Automatic continuous online monitoring of polymerization reactions (ACOMP) was adapted to the monitoring of acrylamide polymerization in inverse emulsions. This is the first application of ACOMP to heterogeneous phase polymerization. The conversion and reduced viscosity were monitored by continuously inverting and diluting the emulsion phase using a small reactor sample stream and a breaker surfactant solution, followed by UV absorption and viscometric detection. This inversion into a stable portion of the polymer/surfactant phase diagram is accomplished in tens of seconds, yielding dilute solutions containing acrylamide (Aam), polyacrylamide (PA), oil droplets, and small quantities of surfactant, initiator and other debris, and low molecular weight compounds. After establishing the means of making ACOMP measurements, a first application of the method is made to resolving some of the kinetic issues involved in polymer emulsification, including the evolution of molecular mass, and the simultaneous action of an “intrinsic” initiator and an added chemical initiator.

Various means have been used to analyze aliquots of reacting solutions, such as dynamic light scattering (DLS), static light scattering (SLS), scanning electron microscopy, and small angle neutron scattering (SANS) for particle sizing, SEC on inverted emulsions, and viscometry on diluted or precipitate/redissolved samples for measures of molecular mass. Turbidity and changes in viscosity during the polymerization have been monitored. Simple online measurements have been made by dilatometry. A useful advance in this field would be the introduction of a means for monitoring conversion and measures of polymer molar mass during the reaction, so as to understand both the kinetics and mechanisms and, potentially, to control them during the reaction. Automatic continuous online monitoring of polymerization reactions (ACOMP) was introduced in 1998 and provides a means of implementing this possibility. It is a nonchromatographic technique that requires the continuous withdrawal of a small sample stream from the reactor, which is diluted to the degree that measurements made on the flowing sample are dominated by single particle properties, not by polymer interactions. Typically, combining multi-angle light scattering (MALS), ultra-violet absorption, viscometry, and differential refractometry allows the determination of monomer conversion and measures of polymer molecular mass. It has been successfully applied to many homogeneous polymerization systems: free radical, nitroxide mediated controlled radical polymerization (CRP), CRP gradient copolymerization, step-growth reactions, simultaneous determination of average composition and molecular mass distributions in free radical copolymerization, and for continuous reactors. Although no chromatographic columns

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**Online Monitoring of Polymerization Reactions in Inverse Emulsions**

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are used, means for obtaining molecular mass distributions and indices of polydispersity have been presented.23

Until now, however, ACOMP has been applied only to homogeneous phase polymerization reactions, so that extension to heterogeneous phase reactions represents an advance for ACOMP, as well as understanding the polymerization reactions themselves. ACOMP is becoming a routine analytical technique for laboratory scale use, where kinetics can be quickly obtained and mechanisms modeled. It is hoped that it will also prove useful for optimization of reactions at the pilot plant level and, ultimately, be used in feedback control in full scale industrial reactors. This latter application promises significant advances in product quality and the efficient use of energy, nonrenewable resources, and plant and labor time.

To make absolute measurements on an inverse emulsion system containing oil, water, monomer, polymer, initiator, and surfactant, special means of online sample “conditioning” and data interpretation need to be found. Stated simply, the monomeric and polymeric contents of the inverse emulsion/latex must be “spilled” out from the discrete phase droplet in a period of seconds, and the resulting detectors signals must be interpreted to allow differentiating among the complex mixture of components. Another concern is that, upon diluting and conditioning such a complex mixture, the multiple components will be displaced to different portions of a complex phase diagram, and this must be stable enough for equilibrium or quasiequilibrium measurements to be made.

This work is meant to (1) establish a means of continuously inverting and conditioning the reactor liquid into a stable portion of the phase diagram, determining the type of behavior that occurs in the multicomponent system upon conditioning, and how the relevant components can be tracked with the detector train, and (2) to make initial ACOMP measurements with the goal of obtaining preliminary kinetic data. Although various schemes for breaking the emulsions can be conceived, this work concentrates on the use of HLB (high lyophilic balance) surfactant (or “breaker surfactant”) to invert the water-in-oil inverse emulsion droplets used in polymerization to an oil-in-water system. The generality of ACOMP for polymerization monitoring has been amply demonstrated. It is probable that the type of approach taken to phase inversion here will find wide applicability to both oil in water and water in oil systems, although the details of the inversion will have to be experimentally determined for each case.

