

Semiannual Progress Report

For Stimuli-Responsive Polymers with Enhanced Efficiency in Reservoir Recovery Processes

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Abstract

To date, our synthetic research efforts have been focused on the development of stimuli-responsive water-soluble polymers designed for use in enhanced oil recovery (EOR) applications. These model systems are structurally tailored for potential application as viscosifiers and/or mobility control agents for secondary and tertiary EOR methods. The following report discloses the progress of our ongoing research of polyzwitterions, polymers derived from monomers bearing both positive and negative charges, that show the ability to sustain or increase their hydrodynamic volume (and thus, solution viscosity) in the presence of electrolytes. Such polymers appear to be well-suited for use under conditions similar to those encountered in EOR operations. Additionally, we disclose the synthesis and characterization of a well-defined set of polyacrylamide (PAM) homopolymers that vary by MW. The MW of the PAM samples is controlled by addition of sodium formate to the polymerization medium as a conventional chain transfer agent. Data derived from polymer characterization is used to determine the kinetic parameter C_{CT} , the chain transfer constant to sodium formate under the given polymerization conditions. The PAM homopolymer series will be employed in future set of experiments designed to test a simplified intrinsic viscosity equation.

The flow resistance of a polymer solution through a porous medium is controlled by the polymer's hydrodynamic volume, which is strongly related to its intrinsic viscosity. However, the hydrodynamic volume of a polymer molecule in an aqueous solution varies with fluid temperature, solvent composition, and polymer structure. This report on the theory of polymer solubility accentuates the importance of developing polymer solutions that increase in intrinsic viscosity when fluid temperatures are elevated above room conditions. The intrinsic viscosity response to temperature and molecular weight variations of three polymer solutions verified the modeling capability of a simplified intrinsic viscosity equation. These results imply that the simplified intrinsic viscosity equation is adequate in modeling polymer coil size response to solvent composition, temperature and polymer molecular weight. The equation can be used to direct efforts to produce superior polymers for mobility control during flooding of reservoirs at elevated temperatures.

Table of Contents

Executive Summary

TASK 1: Polymer Synthesis

Part I: Polyzwitterions

- Experimental
- Results and Discussion
- Conclusions
- References

Part II: Well-defined Polyacrylamides

- Experimental
- Results and Discussion
- Conclusions
- References

TASK 5: Polymer Mobility Characterization

- Polymer Solubility At Elevated Temperatures
- Background
- Polymer Hydrodynamic Volume
- Polymer-Solvent Interaction
- Polymer Solution Temperatures During Flooding
- Intrinsic Viscosity Dependence Upon Solution Temperature
- Flory Theory
- Polymer-Solvent Interaction Parameter
- Relating Intrinsic Viscosity to the Solvent-Polymer Interaction Parameter
- Explanation of Intrinsic Viscosity Relationship
- Working Equation Relating Solution Intrinsic Viscosity to Polymer and Solvent
- Application to Literature Data
- Intrinsic Viscosity Equation Interpretation
- Conclusions
- Nomenclature
- References

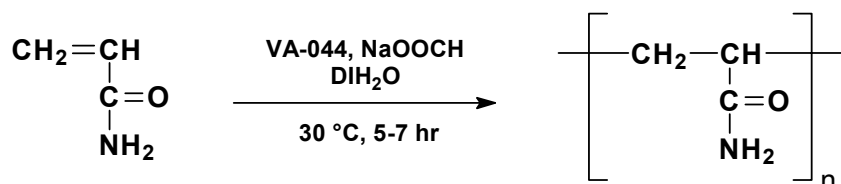
EXECUTIVE SUMMARY

TASK 1: Polymer Synthesis

Our research efforts have been focused on the development of stimuli-responsive water-soluble polymers designed for use in oil field applications, particularly enhanced oil recovery (EOR). These model systems are tailored for potential application as viscosifiers and/or mobility control agents for secondary and tertiary EOR methods. The following report discloses the progress of our ongoing research of polyzwitterions, polymers derived from monomers bearing both positive and negative charges, that show the ability to sustain or increase their hydrodynamic volume (and thus, solution viscosity) in the presence of electrolytes. Such polymers appear to be well-suited for use under conditions similar to those encountered in EOR operations.

Recently, our group has been investigating the solution behavior of amphoteric copolymers of the carboxybetaine monomer 4-(2-acrylamido-2-methylpropyl dimethylammonio) butanoate (AMPDAB), 1, with the sulfobetaine monomer 3-(2-acrylamido-2-methylpropyldimethylammonio) propanesulfonate (AMPDAPS), 2 (Scheme 1). In previous studies, turbidimetry was used to study the solubility behavior of the copolyzwitterion series, C(X:Y) (where X = mol % 1 and Y = mol % 2), and as functions of copolymer composition, pH, and added electrolytes. This report discusses the investigation this copolymer series using rheological techniques.

This current report also discloses the synthesis and characterization of a well-defined set of PAM homopolymers that vary by MW. PAM is synthesized *via* free-radical solution polymerization, under conditions that yield highly linear polymer with minimal levels of hydrolysis (Scheme 1). The MW of the PAM samples is controlled by addition of sodium formate to the polymerization medium as a conventional chain transfer agent. MWs and hydrodynamic sizes of the polymers are determined *via* size exclusion chromatography and dilute solution viscometry, respectively. Data derived from polymer characterization is used to determine the kinetic parameter C_{CT} , the chain transfer constant to sodium formate under the given polymerization conditions.



Scheme 1. Synthesis of PAM.

TASK 5: Polymer Solution Mobility Characterization

Polymer molecules in aqueous solutions that are flowing through porous media are deformed by fluid shear and extensional strain forces. Energy is needed to deform the polymer macromolecules as they pass through the porous media. This deformation energy is extracted from the kinetic energy of the flow field causing a decrease in fluid mobility. It has been observed that fluid mobility decreases with an increase in the size

of the polymer molecules dissolved in the solution. Polymer size varies with fluid temperature, solvent composition and polymer structure. Thus, an understanding of how these factors influence polymer size in solution is important for efficient mobility control when flooding an oil reservoir. Polymer hydrodynamic size is directly proportional to a measurable parameter, the intrinsic viscosity.

This report on the theory of polymer solubility accentuates the importance of developing polymer solutions that increase in intrinsic viscosity when fluid temperatures are elevated above room conditions. Ideally it is desired that a polymer flooding solution's intrinsic viscosity remain constant or preferably increase as it leaves the injection well and heats up to the reservoir temperature. This advantageous polymer solution property would ensure that fluid mobility control would not be diminished as the solution migrates into and through a hot reservoir and thereby would improve sweep efficiency and oil recovery. The theory developed in this work will enable an interpretation of what effects both polymer structure and solvent properties have on solution intrinsic viscosities at elevated temperatures.

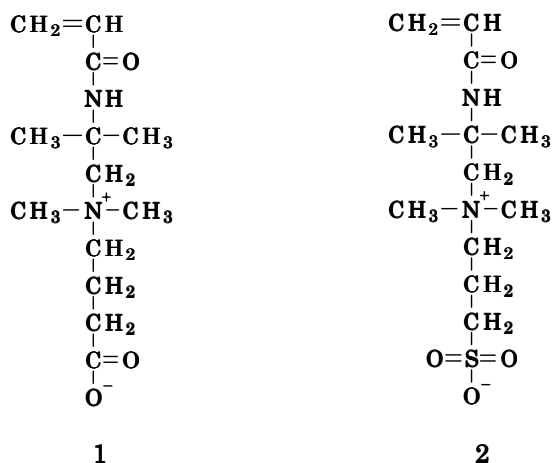
TASK 1, Part I: Polyzwitterions

SUMMARY

Our research efforts have been focused on the development of stimuli-responsive water-soluble polymers designed for use in enhanced oil recovery (EOR) applications. These model systems are tailored for potential application as viscosifiers and/or mobility control agents for secondary and tertiary EOR methods. The following report discloses the progress of our ongoing research of polyzwitterions, polymers derived from monomers bearing both positive and negative charges, that show the ability to sustain or increase their hydrodynamic volume (and thus, solution viscosity) in the presence of electrolytes.¹⁻¹¹

Such polymers appear to be well-suited for use under conditions similar to those encountered in EOR operations.

Recently, our group has been investigating the solution behavior of amphoteric copolymers of the carboxybetaine monomer 4-(2-acrylamido-2-methylpropyl dimethylammonio) butanoate (AMPDAB), **1**, with the sulfobetaine monomer 3-(2-acrylamido-2-methylpropyldimethylammonio) propanesulfonate (AMPDAPS), **2** (Scheme 1). In previous studies, turbidimetry was used to study the solubility behavior of the copolyzwitterion series, **C(X:Y)** (where *X* = mol % **1** and *Y* = mol % **2**), and as functions of copolymer composition, pH, and added electrolytes. This report discusses the investigation this copolymer series using rheological techniques. It is shown that changes in pH, electrolyte concentration, and the nature of the anionic moiety incorporated into the zwitterionic mer unit dramatically affect the viscosities of the polybetaine solutions.



Scheme 1. 4-[(2-acrylamido-2-methylpropyldimethylammonio)]butanoate (AMPDAB, **1**), and 3-[(2-acrylamido-2-methylpropyldimethylammonio)]propanesulfonate (AMPDAPS, **2**).

EXPERIMENTAL

Viscosity Measurements

Copolymer stock solutions were prepared by dissolving designated amounts of the copolymer in the stock electrolyte solutions. The solutions were then isoionically diluted

to appropriate concentrations and allowed to age for seven to ten days on an orbital shaker. pH adjustments were performed by adding small aliquots of a concentrated HCl or NaOH solution *via* a microsyringe. Rheological measurements were performed on a Contraves LS-30 low shear rheometer at constant shear rate (5.96 s^{-1}) and temperature ($25 \text{ }^{\circ}\text{C}$).

RESULTS AND DISCUSSION

Effects of Electrolytes

The effect of sodium chloride on the reduced viscosity was studied at pH 9.5 at a polymer concentration of 0.5 g/dL . The results are shown in Figure 1. The reduced viscosities of **C(75:25)** and **C(100:0)** are relatively unaffected by the presence of added electrolytes. **C(0:100)**, **C(25:75)**, and **C(50:50)**; however, do exhibit significant enhancements in viscosity as the concentration of sodium chloride is increased. As noted in previous solubility studies, the copolymers with a higher incorporation of the sulfobetaine mer units are more influenced by the concentration of sodium chloride. Accordingly, these copolymers also display the largest increases in hydrodynamic volume as the concentration of electrolytes increases.

