM 15-15 display complex behavior with increasing salt concentration. The presence of a small amount of electrolyte is required to solubilize both terpolymers. A slight increase in the ionic strength initially produces a decrease in intrinsic viscosity, likely due to the elimination of intermolecular molecular interactions with increasing ionic strength . As the ionicstrength increases further, the intrinsic viscosities increase as intramolecular interactions are reduced and chain solvation is enhanced.

AM/APS COPOLYMERS

Viscosity measurements were performed on solutions ranging from 20 to 200 mg/dL in concentration. Measurements were recorded with a Contraves LS-30 rheometer at 25°C and a shear rate of 6.0 sec^{-1}.

Steady-state fluorescence emission studies were performed on a Spex Fluorolog-2 fluorescence spectrophotometer equipped with a DM3000F data system. All samples were run in the front-face mode to avoid inner filter effects. Slit widths were varied from 0.5 to 2.5 nm, depending on sample concentration. Samples were deaerated by bubbling with nitrogen for 25-30 min. Particularly "foamy" samples were sparged by first bubbling with helium and then with argon.

Results and Discussion

In Figure 7, I_E/I_M and the reduced viscosity of copolymer **1** are plotted as a function of concentration. Viscosity and I_E/I_M both increase dramatically above an initial concentration, C^* (ca. 0.1 g/dL), providing strong evidence that intermolecular hydrophobic association of the labels is facilitated. It has been proposed that hydrophobic molecules can locate each other at distances greater than 100 angstroms due to the strong influence of water-structuring[9]. This is reflected on a molecular level by enhancement of I_E/I_M values. On a macroscopic scale, hydrophobic associations are indicated by a sharp increase in the viscosity profile at C^*.

Copolymerization dependencies of reduced viscosity and I_E/I_M are shown in Figure 8 for copolymer **2** prepared in DMF/H_2O. The zero Huggins constant of the reduced viscosity vs. concentration curve suggests a compact polymer conformation that is independent of polymer concentration. The I_E/I_M values confirm this premise. The microstructure of this polymer - random label distribution - no doubt strongly influences the polymer conformation. In water, the hydrophobic labels are compelled to aggregate by the hydrophobic effect. The homogeneous polymerization medium results in a random microstructure. The random interspacing of the hydrophobe along the polymer backbone leads to compaction of the polymer coil due to intramolecular associations. Such a compact structure is reflected in the viscosity profile of **2**.

Although **1** contains less pyrenesulfonamide label than **2**, excimer emission intensity (I_E) of **1** is enhanced relative to **2**. A greater local concentration therefore exists for **1**, suggesting that microstructural differences exist between these polymers. We believe that **1** has a more blocky microstructure due to partitioning of the pyrenesulfonamido monomer within the micelle during copolymerization, allowing some degree of blockiness even at low feed composition.

References

1) Turner, S. R.,; Siano, D. B. and Bock, J., US Patent 4 426 485, 1984.
2) Valint, P. L. Jr.; Bock, J. and Schultz, D., Polym, Mater. Sci. and Eng. Prepr., 57, 482, 1987.
3) McCormick, C. L.; Middleton, J. C. and Cummins, D. F., Macromolecules, 25 ,1201, 1992.
4) McCormick, C. L. and Johnson, C. B., Macromolecules, 21,686, 1988.
5) McCormick, C. L. and Johnson, C. B., Macromolecules, 21,694, 1988.
6) McCormick, C. L. and Johnson, C. B., Polymer, 31,1000, 1990.
7) McCormick, C. L. and Blackmon, K. P., Polymer, 27, 1971, 1986..
8) Ezzell, S.A.; McCormick, C.L. Macromolecules 1992, 25, 1881.
9) Israelachvili, J.; Pashley, R. Nature 1982, 300, 341.