Materials and Methods

ACOMP Instrumentation. This work represents the first application of ACOMP to heterogeneous phase polymerization, and as such, it presented considerable challenges both for the design and implementation of the ACOMP “front-end” and the ACOMP detector train “back-end”. The front-end comprises the components needed to extract a small stream from the reactor and produce the continuous, conditioned, diluted, phase inverted emulsion sample stream to the detectors. The back-end comprises the series of detectors which provide the raw data for full polymerization reaction analysis.

ACOMP Front-End. An advantage of the emulsion polymerization reaction is that the viscosity of the reaction liquid increases very little during the reaction, typically 2× to 4×, compared to solution or bulk polymerizations where the viscosity can increase by a factor of well over 105. Hence, it was possible to use an HPLC pump (Knauer K-120) to withdraw sample continuously from the reactor, instead of a heavy duty gear pump needed in homogeneous phases reaching high reactor liquid viscosities (i.e., well in excess of 105 cP). The reaction stream reached a low pressure mixing chamber (LPMC), consisting of a stirred, 30 mL vial, vented to atmospheric pressure. The LPMC was also fed with an HPLC pump (Eldex), delivering the breaker surfactant solution at a much higher rate than the reactor withdrawal pump, and any excess flow into the LPMC was continuously pumped off by a peristaltic pump, thus maintaining a fixed fluid level in the LPMC. The inverted and diluted emulsion was withdrawn from the LPMC by a third HPLC pump (Agilent 1100) and diluted further by mixing it with 0.1 M NaCl solvent brought by another Agilent 1100 HPLC pump into an Upchurch Microbore high pressure mixing chamber (HPMC). The outlet stream from the high pressure mixing chamber passed through a 10 micron inline filter, and the stream from this filter constituted the highly diluted, conditioned, phase inverted emulsion sample that fed the detector train.

ACOMP Back-End. The ACOMP detector train, or back-end, consisted of a Shimadzu SPD-10AVp dual wavelength Ultraviolet (UV) spectrophotometer (used to monitor the monomer disappearance during the polymerization) and a home-built single capillary viscometer.24 A Waters 410 refractive index detector (RI) and a home-built seven angle multi-angle light scattering detector were also in the detection train but, as described below, provided signals which were much harder to interpret. The principles, details, and data analysis method for each detector have been previously described.10–16

For the viscometer, it is recalled here that the Poisseuille solution or bulk polymerizations where the viscosity can increase by a factor of well over 105. Hence, it was possible to use an HPLC pump (Knauer K-120) to withdraw sample continuously from the reactor, instead of a heavy duty gear pump needed in homogeneous phases reaching high reactor liquid viscosities (i.e., well in excess of 105 cP). The reaction stream reached a low pressure mixing chamber (LPMC), consisting of a stirred, 30 mL vial, vented to atmospheric pressure. The LPMC was also fed with an HPLC pump (Eldex), delivering the breaker surfactant solution at a much higher rate than the reactor withdrawal pump, and any excess flow into the LPMC was continuously pumped off by a peristaltic pump, thus maintaining a fixed fluid level in the LPMC. The inverted and diluted emulsion was withdrawn from the LPMC by a third HPLC pump (Agilent 1100) and diluted further by mixing it with 0.1 M NaCl solvent brought by another Agilent 1100 HPLC pump into an Upchurch Microbore high pressure mixing chamber (HPMC). The outlet stream from the high pressure mixing chamber passed through a 10 micron inline filter, and the stream from this filter constituted the highly diluted, conditioned, phase inverted emulsion sample that fed the detector train.