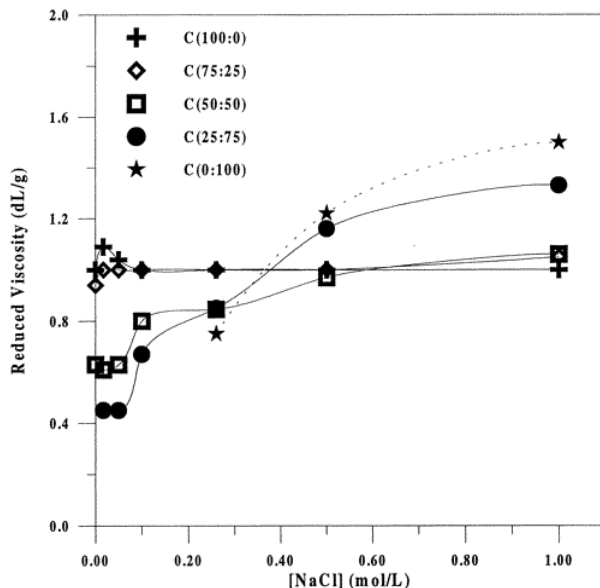


Figure 1. Reduced viscosity of **C(X:Y)** copolymers as a function of increasing NaCl concentration at pH = 9.5 ($C_p = 0.5 \text{ g/dL}$). (Full line drawn as a guide.)

Effects of pH

The reduced viscosity of the copolymers was also studied as a function of pH (Figure 2). The presence of the carboxylate group allows the polymers to acquire an overall cationic charge as the pH is lowered. As this occurs, the polymer coil exhibits an increase in hydrodynamic volume as a result of coulombic repulsions. **C(100:0)** experiences an increase in viscosity around pH 8.5 - 9.0. **C(50:50)** and **C(75:25)** require lower pH values for an increase in viscosity to be observed. It should be mentioned that

small molecule studies on surfactants possessing a carboxybetaine head group with three methylene units between charged centers have pK_a values of approximately 4. For the copolymers in this study, the protonation of the carboxylate group of **1** appears to be more facile and occurs at suprisingly high pH values. The magnitude of the increase in viscosity is also dependent on the mol % of **1** incorporated into the copolymer. The higher the percentage of **1** incorporated, the greater the increase in viscosity as a result of enhanced charge-charge repulsions between the cationic centers. The eventual reduction in viscosity at very low pH values is due to an increase in the ionic strength of the medium.

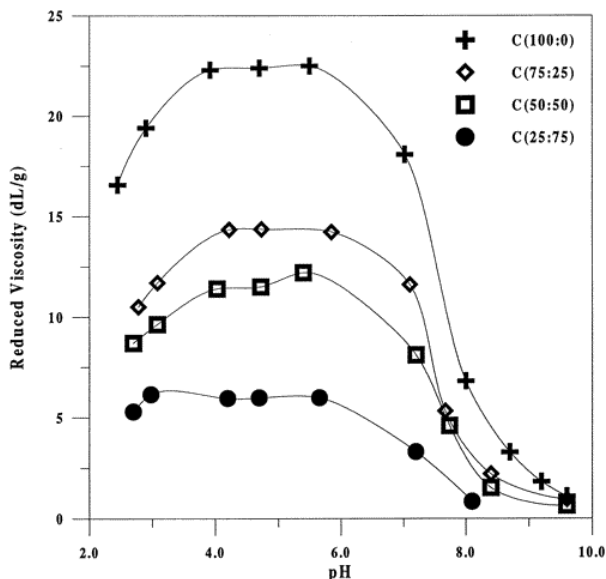


Figure 2. Reduced viscosity of C(X:Y) copolymers as a function of pH in deionized water ($C_p = 0.5$ g/dL). (Full line drawn as a guide.)

The effects of pH on the reduced viscosity were also studied in the presence of added sodium chloride for C(75:25) and C(25:75) and the results are given in Figures 3 and 4, respectively. For C(75:25), at all but the highest pH values, the reduced viscosity decreases as the concentration of sodium chloride is increased. In 0.5 M NaCl, no change in viscosity is observed throughout the pH range. These results are due to shielding of coulombic repulsions, behavior typical of polyelectrolytes. Similar behavior is observed for C(25:75).

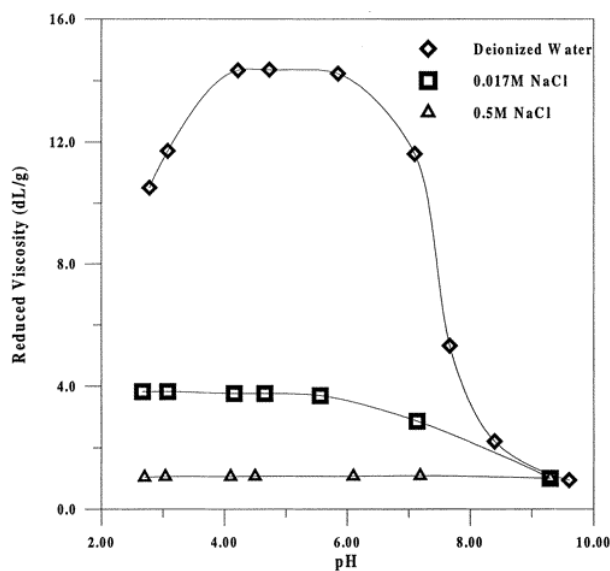


Figure 3. Reduced viscosity of C(75:25) as a function of pH in deionized water and NaCl solutions ($C_p = 0.5$ g/dL). (Full line drawn as a guide.)

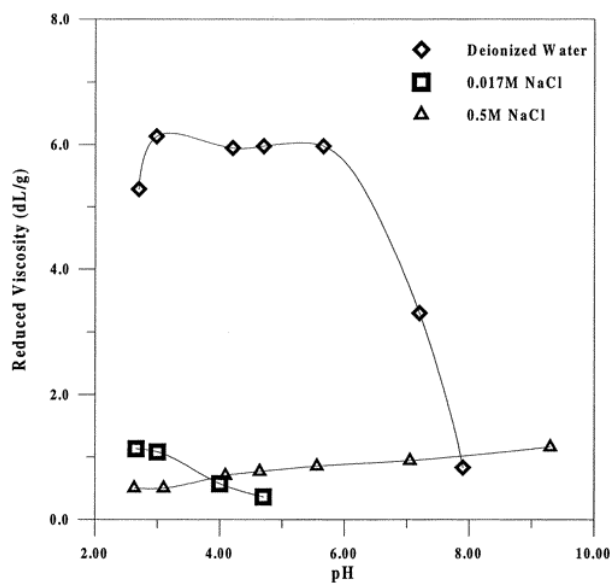


Figure 4. Reduced viscosity of C(25:75) as a function of pH in deionized water and NaCl solutions ($C_p = 0.5$ g/dL). (Full line drawn as a guide.)

Effects of Counterions

The effects of various electrolytes on the viscosity of **C(50:50)** were studied (Figure 5). As observed for the solubility studies reported earlier, the nature of the added electrolytes influences the phase behavior of the copolymers. The results follow the Hoffmeister series and the larger, more polarizable ions lead to higher solution

viscosities. This is likely a result of stronger interactions with the ionic moieties along the polymer chain; however, water structuring effects may also be operative.

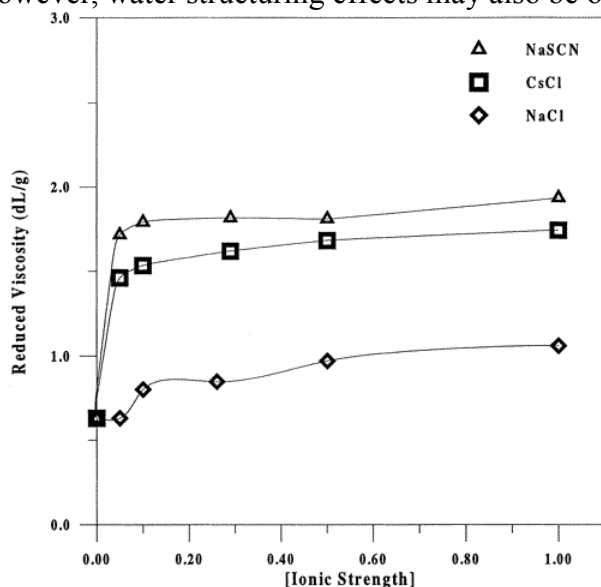


Figure 5. Reduced viscosity of C(50:50) as a function of increasing electrolyte concentration. (Full line drawn as a guide.)

CONCLUSION

Viscosity behavior was examined as a function of pH and added electrolytes. C(25:75), C(50:50), and C(0:100) exhibited the greatest increase in viscosity as the concentration of electrolytes was increased due to the higher incorporation of the sulfobetaine mer units into these polymers. Copolymers containing the highest mol % of the carboxybetaine mer unit displayed the greatest enhancement in viscosity as the pH of the aqueous medium was lowered. This behavior is a result of the polyelectrolyte-to-polycation transition as the carboxybetaine mer units become protonated and is evidenced by the decrease in viscosity in the presence of electrolytes.

TASK 1, Part II: Well-defined Polyacrylamides

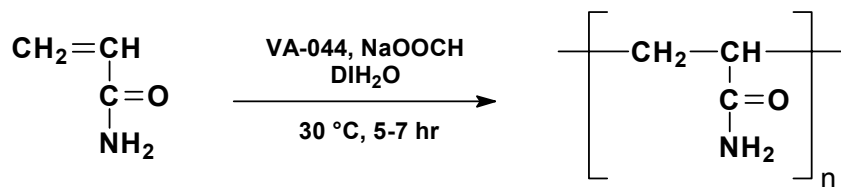
SUMMARY

To date, our synthetic research efforts have been focused on the development of stimuli-responsive water-soluble polymers designed for use in enhanced oil recovery (EOR) applications. These model systems are structurally tailored for potential application as viscosifiers and/or mobility control agents for secondary and tertiary EOR methods. The goal of previous synthetic work has been to design novel polymers that exhibit large dilute solution viscosities in the presence of the adverse conditions normally encountered in oil reservoirs (such as high salt concentrations, the presence of multivalent ions, and elevated temperatures). The polymers are also designed to have “triggerable” properties that can be elicited by external stimuli, such as changes in pH and/or salt concentration.

The Hester Research Group recently began exploring the thermodynamics of water-soluble polymers to better understand polymer solution behavior.¹ Theoretical relationships have been developed that can predict the reduced and intrinsic viscosities of polymer solutions as functions of molecular weight (MW), temperature, and polymer concentration. Such relationships are powerful tools that enable a comprehensive understanding of polymer solution behavior over a wide range of conditions. By applying these theoretical models to actual experimental systems, information that is critical for the successful design of future EOR polymers can be obtained.

To test the theories developed by the Hester Research Group, it is necessary to perform viscosity measurements on well-defined sets of model polymers. Polyacrylamide (PAM) homopolymer was selected for initial experimentation because it is the base polymer from which most synthetic EOR polymers are derived (either *via* copolymerization with functional monomers or *via* hydrolysis to anionic PAM). PAM is a simple (e.g. nonionic and entirely hydrophilic) and well-studied polymer; thus, it is an ideal candidate for this preliminary experimental work. Once results are obtained for PAM, copolymers of acrylamide and other water-soluble monomers will be analyzed to determine the effects of functional group incorporation on the (co)polymer solution thermodynamic behavior. The theories developed by the Hester Research Group will allow us to quantify changes in polymer-solvent interaction that occur due to altering the chemical composition of the (co)polymer.