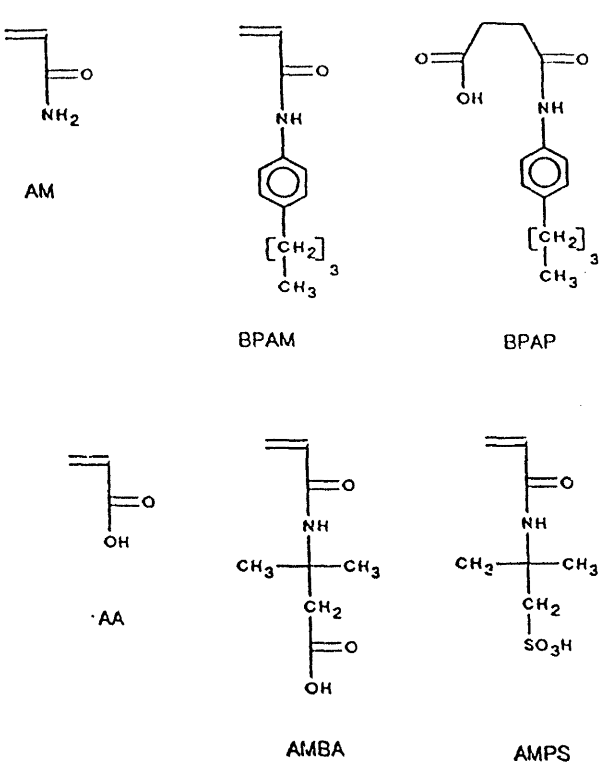


Figure 1. Monomers used in polymer synthesis and the BPAM model compound.

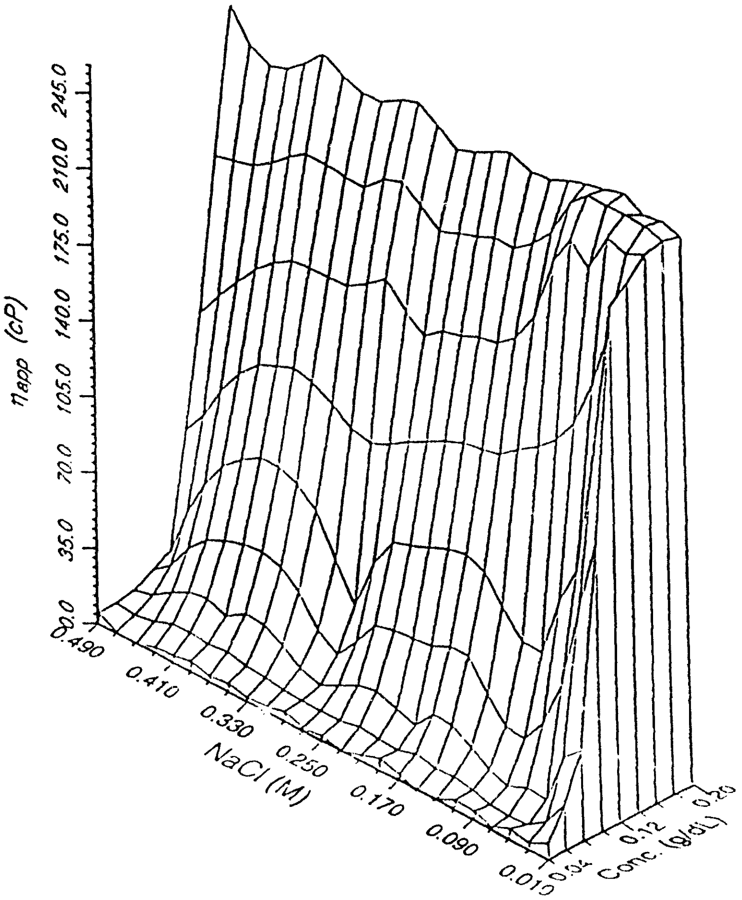
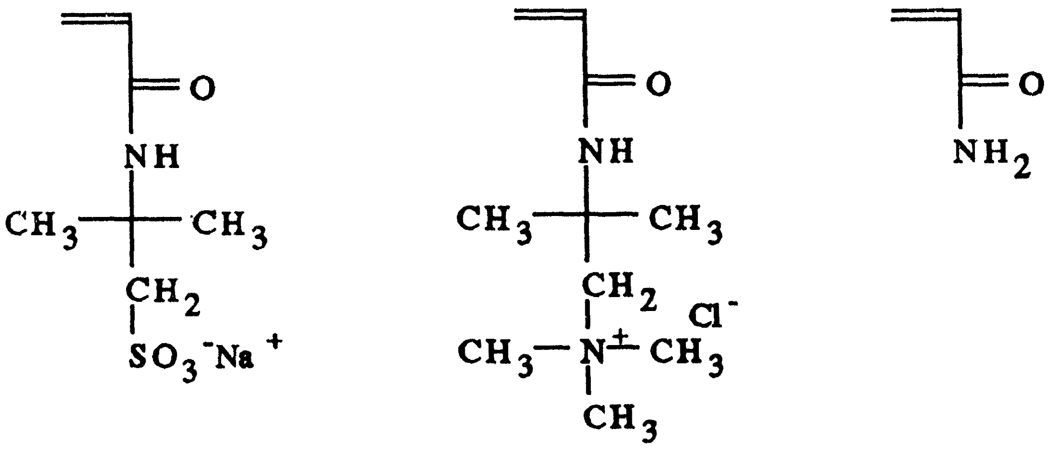