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Automatic Continuous Mixing (ACM) Instrumentation. The ACM technique has been described in detail in a previous work.25,26 ACM is used to determine equilibrium properties of multicomponent solutions, such as weight average molecular mass, Mw, second virial coefficient A2, and weight average intrinsic viscosity [η]w, by forming continuous gradients along chosen paths in composition space. A programmable HPLC Shimadzu LC-10ATvp mixing pump was used to pass the solutions through a detector train comprising a Waters 410 refractive index detector, a single capillary viscometer and another home-built 7 angle MALS detector. Multidetector Size Exclusion Chromatography (SEC). The SEC instrumentation contained the same detectors described in the first sections, except that a commercial BI-MwA MALS detector was used. A Shodex OH-pak 806M HQ chromatographic column was used, in conjunction with a 100 μL injection loop. The solvent (NaCl 0.1 M, the same as in ACOMP) passed through the system at 0.8 mL/min. This type of multidetector SEC instrumentation has been analyzed in detail.27

The SEC was useful for separating monomer from polymer, allowing the continuous ACOMP conversion data to be cross-checked with
discrete, manually withdrawn aliquots from the waste line, and/or from the reactor. The agreement was always very good. The SEC data, however, were not particularly useful for determining molecular mass and viscosity distributions, simply because the polymers produced were so large that they all eluted in the exclusion limit of the 806 column and so no useful separation took place. Hence, ACM proved more valuable in offline characterization of $M_w$ and $[\eta]_w$ than SEC, and the SEC results in this work were restricted to cross-checking conversion.

**Dynamic Light Scattering (DLS).** A Brookhaven Instruments 90-Plus DLS system, with fixed detection at 90°, was used, together with the usual Cumulant Analysis of the scattered electric field autocorrelation function, obtained via the Gaussian approximation from the directly measured and computed scattered intensity autocorrelation function. This yielded $z$-average diffusion coefficient $D_z$. DLS was used to assess emulsion droplet size and evolution, and to help establish the stability behavior of the inverted phase.

**Reagents and Polymerization Procedure.** The components of the inverse emulsion were as follows: acrylamide from Polysciences (Chemzymes, Ultrapure; in early experiments, not reported here), acrylamide 50 wt %, inhibited with 25 ppm Cu$^{2+}$ was used), deionized water, Exxsol D80 as oil phase (aliphatic hydrocarbon), and HAMP-EX 80 chelant (40 wt % pentasodium DTPA solution). Span 80 (sorbitan monooleate) was used as the emulsifier. Two different lots of Span 80 were used, lot A and lot B, which both had different appearances (lot A was lighter in color). Additionally, lot A appears to have included some form of “intrinsinc initiator”, as discussed below. Phase separation of the monomer containing emulsions occurred slowly, over several days, which is a long time scale compared to that of the reaction hours. The emulsion after polymerization was stabler over much longer periods of time.

The strategy was to use a second (“breaker”) surfactant and high aqueous dilution to invert the phase to oil-in-water as soon as the emulsion is withdrawn from the reactor, hence spilling the polymeric and monomeric components of the emulsion into the continuous aqueous phase. In this way, the detectors can distinguish the polymer and monomer in the aqueous phase, amidst the oil droplets. Sulfonic N-95 (alkylphenol ethoxylate), a nonionic surfactant, was chosen to make the phase inversion. Initially, a photoinitiator was used, Irgacure 2959 (2-hydroxy-1-[4-(hydroxyethoxy) phenyl]-2-methyl-1-propanone), which activates as soon as a mercury lamp illuminates the reactor. The photoinitiated reactions took place at room temperature. Although the UV photoinitiation experiments were successful, and allowed the reactions to be quenched by merely turning off the UV source, it was too difficult to control the illumination and consistently measure the UV dosage for subsequent quantitative analysis, so chemical initiation was used for the work reported here. The initiator chosen was 2,2′-azobis (2-amidinopropane) dihydrochloride (V50), added to the reactor (1 mL solution in water, purged with N$_2$ for a few minutes) as soon as the reaction temperature has been reached and a monomer emulsion baseline has been acquired.

The emulsions were prepared as follows: Exxsol D80 (30% total mass) was mixed with Span 80 (2.15% total mass), and separately a 50% acrylamide solution was prepared in water then the solutions are combined and homogenized using a high-speed homogenizer at 4000 rpm. The emulsion was sparged with nitrogen for at least one-half hour before the reaction, and continuously during the reaction.