This current report discloses the synthesis and characterization of a well-defined set of PAM homopolymers that vary by MW. PAM is synthesized *via* free-radical solution polymerization, under conditions that yield highly linear polymer with minimal levels of hydrolysis (Scheme 1). The MW of the PAM samples is controlled by addition of sodium formate to the polymerization medium as a conventional chain transfer agent. MWs and hydrodynamic sizes of the polymers are determined *via* size exclusion chromatography and dilute solution viscometry, respectively. Data derived from polymer characterization is used to determine the kinetic parameter C_{CT} , the chain transfer constant to sodium formate under the given polymerization conditions.



Scheme 1. Synthesis of PAM.
Task 1: Polymer Synthesis

EXPERIMENTAL

Materials

All materials were purchased from Aldrich and used as received, unless otherwise noted. Acrylamide (AM, 97%) was recrystallized three times from acetone and dried *in vacuo* prior to use. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was a gift from Wako Pure Chemical Industries, Ltd. and used as received. Deionized water (DIH₂O) was obtained from a Barnstead NANOPure reverse osmosis/filtration unit (resistivity = 18.0 MΩ).

Polymer Synthesis

Polyacrylamide (PAM) was synthesized *via* conventional free radical polymerization in DIH₂O. Sodium formate (NaOOCH) was added as a chain transfer agent to control polymer MW. The monomer concentration was held constant at 0.46 M, and the concentration of NaOOCH was adjusted to yield PAM samples of different MWs. The monomer-to-initiator ratio was held constant at 1000:1, and the reaction pH was 7.0 ± 0.5. A typical polymerization procedure is described as follows:

Degassed DIH₂O (1500 mL) was charged to a 2 L, three-neck round bottom flask equipped with mechanical stirrer and N₂ inlet/outlet. The flask was placed in a 30 °C constant temperature bath, and the contents were sparged with N₂ for 20 min. AM (48.62 g) and NaOOCH (11.63 g) were charged to the flask and allowed to stir for 10 min. VA-044 (0.22 g, dissolved in 10 mL DIH₂O) was charged to the flask *via* syringe to initiate polymerization. The polymerization was allowed to proceed under N₂ atmosphere for 5.5 hr. Stirring speed was adjusted to maintain a shallow vortex in the reaction medium. The reactor contents were discharged to Spectra-Por No. 4 dialysis tubing (MWCO = 12-14,000 g/mol) and dialyzed against DIH₂O for one week, with the dialysis water being changed every 24-48 hr. The purified PAM was isolated *via* lyophilization to yield a white, cotton-like solid.

Size Exclusion Chromatography

Aqueous size exclusion chromatography (SEC) was used to determine polymer MW and polydispersity index (PDI). The SEC system consisted of an Agilent 1100 series isocratic pump, two Viscogel columns (GPW_{XL} 5000 and 6000, Viscotek) connected in series, a DAWN EOS® 18-angle laser light scattering detector (Wyatt Technologies), and an Optilab® DSP interferometric refractometer (Wyatt Technologies). Data acquisition and analysis was performed using ASTRA® chromatography software (Wyatt Technologies). A mixed aqueous-organic eluent (0.05 M Na₂SO₄/acetonitrile, 80/20 v/v) was used for SEC. The refractive index increment (dn/dc) of PAM in the mixed eluent was determined using the refractometer in offline mode (dn/dc = 0.1603 ± 0.0007). To prevent overloading of the columns, the

concentrations of injected samples ranged from 0.5-9.0 mg/mL, depending on the MW of the polymer (estimated from intrinsic viscosity data). The error associated with the reported weight-average MWs (M_w) was determined to be $\leq \pm 2\%$.

Dilute Solution Viscometry

Intrinsic viscosities were determined using a Contraves LS-30 low shear rheometer operating at 5.96 s^{-1} and $25\text{ }^{\circ}\text{C}$. PAM stock solutions were prepared in 0.514 M NaCl and allowed to age 24-48 hr while stirring gently on an orbital shaker. Sodium azide (NaN_3) was added to the 0.514 M NaCl to prevent microbial growth ($[\text{NaN}_3] = 1\text{ mM}$). The stock solution concentrations were corrected for the moisture content of the lyophilized PAMs (determined *via* weight loss on vacuum drying at $60\text{ }^{\circ}\text{C}$). Dilutions of the stock solutions were prepared using 0.514 M NaCl and allowed to age overnight on the orbital shaker prior to analysis. Measurements of apparent viscosity on each sample were repeatable with a precision of $\pm 1\%$. Intrinsic viscosities were determined by plotting reduced viscosity versus concentration and extrapolating to zero concentration.

RESULTS AND DISCUSSION

Polymer Synthesis

PAM homopolymers were synthesized *via* thermally-initiated free radical polymerization in DIH_2O at $30\text{ }^{\circ}\text{C}$. The polymerizations were conducted slightly above room temperature to minimize chain branching and hydrolysis reactions which can occur at higher temperatures.^{2,3} The use of NaOOCH as a chain transfer agent in the synthesis of acrylamide (co)polymers has been previously reported in both patent and open literature.^{4,5} The compound was selected for these experiments because it is inexpensive, non-toxic, and non-odorous, unlike the thiol compounds (e.g. β -mercaptoethanol) normally used as chain transfer agents. NaOOCH is also easily removed from the polymer *via* dialysis or precipitation of the reactor product. VA-044 was selected as the initiator due to its high efficiency at lower temperatures. Based on data obtained from VA-044 product literature,⁶ it was determined that only five percent of the initiator charged to reactor decomposed during the polymerization period. Thus, the rate of initiation was assumed to be constant throughout the entire polymerization, and primary radical termination of propagating chains was considered negligible.

The $[\text{AM}]:[\text{NaOOCH}]$ ratio was varied from 32 to 4 (i.e. from 3.1 mol % to 25.0 mol %, based on $[\text{AM}]$); a control polymerization in the absence of NaOOCH was also conducted. Polymerizations were typically conducted from 5-7 hr, and conversions of 85-94% were achieved (Note: the control polymerization was halted at 65% conversion due to the extreme increase in viscosity of the reaction medium). Table 1 shows the parameters used in the synthesis of each sample and the conversions obtained. Evidence of hydrolysis was not detectable by ^{13}C NMR analysis of the PAM samples in D_2O (i.e. only the amide carbonyl of PAM was observed in the ^{13}C spectrum).

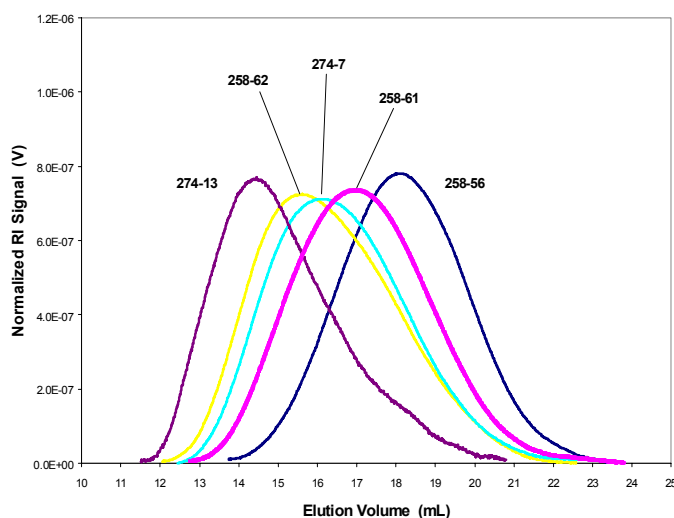
Table 1. Synthetic parameters and characterization results for PAM series.

Sample ID	[M]:[CT] ^a	Reaction Time (hr)	Conversion (%)	M _w ^b (10 ⁶ g/mol)	PDI ^b	R _g ^b (nm)
258-46	no CT	4.0	65	6.19	-	120
258-56	4	5.3	86	0.23	1.97	-
258-61	8	5.5	87	0.43	2.10	25
274-7	12	6.0	85	0.64	2.05	37
258-62	16	7.3	94	0.77	2.07	42
274-13	32	5.1	85	1.38	2.19	58

^a M = AM, CT = NaOOCH^b determined *via* aqueous SEC/MALLS analysis

SEC-MALLS Characterization

MW and polydispersity index (PDI) data were obtained *via* SEC coupled with multi-angle laser light scattering (MALLS) detection. MALLS detection enabled determination of absolute MWs without the use of polymer standards and universal calibration techniques. Figure 1 shows the SEC chromatograms (refractometer signal is plotted) of the five PAM samples polymerized in the presence of NaOOCH. (Note: To provide a meaningful visual comparison, the chromatograms have been normalized for the mass of polymer injected in each run. Since the refractive index (RI) signal is proportional to the concentration (i.e. mass per unit volume) of analyte detected, one may normalize the RI signals by dividing the raw voltages by the concentrations of analyte injected in each run.) The results of the SEC-MALLS analysis for the series of PAM homopolymers are given in Table 1.

**Figure 1. Normalized SEC chromatograms of PAM samples synthesized in the presence of NaOOCH.**

Weight-average MWs (M_w) for PAM synthesized in the presence of NaOOCH ranged from 230,000 g/mol to 1,380,000 g/mol, depending on the ratio of monomer to chain transfer agent employed. The PDIs of the PAM samples prepared using NaOOCH were approximately equal to 2.0, the value expected for a normal free radical solution polymerization in the absence of Trommsdorf or gel effects.⁶ The control PAM (sample #258-56) prepared in the absence of NaOOCH exhibited a much higher M_w (6,190,000 g/mol) compared to the other samples. The reactor product of the control polymerization was observed to be extremely viscous at lower conversion; thus, the substantially greater value of M_w observed for the control PAM was attributed to the Trommsdorf effect. An accurate PDI could not be obtained for the control PAM due to the inability to completely separate the high MW sample with the given SEC column set.

The MALLS detector also allowed weight-average radii of gyration (R_g) to be determined; these values are reported in Table 1 and coincide with the values of M_w . An accurate value of R_g could not be calculated for PAM sample #258-56, as the low MW polymer did not exhibit sufficient angular-dependent scattering behavior.

Determination of Chain Transfer Constant to Sodium Formate

While the use of NaOOCH as a chain transfer agent in PAM synthesis has been documented in the literature, the kinetics of this chain transfer reaction remain largely unexamined. One of the primary objectives of this work was to determine the chain transfer constant (C_{CT}) to NaOOCH in the aqueous solution polymerization of AM at 30 °C. The determination of C_{CT} will allow us to target specific MW PAMs in future synthetic work. It will also allow us to estimate the anticipated MWs of (co)polymers of AM and acrylamido monomers of similar reactivity when prepared under similar conditions.