Figure 2. Apparent viscosity as a function of polymer contration and NaCl concentration for the BPAM/NaAMB-5 terpolymers.



NaAMPS **AMPTAC** **AM**

Figure 3. Monomers used in ATAS and ATASAM polymer series.

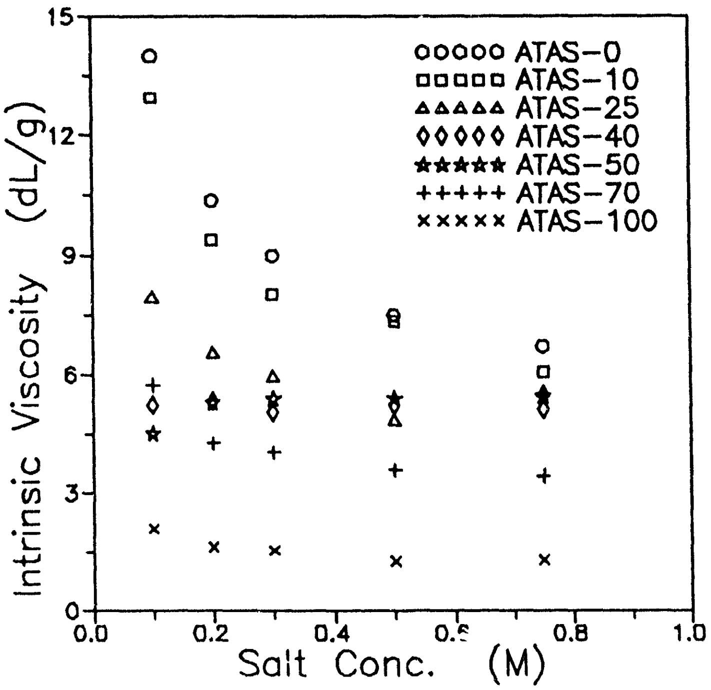


Figure 4. Intrinsic viscosities for the ATAS copolymers as a function of NaCl concentration determined at a shear rate of 5.96 sec^{-1}.

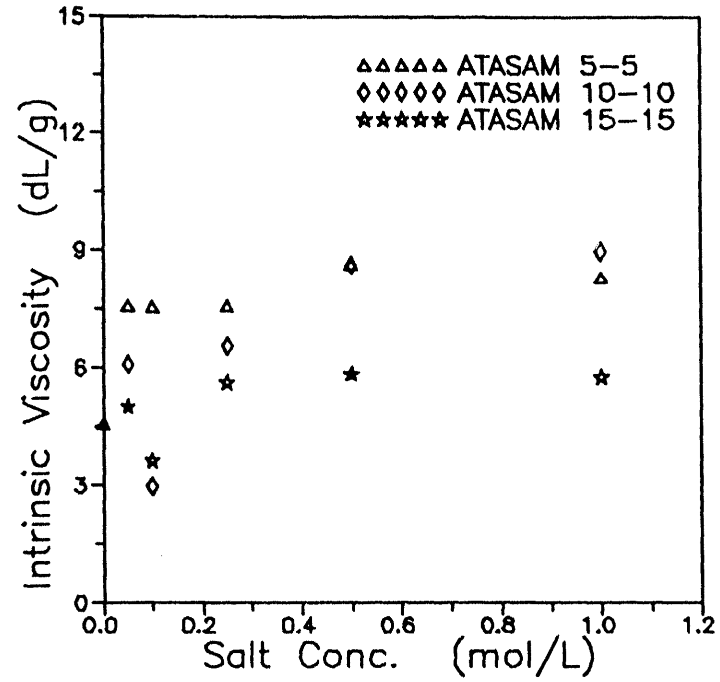
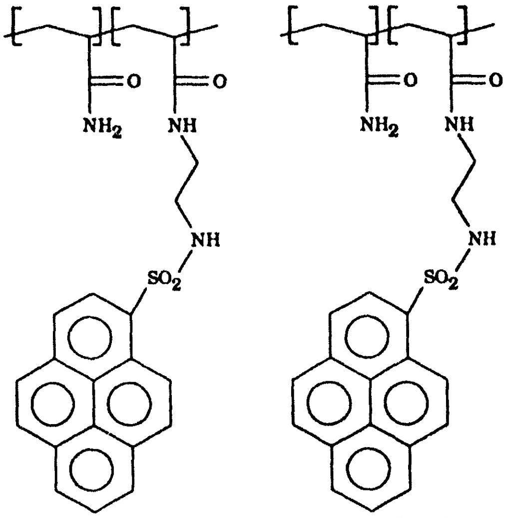