**Results**

**I. Establishing ACOMP Conditions.** ACM Characterization of the Breaker Surfactant. The N-95 surfactant (breaker surfactant) was characterized by ramping its concentration from 0 to $1 \times 10^{-3}$ g/mL in aqueous 0.1 M NaCl. Shown in Figure 1 are Rayleigh scattering ratios at zero scattering angle divided by an optical constant $K$ and polymer concentration $c$. The inset to Figure 1 shows $I(q = 0)/Kc$, weight-average reduced viscosity $\eta_r$, and effective hydrodynamic diameter data versus concentration. The upward trend of $I(q)/Kc$ vs $c$ indicates that N-95 itself presents strongly concentration dependent aggregation, which is reversible.

**ACM Characterization of Polyacrylamide Shear Sensitivity.** Because of the high molecular mass of the PA, non-Newtonian behavior was a concern, as well as possible breakage of the high mass chains when forced through small pores in filters. Hence, both the inline filtration system and the shear rate at which the viscosity of the inverted emulsion is measured were important considerations.

Figure 2 shows $\eta_r$ vs shear rate, for a 0.277 mg/mL polymer emulsion in 0.5% N-95 surfactant solution (a 10 $\mu$m inline filter was used). The shear rate was varied by varying the flow rate from 0 to 3 mL/min. Even lower shear rates were investigated by doubling the internal radius of the capillary in the viscometer (and increasing their length to 100cm, to counteract the drop in pressure). With this, the average shear rate (eq 2) decreases by a factor of 8 for any given flow rate.

To assess the effect of filtration, a 0.55 mg/mL polymer emulsion in 0.5% N-95 surfactant solution was passed through detectors at 0.8 mL/min, through filters of different pore size. The inset to Figure 2 shows $\eta_r$ data computed based on these experiments. The 0.5 $\mu$m filter leads to irreversible breakage of

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the polymer, leading to a much smaller
filtration. In contrast, there is virtually no breakage when a
dry polymer was dissolved in 0.1 M NaCl for ACM experiments.
acetone/2-propanol mixture, and dried in an oven for 24 h. The
ACM characterization was made on dry polyacrylamide, obtained
by precipitation of the reactor contents (B1, Table 1b) in an
emulsion 520 450 220 212 200
emulsion 2.9 \times 10^6 2.0 \times 10^6 6.9 \times 10^5 6.6 \times 10^5 6.2 \times 10^5
dry polymer\textsuperscript{e} 680 1000 1280 950 700
M\textsubscript{w,app}\textsubscript{ACOMP}\textsuperscript{d} (g/mol)
dry polymer\textsuperscript{e} f=0.37 3.53 \times 10^6 6.52 \times 10^6 5.49 \times 10^6 3.57 \times 10^6 4.27 \times 10^6
\textsuperscript{a} In all of the experiments, the monomer concentration was 3.338 M. \textsuperscript{b} M\textsubscript{w} values obtained by viscosity from eq 10.
\textsuperscript{c} Viscosity extrapolated to f = 1. \textsuperscript{d} M\textsubscript{w} values obtained by viscosity (extrapolated to f = 1) from eq 10. \textsuperscript{e} Data are for PA that was precipitated in acetone/2-propanol, dried, and redissolved in NaCl 0.1 M prior to measurements. \textsuperscript{f} M\textsubscript{w} obtained by extrapolation of ACM light scattering data to q = 0 and c = 0 (method of Zimm).

the polymer, leading to a much smaller \eta\textsubscript{i} value than when no filter is used. In contrast, there is virtually no breakage when a 10 \mu m filter was used, and so this size filter was used throughout the work.

**Polyacrylamide Does Not Interact with the N-95 Surfactant.** ACM characterization was made on dry polyacrylamide, obtained by precipitation of the reactor contents (B1, Table 1b) in an acetone/2-propanol mixture, and dried in an oven for 24 h. The dry polymer was dissolved in 0.1 M NaCl for ACM experiments. Figure 3 shows \( KcIq @ q = 0 \) and \( \eta_i \) for the experiment described above. \( KcIq \) and \( \eta_i \) both increase with polymer concentration in the way expected for a random coil polymer with positive excluded volume. These data allowed the effects of \( A_2 \) and hydrodynamic interactions to be assessed, so that proper dilution conditions in the ACOMP detector train could be determined.

It was also important to ascertain whether there was any significant interaction between PA and the N-95. Using ACM, N-95 was added continuously from zero to 3 mg/mL to a polymer solution at fixed concentration (0.25 mg/mL). It was found that the MALs and viscosity signals were simply additive. Hence, it was concluded that PA and N-95 do not interact significantly.