C_{CT} for NaOOCH in our AM polymerizations was determined by the method of Gregg and Mayo.⁷ In the absence of chain transfer to monomer, polymer, solvent, and initiator, the number-average degree of polymerization (X_n) is given by the following expression:

$$\frac{1}{X_n} = \frac{1}{(X_n)_o} + C_{CT} \frac{[CT]}{[M]} \quad (1)$$

where $(X_n)_o$ is the value of X_n when $[CT] = 0$, $[CT]$ is the chain transfer agent concentration in mol/L, and $[M]$ is the monomer concentration in mol/L. For the polymerization of AM under the given conditions, chain transfer to monomer, polymer, and solvent is insignificant.^{2,8} Chain transfer to the VA-044 initiator in these polymerizations is also negligible because a) a very low concentration of initiator ($[AM]:[VA-044] = 1000$) was employed in the PAM synthesis,⁷ and b) azo initiators are not prone to such reactions.⁹ Thus, the only significant mode of chain transfer is assumed to be the reaction of a propagating PAM chain with NaOOCH.

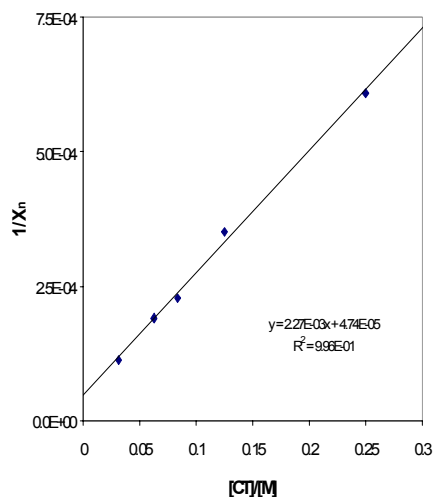


Figure 2. The effect of NaOOCH on the degree of polymerization of AM in DIH₂O ([AM] = 0.46 M, [AM]:[VA-044] = 1000, temperature = 30 °C).

Values of $1/X_n$ ($X_n = (M_w/PDI)/71.08$ g/mol AM) were calculated from the data in Table 1 and plotted versus $[CT]/[M]$ (Figure 2). The slope of the line is $C_{CT} = (2.27 \pm 0.08) \times 10^{-3}$. In the absence of NaOOCH, the predicted M_w (assuming $PDI = 2.0$) is 3,000,000 g/mol; however, the actual M_w of the control PAM was 6,190,000 g/mol. The departure from the theoretical value predicted by the Mayo relationship is due to the Trommsdorf effect in the reaction medium with increasing monomer conversion.⁶ For comparison, literature values of chain transfer constants to other compounds (including the monomer, polymer, and solvent) are listed in Table 2. (Only values determined under experimental conditions similar to those described in this paper are reported in Table 2.)

Table 2. Literature values of chain transfer constants in acrylamide polymerization.

Chain transfer species	T (°C)	$C_{CT} \times 10^4$
NaOOCH	30	22.7
Acetonitrile ^a	N/A	5.5
tris(2-Carbamoylethyl)amine ^a	N/A	85
Hydrogen peroxide ^{a,b}	25	5
Iron(III) chloride ^a	25	4.26×10^4
Isopropanol ^{a,b}	50	19
Methanol ^{a,b}	30	0.13 - 0.19
AM ^{a,b}	25	0.08 - 0.2
PAM ^b	< 50	negligible
Water ^{a,b}	25	near zero - 0.204

^a Ref. 8

^b Ref. 2

When highly reactive chain transfer agents, such as NaOOCH, are used to control polymer MW, the concentration of transfer agent will decrease with increasing monomer

conversion if the transfer agent cannot be replenished.⁸ It is critical that a sufficient amount of chain transfer agent is present over the entire range of conversion, otherwise a broad PDI will result. To verify that a chain transfer agent will be present in sufficient quantities during a polymerization, one may calculate the half-conversion of the transfer agent.⁸ The half-conversion, $U_{1/2}$, is defined as the monomer conversion where half of the chain transfer agent has been consumed and is given by the following equation:

$$U_{1/2} = 100 \left(1 - 0.5 \frac{1}{C_{CT}} \right) \quad (2)$$

Using the C_{CT} value for NaOOCH in DIH₂O at 30 °C, $U_{1/2}$ for AM was determined to be 100%. This indicates that the polymerization will reach full conversion without suffering from the effects of chain transfer agent consumption (e.g. broadening of PDI). The PDI data in Table 1 provide further evidence that chain transfer agent supply is not being exhausted during the course of the polymerizations.

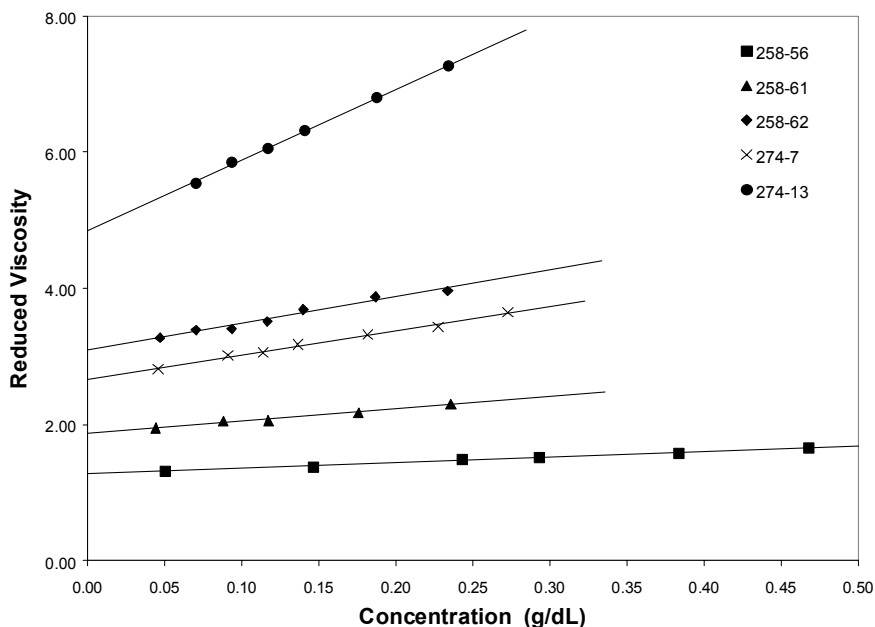


Figure 3. Huggins plots for PAM samples in 0.514 M NaCl.

Dilute Solution Viscometry

Figure 3 depicts the Huggins plots used to determine the intrinsic viscosities of the various PAM samples in 0.514 M NaCl at 25 °C (sample #258-46 is omitted for visual purposes). The PAM solutions were observed to be Newtonian fluids (i.e. non-shear thinning); thus, the intrinsic viscosity determined at 5.96 s⁻¹ may be considered the zero-shear intrinsic viscosity. Intrinsic viscosities are reported in Table 2.

Table 3. Results of dilute solution viscometry.

Sample ID	$[\eta]^a$ (dL/g)	M_v^b (10^6 g/mol)	d_H^b (Angstroms)	M_v^c (10^6 g/mol)	d_H^c (Angstroms)	M_v^d (10^6 g/mol)	d_H^d (Angstroms)
258-46	20.6	11.2	3065	10.3	2981	12.2	3157
258-56	1.28	0.27	350	0.25	341	0.33	376
258-61	1.87	0.45	472	0.41	459	0.54	502
274-7	2.68	0.73	624	0.67	607	0.86	662
258-62	3.10	0.88	698	0.81	680	1.04	740
274-13	4.88	1.61	995	1.49	969	1.88	1047

^a intrinsic viscosity measured in 0.514 M NaCl at 25 °C and 5.96 s⁻¹

^b calculated using K and a values (no heterodispersity correction) of McCarthy *et al.*¹⁰

^c calculated using K and a values (with heterodispersity correction) of McCarthy *et al.*¹⁰

^d calculated using K and a values of Klein and Conrad¹¹

Determination of Mark-Houwink-Sakurada parameters

Mark-Houwink-Sakurada (MHS) parameters (i.e. K and a values) for PAM in 0.514 M NaCl at 25 °C were determined from the M_w and intrinsic viscosity ($[\eta]$) data. Figure 4 shows the log-log plot of $[\eta]$ versus M_w from which the K and a values were calculated. The MHS parameters determined in this work were $K = 1.09 \times 10^{-4}$ dL/g (g/mol)^{-0.756} and $a = 0.756$.

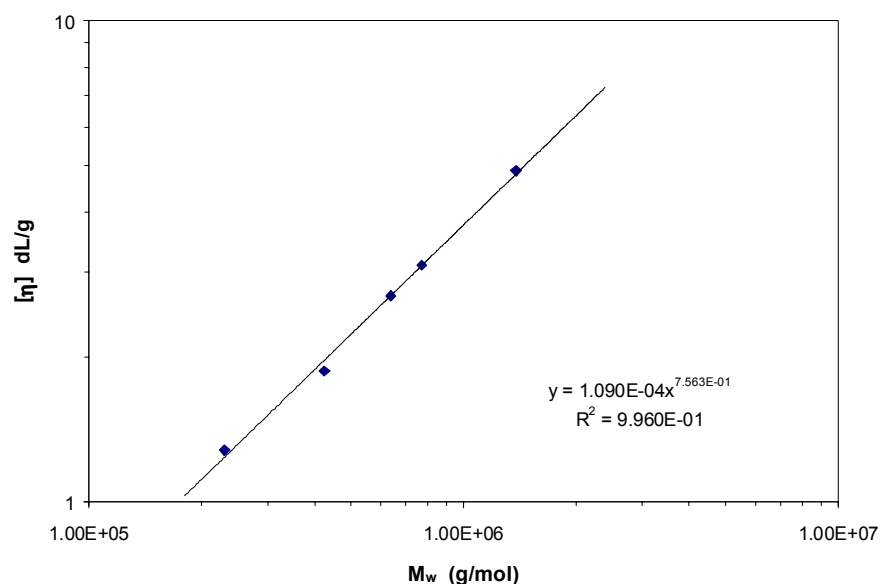


Figure 4. Mark-Houwink-Sakurada plot for PAM in 0.514 M NaCl at 25 °C. $K = 1.09 \times 10^{-4}$ dL/g (g/mol)^{-0.756} and $a = 0.756$.

MHS parameters for unfractionated PAM in 0.5 M NaCl at 25 °C have been reported in the literature by McCarthy *et al.*¹⁰ and Klein and Conrad¹¹ (Table 4). The MHS relationship ($[\eta] = K(M_v)^a$) and the various reported K and a values were used to calculate the viscosity-average MWs (M_v) of the PAM samples shown in Table 3. Hydrodynamic diameters (d_H) were also calculated using the following relationship: $d_H =$

$5([\eta] \cdot M_v)^{1/3}$.¹² In all cases, the MHS relationship overestimates the MWs of our PAM samples when the MHS parameters found in the literature results are used. This overestimation may be attributed to differences in experimental techniques employed by our group (i.e. the use of 0.514 M NaCl vs. 0.5 M NaCl as the solvent, the determination of viscosity with a low shear rheometer vs. an Ubbelodhe (capillary) viscometer, etc.).