Figure 5. Effects of sodium chloride on the intrinsic viscosities of ATASAM terpolymers determined at 25°C at a shear rate of 5.96sec^{-1}.



(0.25 Mol. %)
1

(0.35 Mol. %)
2

Figure 6. Surfactant-Polymerized (**1**) and Solution-Polymerized (**2**) AM/APS.

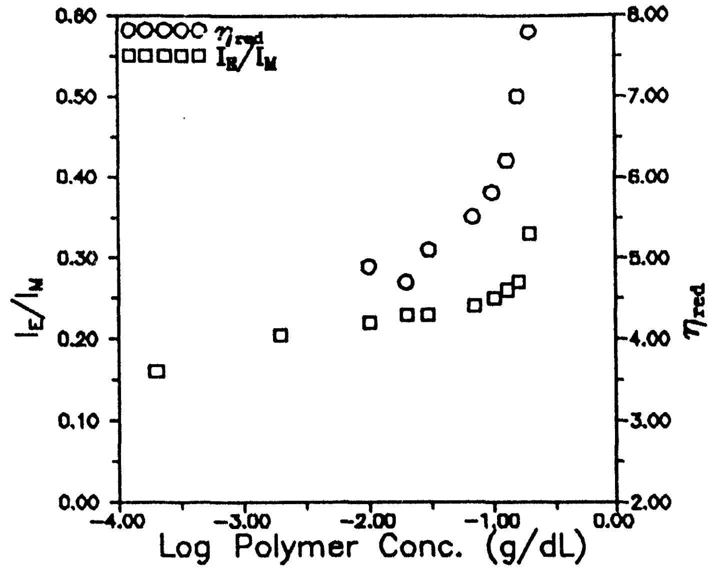


Figure 7. η_{red} and I_E/I_M as a Function of the Concentration for **1** in Deionized H_2O.

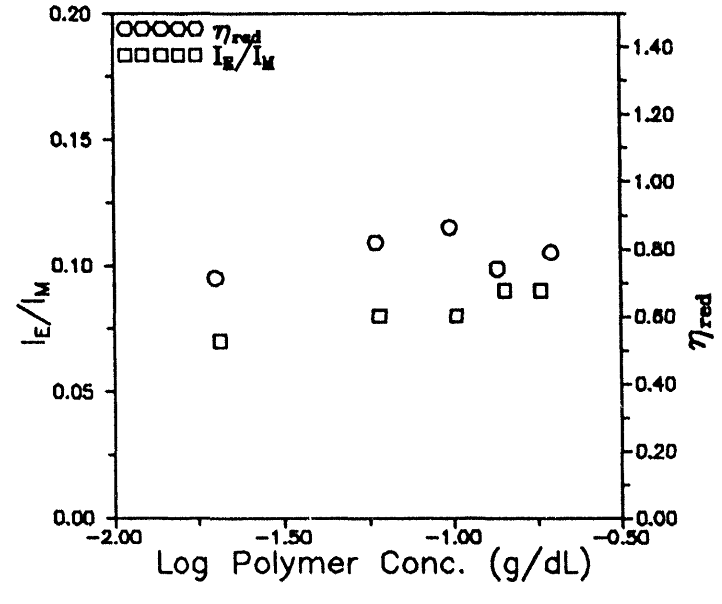


Figure 8. η_{red} and I_E/I_M as a Function of the Concentration for **2** in Deionized H_2O.

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