**To Establish Detector Response to Phase Inverted Solutions.** A series of experiments was made to determine how each detector responds to the different components of the diluted, phase inverted emulsion. Thus, two experiments were performed: In the first one, all of the components of emulsion but the polymer were mixed in the same proportions as in the reaction, then phase inverted by mixing discrete amounts of this emulsion into a 0.05% N-95 breaker surfactant solution, producing the series of emulsion concentrations shown on the abscissa of Figure 4. Strikingly, the viscometer is insensitive to the oil droplets and possible other debris produced when the emulsion without polymer is broken. The inset to Figure 4 shows, however, that

![Figure 3. ACM for PA: \( KcIq @ q = 0 \) and reduced viscosity curves versus concentration. The polymer was obtained by precipitation of the reactor contents (B1, Table 1b) in an acetone/2-propanol mixture and dried for 24 h.](image-url)
the light scattering increases significantly. In the second experiment, polymer is included in the emulsion and the same dilution procedure and use of constant 0.05% N-95 surfactant is followed. The most prominent effect is the fact that, while the viscometer is insensitive to the oil droplets produced when the emulsion is broken, it responds linearly to the polymer concentration. As seen in the inset, which shows light scattering response with and without polyacrylamide in the microemulsion, the light scattering is sensitive to the droplets and debris, in addition to the polymer, so that these data are much more complicated to analyze. It was hence decided to rely on the viscometer to provide a measure of polymer mass.

**Determination of the Time to Create Phase Inverted Solutions.**
A major factor in establishing the feasibility of the phase inversion approach to ACOMP is the amount of time it takes to make the phase inversion. In general, there is a “time budget” in ACOMP, that is, an acceptable amount of delay between withdrawal from the reactor and measurement by the detector train.

To measure the inversion time, a few drops of the emulsion sample from one of polymerization reactions performed (A2, Table 1a) were added into 50 mL of an N-95 0.5% solution (0.5 mg/mL polymer) and the dissolving mixture was continuously circulated through the same detectors as used in ACOMP. A second experiment on an emulsion sample supplied by Cytec Industries, is also shown in Figure 5. The figure shows that polymer-containing emulsion inverts in tens of seconds when diluted with the breaker surfactant, the fraction of dissolved polymer was determined from the build-up of the UV and RI signals to yield the polymer concentration, since the total concentration of polymer plus monomer is known. This time is well within a typical ACOMP time budget. By way of contrast, the experiment was repeated with the dry polymer obtained by precipitation from the Cytec sample, and the data show that the dissolution time of pure, dry PA is thousands of seconds. This demonstrates another advantage of ACOMP, in that sample preparation of liquid reactor contents is orders of magnitude faster than post-polymerization analyses of dried polymer. The same trends are seen in the viscosity curves.

**Phase Behavior of PA/N-95 Determined by DLS Experiments.**
DLS experiments were done in order to find the range of ratios of polymer/surfactant yielding stable solutions. A few polymer concentration values were chosen for each N-95 surfactant %, the solutions were prepared 12 h before measurements, without filtration. Readings were then made at various time intervals over several days to check the stability of the solutions. Figure 6 is the stability or phase diagram based on these experiments. If no change in $D_z$ occurred over several days the solution was termed “stable” (filled circles in the figure). If $D_z$ changed in time, i.e., decreased due to particles becoming larger, but did not become visually cloudy over several days the solution was termed “metastable” (diamond symbols). Solutions which became visually cloudy and/or precipitated within a day were termed “unstable” (triangle symbols). The stable regions of the diagram were used to determine the polymer/N-95 composition ranges into which the reactor contents could be diluted for ACOMP measurements.