Table 4. Values of K and a for unfractionated PAM in 0.5 M NaCl at 25 °C.

Source	K ($\times 10^{-4}$ dL/g)	a
McCarthy, et al. ¹⁰		
with heterodispersity correction	1.21	0.746
without heterodispersity correction	1.14	0.746
Klein and Conrad ¹¹	0.719	0.77
Present work ^a	1.09	0.756

^a determined in 0.514 M NaCl

The MHS parameters determined in this work correlate quite well with those determined by McCarthy *et al*, with the non-heterodispersity corrected K and a values showing the best agreement (Table 4). McCarthy and coworkers determined their MHS parameters at a slightly lower ionic strength (0.5 M NaCl) and over a wider range of PAM MWs (91,000 – 3,243,000 g/mol) in their work. Hence, the differences in solvent ionic strength and range of PAM MWs examined most likely account for the slight deviations from the K and a values reported here. In both our work and the work of McCarthy *et al.*, SEC and light scattering were utilized for MW determination. Klein and Conrad instead used sedimentation to determine MWs in their work. Thus, the large difference in Klein and Conrad's K and a values may be attributed to differences in analytical technique for MW.

CONCLUSION

A well-defined series of PAM homopolymers has been prepared *via* free-radical polymerization in aqueous solution. NaOOCH was employed as a chain transfer agent to control the polymer MW. The series of PAM samples was characterized using SEC-MALLS and dilute solution viscometry. PAM M_w s ranged from $0.23 - 6.19 \times 10^6$ g/mol, depending on the amount of NaOOCH added to the polymerization medium. The chain transfer constant (C_{CT}) for NaOOCH in AM polymerization was determined to be $(2.27 \pm 0.08) \times 10^{-3}$. Intrinsic viscosities for the PAM samples in 0.514 M NaCl at 25 °C ranged from 1.28 – 20.8 dL/g. Using the MW and intrinsic viscosity data, MHS K and a values were determined; the values were found to correlate well with values found in the literature. The PAM homopolymer series will be employed in a three-level, full factorial design of experiments to test theoretical relationships developed by the Hester Research Group.

Task 5: Polymer Solution Mobility--Macromolecular Hydrodynamic Volume At Elevated Temperatures

Background

As explained in previous reports^{1, 2}, polymer molecules in aqueous solutions that are flowing through porous media are deformed by fluid shear and extensional strain forces. Each polymer molecule in solution can be considered a spherical coil swollen with solvent and having a large hydrodynamic volume. Energy is needed to deform the polymer macromolecules as they pass through the porous media. This deformation energy is extracted from the kinetic energy of the flow field causing a decrease in fluid mobility. It has been observed that fluid mobility decreases with an increase in the hydrodynamic size of the polymer molecules dissolved in the solution. Polymer hydrodynamic size varies with fluid temperature, solvent composition and polymer structure. Thus, an understanding of how these factors influence polymer hydrodynamic volume is important for understanding mobility control when flooding an oil reservoir.

Polymer Hydrodynamic Volume

Polymer hydrodynamic volume is directly related to a measurable parameter, the intrinsic viscosity. The intrinsic viscosity is the fluid volume occupied by a given mass of polymer. Each polymer coil contains one polymer molecule surrounded by a much larger volume of solvent. The volume of solvent associated with a given polymer mass is called the intrinsic viscosity, η_{intr} ; a parameter that can be determined by dilute solution viscosity experiments. The usual dimensions of intrinsic viscosity are milliliters of fluid per gram of polymer. Intrinsic viscosity is also reported using dimensions of deciliters per gram. The intrinsic viscosity is dependent upon polymer type, solvent composition and temperature. A large intrinsic viscosity value implies that the polymer coils are greatly expanded by the solvent. A low intrinsic viscosity value indicates that the polymer coil volume is small.

The hydrodynamic volume of a single polymer coil, V_c , is the product of the intrinsic viscosity and the mass of a single polymer molecule. The mass of a single polymer molecule is the polymer molecular weight, M , divided by Avogadro's number, N_o .

$$V_c = M \eta_{intr} / N_o \quad (1)$$

To have improved oil recovery when flooding reservoirs with polymer solutions, larger polymer coil hydrodynamic volumes are desired. As shown by Equation (1), coil hydrodynamic volumes can be estimated from intrinsic viscosity and polymer molecular weight measurements.

Polymer - Solvent Interaction

A polymer's intrinsic viscosity depends upon the degree of solvent-polymer thermodynamic interaction. Favorable solvent-polymer thermodynamic interaction increases polymer coil hydrodynamic volume by increasing the polymer's intrinsic viscosity. When the solvent-polymer interactions are not favorable, the polymer coil volume decreases. With very unfavorable solvent-polymer interactions, the polymer coil will completely collapse and will no longer be soluble in the solvent. Solvent-polymer thermodynamic interaction depends upon polymer molecular structure and concentration, solvent molecular structure, and solution temperature.³ Dilute polymer solutions are used for flooding oil reservoirs and these solutions become even more diluted as they flow away from the injection well. At dilute conditions, polymer coils do not interact and respond to fluid flow conditions independently of one another.

Polymer Solution Temperatures During Reservoir Flooding

After injection, a polymer solution increases in temperature and rapidly approaches the reservoir temperature. Usually reservoir temperatures are greater than room temperature conditions. Ideally, the flooding solution's intrinsic viscosity should remain constant or preferably increase as it leaves the injection well and heats up to the reservoir temperature. This desirable property would ensure that the displacing fluid mobility would not increase due to a reduction in polymer coil hydrodynamic volume as the solution migrates into the reservoir. Thus, synthesis efforts for producing superior polymers for reservoir flooding should be directed to creating polymers that maintain or increase their intrinsic viscosity as the fluid temperature is elevated.

Intrinsic Viscosity Dependence Upon Solution Temperature

Figure 1 shows a phase diagram for a typical polymer solution. Polymer solutions may have both a lower critical solution temperature, LCST, and an upper critical solution temperature, UCST. At temperatures above the LCST or at temperatures below the UCST, phase separation can occur. At solution temperatures between the UCST and LCST, a single phase region exists. The two-phase regions are separated from the single phase region by boundary curves (binodal curves). Polymer-solvent mixtures inside a binodal curve separate into two liquid phases having compositions on the binodal curve. The LCST usually occurs at about 0.8 of the pure solvent gas-liquid critical temperature.⁴ Using this estimation technique, the LCST for water is expected to be about 518 °K or 245 °C; a temperature much greater than temperatures existing in oil reservoirs.

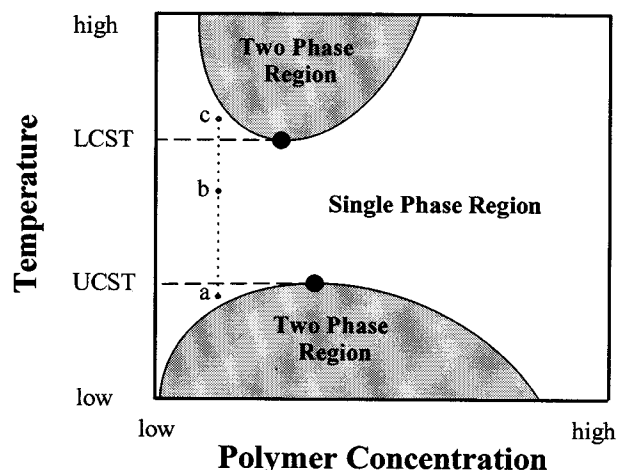


Figure 1: Polymer Solution Phase Diagram

For dilute polymer solutions at a low temperature (point “a” in Figure 1), the polymer coils in the solution usually increase in hydrodynamic volume as the temperature increases to temperatures greater than the upper critical solution temperature. As the solution temperature continues to increase, the polymer coil volume eventually reaches a maximum (point “b”) and thereafter decreases in volume as the solution temperature (point “c”) approaches the upper critical temperature.

Several theories have been proposed to explain the relationship between a polymer coil's hydrodynamic volume and solution temperature. Most theories are based on the work of Paul Flory in which a theta temperature, θ , is defined as the critical miscibility temperature for a given solvent-polymer system in the limit of infinite polymer molecular weight.⁵ At theta conditions, the excess chemical potential of mixing is zero. If the heat of polymer-solvent mixing is endothermic, an increase in solution temperature (to temperatures greater than the theta temperature) will increase polymer coil hydrodynamic volume. If the heat of polymer-solvent mixing is exothermic, a decrease in solution temperature (to temperatures less than the theta temperature) will increase polymer coil hydrodynamic volume.

Flory Theory

Theoretical relationships of Paul Flory showed that a polymer coil volume expansion, α_p , was a function of solution absolute temperature, T , and the number of polymer segments, N .

$$\alpha_f^5 - \alpha_f^3 \approx \sqrt{N} \left(1 - \frac{\theta}{T} \right) \quad \text{Flory Equation}$$

The expansion factor, α_f , is the cube root of the ratio of the intrinsic viscosity, η_{intr} , to intrinsic viscosity at the theta temperature, η_θ . The number of polymer segments, N , is approximately equal to the polymer molar volume, V_p , divided by solvent molar volume, V_s .⁶ For high molecular weight polymers that have a large number of segments the α_f^3 term can be neglected when the fluid temperature differs significantly from the theta temperature. After inserting $(\eta_{\text{intr}} / \eta_\theta)^{1/3}$ for α_f , the simplified equation becomes linear.

$$\left(\frac{\eta_{\text{intr}}}{\eta_\theta} \right)^{5/3} \approx \sqrt{N} \left(1 - \frac{\theta}{T} \right) \quad \text{Simplified Flory Equation}$$

$$\left(\eta_{\text{intr}} \right)^{5/3} \approx \sqrt{N} \left(\eta_\theta \right)^{5/3} - \sqrt{N} \left(\eta_\theta \right)^{5/3} \theta \left(\frac{1}{T} \right) \quad \text{Linear Equation}$$

The equation above indicates that a plot of $(\eta_{\text{intr}})^{5/3}$ versus $\frac{1}{T}$ should yield data points that fall on a straight line. The intercept, A , and slope, B , of the line will be $\sqrt{N} (\eta_\theta)^{5/3}$ and $-\sqrt{N} (\eta_\theta)^{5/3} \theta$, respectively.

The theta temperature, θ , is equal to $-B/A$. If M_o is the molecular weight of a segment of the polymer macromolecule that has the same volume as a solvent molecule, then $N = M/M_o$. Therefore the intrinsic viscosity at theta conditions, η_θ , is

$$\eta_\theta = \left(A \sqrt{M_o / M} \right)^{3/5}$$

Figure 2 shows the linear form of the Flory plot of two partially hydrolyzed polyacrylamide polymers in brine solution, Alcoflood 1285 (Ciba Specialty Chemicals PLC) in 0.514 molar NaCl and Pusher 700 (Dow Chemical Co.) in 3 wt. % NaCl. The random degree of hydrolysis for both polymers is between 25 and 30%. The molecular weights for the Alcoflood 1285 and

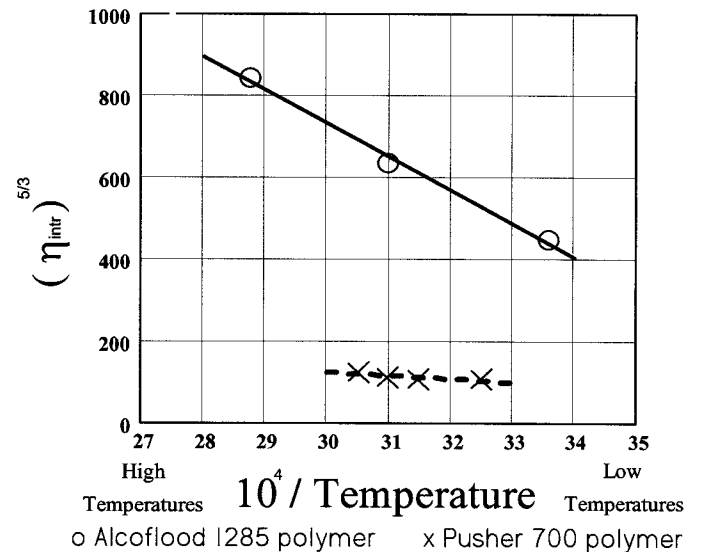


Figure 2 : Polyacrylamide Flory Plots

Pusher 700 polymers are about 20 million and 5 million, respectively. The polymer segment molecular weight, M_o , for both polymers is about 17.7 grams per mole. The Pusher 700 polymer data was from the literature.⁷ Table I gives the Flory parameters that were calculated from the plots given in Figure 2.

Table I: Flory Parameters for Polyacrylamide in 3% NaCl Solvent

Parameter	Units	Pusher 700	Alcoflood 1285
M	g/mole x 10^6	5	20
M_o	g/mole	17.7	17.7
N		2.9×10^5	1.1×10^6
V_p	mL	5×10^6	20×10^6
V_s	mL	17.6	17.6
$\eta\theta$	dL/g	5.0	11.7
θ	$^{\circ}\text{K}$	257	226

Polymer - Solvent Interaction Parameter

Originally, the solvent - polymer interaction parameter, χ , introduced by Flory was intended to only account for the enthalpic contributions during mixing. However, it has been determined that χ has both enthalpic and entropic components. Presently it is common practice to express χ as the sum of an enthalpic and entropic contribution.

$$\chi = \chi_s + (\chi_h / T) \quad (2)$$

χ_h and χ_s are independent of temperature but are functions of polymer and solvent. Recent findings have shown that χ_s is correlated with χ_h and the theta temperature θ .⁸

$$\chi_s = (\frac{1}{2}) - (\chi_h / \theta) \quad (3)$$

At a given polymer molecular weight, the dependence of χ on temperature can be expressed as

$$\chi = \frac{1}{2} - \chi_h [(1/T) - (1/\theta)] \quad (4)$$

At a constant temperature Huggins⁵ found that χ varied with the number of polymer segments, N.

$$\chi = \frac{1}{z} \left(1 - \frac{1}{N} \right)^2 \quad (5) \quad \text{where } z \text{ is the coordination number. The coordination number}$$

is the number of solvent molecules surrounding a segment of the polymer macromolecule. If the solvent molecules form a cube around a polymer segment, then z would have a value of 6. The exact value of z is unknown because it is a complex function of polymer and solvent structure.⁹

Equation (4) can be used to determine the partial change in χ with respect to temperature at constant polymer molecular weight and equation (5) can be used to determine the partial change in χ with respect to the number of polymer segments at constant temperature. The sum of these two partial changes is equal to the total change in χ .

$$d\chi = \left(\frac{\partial \chi}{\partial T} \right)_N dT + \left(\frac{\partial \chi}{\partial N} \right)_T dN = -\frac{\chi_h}{T^2} dT + \frac{2}{z} \left(\frac{1}{N^2} - \frac{1}{N^3} \right) dN \quad (6)$$

For high molecular weight polymers with large N values, $(1/N^2) - (1/N^3) \approx 1/N^2$. Making this approximation and integration of Equation (6) gives $\chi = \frac{\chi_h}{T} - \frac{2}{zN} + \text{constant}$. The constant is determined by requiring χ to be $\frac{1}{2}$ when $T = \theta$ and $N = \infty$. The constant is equal to $\frac{1}{2} - (\chi_h / \theta)$.

$$\text{Thus, } \chi = \frac{1}{2} - \frac{2}{zN} + \chi_h \left(\frac{1}{T} - \frac{1}{\theta} \right) \quad (7)$$

Relating Intrinsic Viscosity to the Solvent-Polymer Interaction parameter

For dilute polymer solutions it has been experientially shown that the second Virial coefficient, A_2 , in the limit of zero polymer concentration is related to the intrinsic viscosity by the relationship¹⁰

$$A_2 \approx \pi (\eta_{intr} - \eta_\theta) / M. \text{ However, } \chi \text{ is related to } A_2 \text{ by the function } \chi = (1/2) - A_2 \rho_p^2 V_s$$

$$\text{where } \rho_p \text{ is the polymer density.}^6 \text{ Therefore, } \chi = \left(\frac{1}{2} \right) - \frac{\pi \rho_p^2 V_s}{M} (\eta_{intr} - \eta_\theta) \quad (8)$$

Equations 7 and 8 can be combined to give Equation 9, shown below.

$$\eta_{intr} = \eta_\theta + \frac{2M}{\pi z \rho_p^2 V_s N} + \frac{M}{\pi \rho_p^2 V_s} \chi_h \left(\frac{1}{\theta} - \frac{1}{T} \right) \quad (9)$$

After substitution of $N = M / M_o$ and $\eta_\theta = K_\theta \sqrt{M}$ where K_θ is the Mark-Houwink K value at the theta temperature, Equation (9) becomes

$$\eta_{intr} = \frac{2M_o}{\pi z \rho_p^2 V_s} + K_\theta \sqrt{M} + \frac{M}{\pi \rho_p^2 V_s} \frac{\chi_h}{\theta} - \frac{M}{\pi \rho_p^2 V_s} \frac{\chi_h}{T} \quad (10)$$

M_o , z , ρ_p , K_θ and χ_h are constants for a given polymer structure and solvent. The solvent molar volume, V_s , for aqueous solvents only varies slightly with temperature, T .

$$V_s = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} \quad (11) \quad \text{where } \alpha, \beta \text{ and } \gamma \text{ are constants for a given solvent.}$$

For aqueous solvents at low pressures the molar volume, V_s , is almost constant from 0 to 100 °C. See Table II below.

Table II : Solvent Molar Volumes¹¹

Aqueous Solvent	α mL / mole	β mL / (°K mole)	γ mL / (°K ² mole)
Water	30.27	-6870	9.59 x 10 ⁵
Water with 3% NaCl	28.36	-5995	8.19 x 10 ⁵
Aqueous Solvent	Molar Volume at 25 °C mL/mole	Molar Volume at 50 °C mL/mole	Molar Volume at 75 °C mL/mole
Water	18.02	18.19	18.45
Water with 3% NaCl	17.46	17.65	17.89

The value of the first term on the right side of Equation (10) is always much smaller than the remaining terms and therefore can be neglected. With this simplification Equation (10) becomes

$$\eta_{intr} = K_{\theta} \sqrt{M} + \frac{M}{\pi \rho_p^2 V_s} \frac{\chi_h}{\theta} - \frac{M}{\pi \rho_p^2 V_s} \frac{\chi_h}{T} \quad (12)$$

Because the parameters in equation (12) are constants for a given polymer solution, Equation (12) can be used to predict the dependence of the solution intrinsic viscosity on temperature and polymer molecular weight. The relationship described by Equation (12) is complex and requires a physical explanation.

Explanation of Intrinsic Viscosity Relationship

The first term on the right side of Equation (12) is the intrinsic viscosity at the theta condition. At the theta condition the polymer coil volume or intrinsic viscosity is at a minimum because at this condition the polymer coil is not swollen by the presence of solvent. At the theta condition $\eta_{intr} = \eta_{\theta} = K_{\theta} M^{1/2}$.

The second term on the right side of Equation (12) is the partial change in the intrinsic viscosity associated with a change in system entropy. This term accounts for changes in system order due to polymer-solvent interaction and is proportional to the ratio of χ_h to θ .

The third term on the right side of Equation (12) is the partial change in intrinsic viscosity associated with a change in system enthalpy. This term accounts for changes in system heat due to polymer-solvent interaction and is proportional to the ratio of $-\chi_h$ to T .

Examination of Equation (12) reveals that four possible solution conditions may exist.

At solution condition **A** : $\chi_h < 0$ & $T > \theta$ then $\eta_{intr} < \eta_{\theta}$ and $\eta_{intr} \downarrow$ as $T \uparrow$.

At solution condition **B** : $\chi_h > 0$ & $T > \theta$ then $\eta_{intr} > \eta_{\theta}$ and $\eta_{intr} \uparrow$ as $T \uparrow$.

At solution condition **C** : $\chi_h > 0$ & $T < \theta$ then $\eta_{intr} < \eta_{\theta}$ and $\eta_{intr} \uparrow$ as $T \uparrow$.

At solution condition **D** : $\chi_h < 0$ & $T < \theta$ then $\eta_{intr} > \eta_\theta$ and $\eta_{intr} \downarrow$ as $T \uparrow$.

The χ parameter characterizes the overall interaction of a polymer segment structure with solvent molecules. The value of χ results from the sum of enthalpic, χ_h/T , and entropic, $\chi_s = 1/2 - (\chi_h/\theta)$, contributions.

A negative value of χ_h indicates that mixing polymer with solvent is exothermic (releases heat) and mixing is favored by enthalpy, i.e., χ becomes less. However, χ_s under these conditions would be positive and mixing would not be favored by entropy, i.e., χ becomes larger. The value of χ depends upon the solution temperature, T , in relationship to the theta temperature, θ . Two possibilities can exist, $T > \theta$ or $T < \theta$; giving dilute solution conditions A and D, respectively.

In contrast, a positive value of χ_h indicates that mixing polymer with solvent is endothermic (gains heat) and mixing is not favored by enthalpy, i.e., χ becomes greater. However, χ_s under these conditions would be less and mixing would be favored by entropy, i.e., χ becomes less. Again, the value of χ depends upon the solution temperature, T , in relationship to the theta temperature, θ . Two possibilities can exist, $T > \theta$ or $T < \theta$; giving dilute solution conditions B and C, respectively.

These dilute solution conditions can be associated with regions on polymer-solvent phase diagrams, as shown in Figure 3 below. Condition B or possibly C is what is desired for polymer flooding; the condition where the intrinsic viscosity or polymer coil hydrodynamic size increases with increasing temperature.

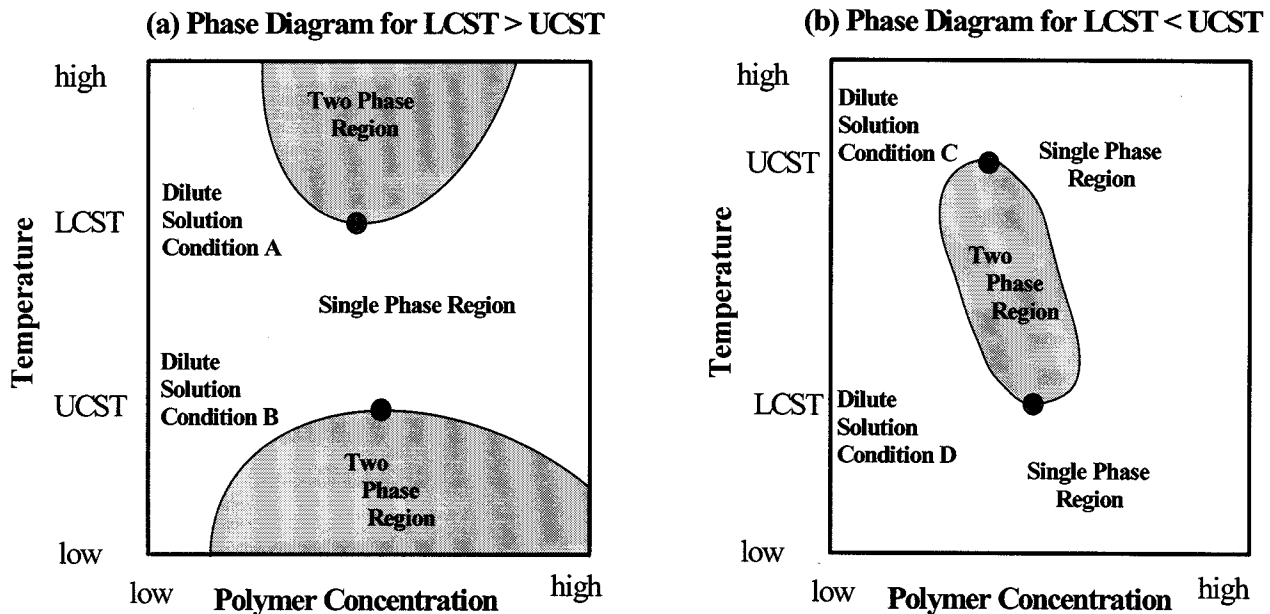


Figure 3 : Polymer - Solvent Phase Diagrams

Working Equation Relating Solution Intrinsic Viscosity to Polymer and Solvent

Equation (12) can be arranged to form Equation (13).

$$\frac{\eta_{intr}}{M} = \frac{\chi_h}{\pi \rho_p^2 V_s} \frac{1}{\theta} + \frac{K_\theta}{\sqrt{M}} - \frac{\chi_h}{\pi \rho_p^2 V_s} \frac{1}{T} \quad (13)$$

Equation (13) is a multi - linear equation of the form $Z = a + b x + c y$ (14) , where

$$Z = \frac{\eta_{intr}}{M}, \quad x = \frac{1}{\sqrt{M}}, \quad y = \frac{1}{T}, \quad a = \frac{\chi_h}{\pi \rho_p^2 V_s \theta}, \quad b = K_\theta, \quad c = -\frac{\chi_h}{\pi \rho_p^2 V_s}$$

Data points defined by experimental measurements of intrinsic viscosity, η_{intr} , at specific polymer molecular weights, M , and solution temperatures, T , can be fitted¹² to Equation (14) by linear regression to determine coefficients a , b and c . Knowledge of these coefficients enables the determination of the unknown parameters K_θ , θ and χ_h .

$$K_\theta = b, \quad \theta = -\frac{c}{a}, \quad \chi_h = -c \pi \rho_p^2 V_s$$

The values of K_θ , θ and χ_h define how the solution's intrinsic viscosity value will vary with polymer molecular weight and fluid temperature.

Using Experimental Data with the Intrinsic Viscosity Working Equation

The linear form of the intrinsic viscosity function, Equation (14), was fitted by multi-linear regression to the data of intrinsic viscosity, molecular weights and solution temperature for the two commercial polyacrylamides previously described in Table I. The regression gave estimates of the parameters K_θ , θ , and χ_h shown in Table III. In these calculations the polymer density, ρ_p , was assumed to be 1.0 g/mL and the solvent molar volume, V_s , was set to 17.6 mL/mole. The values for χ and χ_s were calculated from Equations (2) and (3), respectively. Figure 4 shows a plot of the intrinsic viscosity function versus temperature for three partially hydrolyzed polyacrylamide polymers of different molecular weights in 3 wt. % NaCl aqueous solvent. The molecular weights are 5, 12 and 20 million. As shown in Figure 4, the experimental data for both the 5 and 20 million polyacrylamide solutions fit the function almost perfectly.

The positive value of χ_h , 10 °K, indicates that mixing polyacrylamide with 3 wt. % NaCl solvent is endothermic (gains heat during mixing). Therefore, at higher solution temperatures less heat of mixing is present and this enthalpic effect would increase the solution's intrinsic viscosity at higher fluid temperatures. The value of χ_s , 0.461, that is less than ½. This indicates that the interaction between the polyacrylamide segments and the 3 wt. % NaCl solvent molecules produces disorder during mixing (entropy has increased with mixing). The two theta temperatures obtained using the Flory Equation, shown in Table I, and the single theta temperature estimated using the intrinsic viscosity function, shown in Table III, are, as expected, very similar. Because $\chi_h > 0$ and $T > \theta$, dilute solution condition B exists for the intrinsic viscosity function and the solution's intrinsic viscosity increases with increasing fluid temperatures.

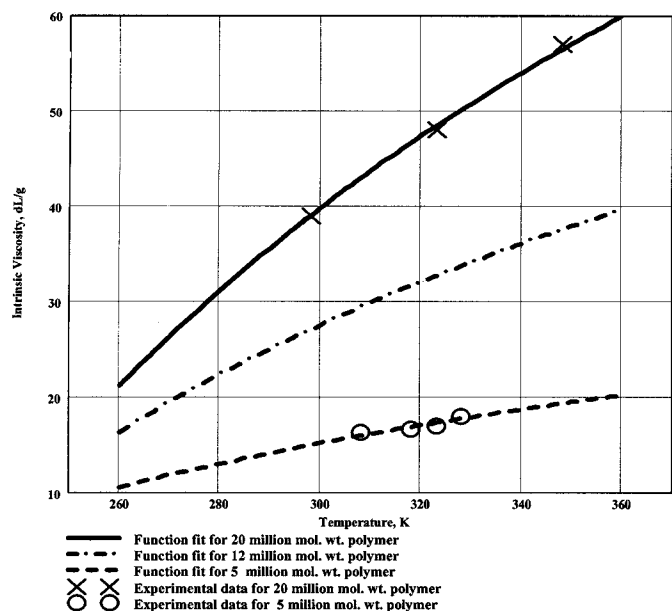


Figure 4: Intrinsic Viscosities of Polyacrylamide in 3 wt. % NaCl Aqueous Solvent

Application to Literature Data

A review of the scientific literature produced several journal papers that contained tabulated data reporting intrinsic viscosity values over a range of polymer molecular weights and fluid temperatures. However in this report, only three data sets are fitted to the simplified intrinsic viscosity equation. These three examples will adequately demonstrate the utility of the intrinsic viscosity relationship.

Data Set I - Poly(isobutylene) in Benzene

This data set was taken from a 1949 paper by T. J. Fox and P. J. Flory.¹³ Poly(isobutylene) molecular weights ranged from 1,260,000 to 48,000 g / mol. Fluid temperatures varied from 25 to 60 °C. Intrinsic viscosities were determined using an Ubbelohde viscometer. Polymer density, ρ_p , and solvent molar volume, V_{s_1} , are 0.915 g / mL and 88.7 mL / mol, respectively.

Parameter	Units	Value
K_θ	$\frac{\text{mL} \cdot \text{mole}^{\frac{1}{2}}}{\text{g}^{\frac{3}{2}}}$	0.466
θ	K	259.3
χ_h	K	10.0
χ_s	dimensionless	0.461
χ at 298K	dimensionless	0.495
χ at 333K	dimensionless	0.491

Table III : Intrinsic Viscosity Function Parameter Fit Values

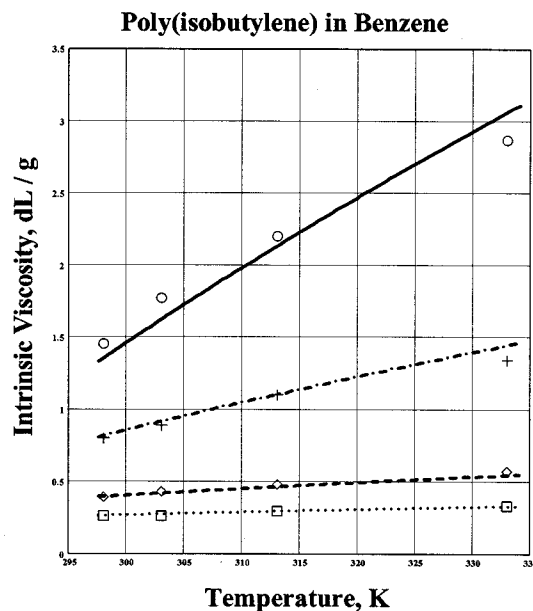


Figure 5: Solution Intrinsic Viscosities of Poly(isobutylene) in Benzene. Solid line & circles are 1,260,000 mol. wt. polymer. Dashed-dot line & pluses are 463,000. Dashed lines & diamonds are 110,000. Dotted line & squares are 48,000.

Figure 5 shows the experimental data and the fit curves resulting from a multi-linear regression of the data to Equation (14). The values determined by the regression for θ , K_θ and χ_h were 297.6 K, 0.119 mL g^{-3/2} mol^{1/2} and 92.9 K, respectively. For this polymer-solvent system, Fox and Flory determined that θ and K_θ had values of 295 K and 0.110 mL g^{-3/2} mol^{1/2}, respectively. Thus, the intrinsic viscosity equation parameters, θ and K_θ , appear to be consistent with the Fox and Flory values.

As shown by Figure 5, the lines produced from the intrinsic viscosity equation give a good fit to the experimental data. The adjusted correlation coefficient between experimental data and corresponding fit values was 0.994. This high value also reflects that the intrinsic viscosity equation is adequate in fitting the experimental data. For this polymer-solvent system, the intrinsic viscosity increases with increasing fluid temperature and increasing polymer molecular weight.

Data Set II - Poly(styrene) in Cyclohexane

This data set was taken from a 1986 paper by F. Gundert and B. A. Wolf.¹⁴ Poly(styrene) molecular weights ranged from 1,800,000 to 17,500 g/mol. Fluid temperatures varied from 32 to 50 °C. Intrinsic viscosities were determined at each solution condition using an Ubbelohde viscometer. Polymer density, ρ_p , and solvent molar volume, V_s , are 1.04 g/mL and 108.1 mL/mol, respectively.

Figure 6 shows the experimental data and the fit curves resulting from a multi-linear regression of the data to Equation (14). The values determined by the regression for θ , K_θ and χ_h were 304.1 °K, 0.079 mL g^{-3/2} mol^{1/2} and 72.8 °K, respectively. For this polymer-solvent system, A. Rudin reported that K_θ had a value of 0.072 mL g^{-3/2} mol^{1/2} for the same polymer.¹⁵ Thus, the intrinsic viscosity equation K_θ parameter appears to be consistent with the Rudin value.

As shown by Figure 6, the lines produced from the intrinsic viscosity equation give a good fit to the experimental data. The adjusted correlation coefficient between experimental data and corresponding fit values was 0.998. This high value also confirms that the intrinsic viscosity equation is adequate in fitting the experimental data.

Data Set III - Poly(vinyl acetate) in Chloroform

This data set was taken from a 1962 paper by W. R. Moor and M. Murphy.¹⁶ Poly(vinyl acetate) molecular weights ranged from 217,000 to 43,000 g/mol. Fluid temperatures varied from 18 to 53 °C. Intrinsic viscosities were determined at each solution condition using a capillary viscometer. Polymer

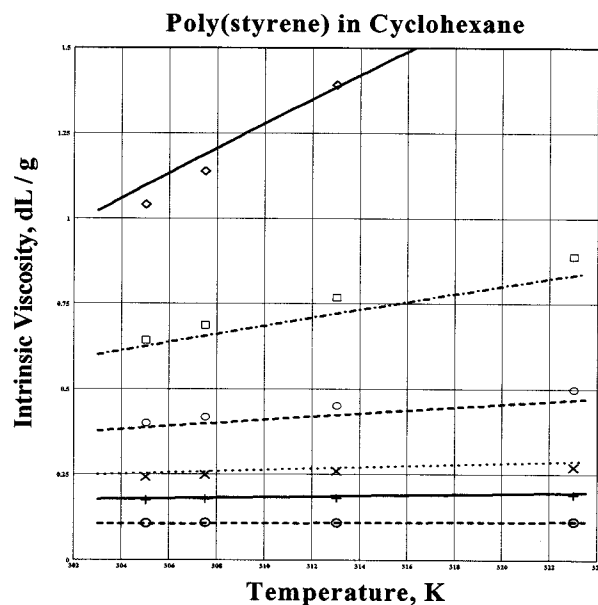


Figure 6: Solution Intrinsic Viscosities of Poly(styrene) in Cyclohexane. Solid line & diamonds are 1.8 million mol. wt. polymer. Dashed-dot line & squares are 600,000. Dashed line and circles are 233,000. Dotted line and x are 100,000. Solid line & pluses are 50,000. Dashed line & circles are 17,500.

density, ρ_p , and solvent molar volume, V_s , are 1.19 g/mL and 80.5 mL/mol, respectively.

Figure 7 shows the experimental data and the fit curves resulting from a multi-linear regression of the data to Equation (14). The values determined by the regression for θ , K_θ and χ_h were 427.1 °K, 0.161 mL g^{-3/2} mol^{1/2} and -106.6 °K, respectively. For this polymer-solvent system, A. Rudin reported that K_θ had a value of 0.093 mL g^{-3/2} mol^{1/2} for the same polymer.¹⁵ Thus, the intrinsic viscosity equation K_θ parameter appears not to be consistent with the Rudin reported value.

As shown in Figure 7, polymer intrinsic viscosity is decreasing as temperature increases. However, the lines produced from the simplified intrinsic viscosity equation give a poor fit to the experimental data. Although the correlation coefficient between experimental data and corresponding fit values is 0.994, the fit points are significantly different from corresponding data points.

It appears that the intrinsic viscosity equation is correctly accommodating for temperature changes but is not adequately adjusting for polymer molecular weight variations. This inadequacy of the fit to the data could be an experimental problem (molecular weight determination error) or it could be associated with the simplifications used to develop the intrinsic viscosity equation, i. e., some of the terms that were omitted could be important for this polymer-solvent system.

Intrinsic Viscosity Equation Interpretation

Table IV gives a summary of the results in fitting the intrinsic viscosity equation to the three sets of experimental data. Included in Table IV is the polymer-solvent enthalpic contribution to the overall interaction parameter, χ_h , the calculated polymer-solvent entropic contribution to the overall interaction parameter, χ_s , and the calculated overall polymer-solvent interaction parameter, χ , for both 25 and 60 °C. The intrinsic viscosity values calculated using the viscosity equation for polymers having a molecular weight of 250,000 g/mol and at 25 and 60 °C are also listed in Table IV.

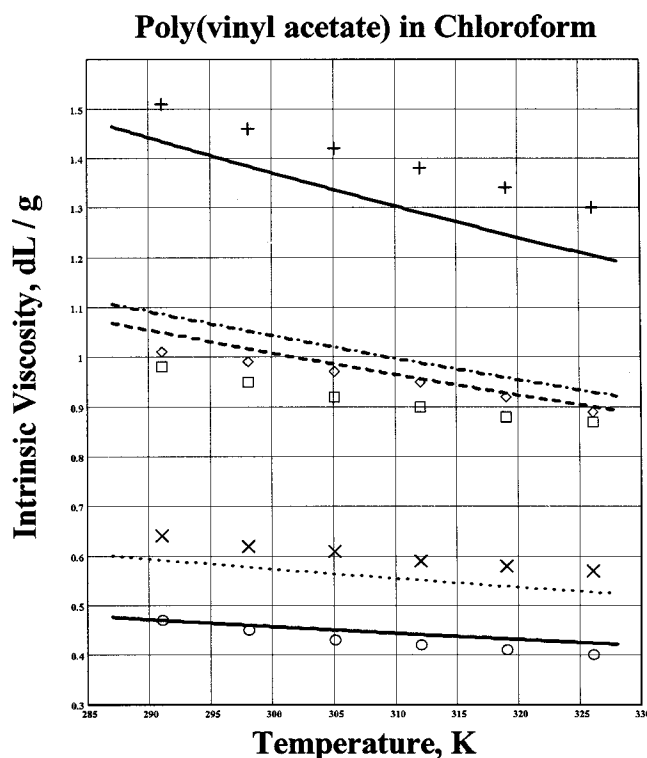


Figure 7: Intrinsic Viscosities of Poly(vinyl acetate) in Chloroform. Solid line and pluses are for 217,000 mol. wt. polymer. Dashed-dot line and diamonds are 148,000. Dashed line and squares are 141,000. Dotted line and x are for 61,000. Solid line and circles are 43,000.

Table IV : Polymer Solubility Parameters

Data Set	θ °K	$K\theta$ mL g ^{-3/2} mol ^{1/2}	χ_h °K	χ_s	χ at 298 K	η_{intr} at 298 K, dl/g M=250,000	χ at 333 K	η_{intr} at 333 K, dl/g M=250,000
I - poly(isobutylene) in benzene	297.6	0.119	92.9	0.188	0.500	0.60	0.467	0.94
II - poly(styrene) in cyclohexane	304.1	0.079	72.8	0.261	0.505	0.36	0.479	0.53
III - poly(vinyl acetate) in chloroform	427.1	0.161	-106.6	0.750	0.392	1.54	0.429	1.28

The entropic contribution to the polymer-solvent interaction parameter, χ_s , can be calculated from the enthalpic contribution to the polymer-solvent interaction parameter, χ_h , and the theta temperature, θ . Recall that this relationship was given by Equation (3).

$$\chi_s = \left(\frac{1}{2} \right) - \left(\frac{\chi_h}{\theta} \right) \quad (3)$$

As previously discussed the overall polymer-solvent interaction parameter, χ , can be calculated for each fluid temperature using Equation (2). This relationship was used to find the χ values at 25 and 60 °C in Table IV.

$$\chi = \chi_s + \left(\frac{\chi_h}{T} \right) \quad (2)$$

When χ is $\frac{1}{2}$, then a theta condition exists for the polymer-solvent system. At χ values greater than $\frac{1}{2}$, the polymer will phase separate from the solution. As χ values become increasing less than $\frac{1}{2}$, polymer coils will expand and the solution's intrinsic viscosity will increase in value.

The expected intrinsic viscosity response to temperature is shown in the last four columns of Table IV. For both the poly(isobutylene) in benzene and the poly(styrene) in cyclohexane solutions where the χ value decreases as the temperature increases from 25 to 60 °C, the intrinsic viscosity values increase by about 50 %. Note that both solutions are almost at the theta condition ($\chi = 0.5$ and polymer coils have minimum size) when the temperature is 25 °C. Above 25 °C, both solvents are expanding the polymer coils to a larger dimension as reflected by smaller χ values and larger intrinsic viscosities at 60 °C.

In contrast, for the poly(vinyl acetate) in chloroform solution where the χ value increases from 0.392 to 0.429 as the temperature increases from 25 to 60 °C, the intrinsic viscosity value decreases by about 17 %. Above 25 °C, the chloroform is less capable of expanding the polymer coils and the coil size collapses as is reflected by a larger χ value and a smaller intrinsic viscosity at 60 °C.

Conclusions

The intrinsic viscosity response to temperature and molecular weight variations of three polymer solutions was used to test the modeling capability of a simplified intrinsic viscosity equation. The simplified intrinsic viscosity equation contains three parameters (θ , $K\theta$, and χ_h) that are related to the thermodynamic properties of polymer solutions. These parameters describe the polymer coil size at unperturbed conditions and the polymer coil expansion capabilities of the solvent as a function of fluid temperature.

V_s	solvent molar volume
x	polymer mol. wt. independent variable in the linear form of the Intrinsic Viscosity Function
y	temperature independent variable in the linear form of the Intrinsic Viscosity Function
z	coordination number (number of solvent molecules associated with a polymer segment)
Z	dependent variable in the linear form of the Intrinsic Viscosity Function
α_f	polymer coil volume expansion factor
α, β	first & second coefficient of the function relating solvent molar volume to temperature
χ	overall polymer-solvent interaction parameter
χ_h	related to the enthalpic contribution to the overall polymer-solvent interaction parameter
χ_s	the entropic contribution to the overall polymer-solvent interaction parameter
η_{intr}	intrinsic viscosity
η_θ	intrinsic viscosity at theta conditions (no polymer-solvent thermodynamic interaction)
γ	third coefficient of the function relating solvent molar volume to temperature
θ	theta temperature (temperature corresponding no polymer- solvent interaction)
ρ_p	polymer density

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