**ACOMP Conditions Defined.** In light of the foregoing experiments, it was possible to establish an extraction/dilution/conditioning sequence for ACOMP. As described above, the reaction takes place in heterogeneous phase: water (acylamide)/oil (Exxsol D80). Since the monomer concentration in the reactor is very high (~25 wt %), a two-step dilution procedure is needed.
in order to produce the 500-fold dilution needed to be both in the desired part of the phase diagram and at a sufficient level of dilution that interpolymer effects are small. The reaction mixture was first diluted and inverted by the 2% N-95 breaker surfactant solution in the LPMC by a factor of 125. The second dilution stage (1:4) took place in a high pressure mixing chamber (HPMC), after which the diluted solution, at 0.47 mg/mL total monomer plus polymer, in 0.5% N-95 is passed through the detector train. All the experiments done with SMO A and SMO B, respectively, are listed in Table 1, parts a and b.

II. ACOMP Results. Features of the ACOMP Raw Data. Shown in Figure 7 is an example of raw ACOMP data for a typical inverse emulsion polymerization reaction (A2, Table 1a), using the conditions established above. Shown are the raw UV, LS (θ = 90°), viscometer, and RI signals. The overall behavior in the different portions of the experiment is more complex than raw ACOMP data from corresponding homogeneous phase polymerization reactions. The second dilution stage (1:4) took place in a high pressure mixing chamber (HPMC), after which the diluted solution, at 0.47 mg/mL total monomer plus polymer, in 0.5% N-95 is passed through the detector train. All the experiments done with SMO A and SMO B, respectively, are listed in Table 1, parts a and b.

At 3500 s extraction of the unreacted contents from the reactor started, and the interval from 3500 to 9000 s was the monomer baseline and temperature stabilization period. This is where the diluted, phase inverted, unreacted emulsion from the reactor begins to flow through the detector train. The excess UV signal in this period is due to double bond adsorption in the acrylamide monomer. The approach of the UV signal to its plateau is perfectly first order (fit not shown), with an exponential time constant of 320 s, reflecting the mixing response time of the LPMC, which contains approximately 30 mL. The delay time between the reactor and the detector train was about 13 min. The viscometer signal decreases very slightly, perhaps due to the removal of N-95 surfactant from micellar phase into the solubilization of oil droplets, where these large entities have negligible intrinsic viscosity. The viscosity signal then quickly stabilizes

Figure 7. Raw ACOMP data for reaction A2, Table 1a, showing LS, RI, viscosity, and UV (215 nm) signals.

The behavior of the RI and LS data is unusual and complex, and is shown only for illustration, and not used in the analysis. As demonstrated earlier (Figure 4), the viscometer is primarily sensitive to just the polymer in the solution. The continued, slow evolution of both RI and LS, however, is surmised to indicate the slow evolution of the emulsion itself in the reactor. At about 8000 s, when the temperature was stabilized, the initiator was added and the effects appear at 9000 s. The decrease in the UV is a direct measure of the monomer conversion, whereas the increase in viscosity measures the production of massive polymers. The increase in RI, which occurs much more quickly than the slow upward evolution of the preceding period, reflects the fact that refractive index increment ddn/dc of polyacrylamide is 0.1939, whereas that of acrylamide is 0.156.30

Kinematic viscosity of the emulsion left in reactor at the end of the reaction was measured with a Cannon viscometer and it was found to be 66.7 centistokes, similar to the viscosity of the emulsion before being polymerized.

Conversion Data and Kinetic Modeling: Surfactant Based Initiators and Radical Scavengers. The ACOMP data were used here to demonstrate the determination of monomer conversion kinetics, and the detection and quantification of both surfactant based initiators and radical scavengers. To this end, the two separate lots of stabilizer surfactant were used, lots SMO A and SMO B described above. For each case as series of reactions was carried out for varying [I] at 53°C. Additionally, for SMO A temperature was varied; see Table 1a,b.

Based on raw UV data and conservation of mass, both monomer and polymer concentrations are simultaneously determined and, hence, the monomer conversion can be computed. Shown in Figure 8 are conversion curves vs time for two reactions with and without initiator added, for SMO A, at 53 °C (A2 and C2, respectively, in Table 1a). First-order fits describe each reaction well. SEC measurements were made on aliquots withdrawn from the ACOMP waste line during the reaction, and the conversion results agree with the data obtained by ACOMP. The discrete SEC data points for conversion are shown, and were determined by integrating the monomer peaks in the SEC data.

Figure 9 shows raw RI and UV chromatograms from SEC for aliquots taken directly from the ACOMP waste stream during

a typical reaction (A2b, Table 1a). As in ACOMP, the RI signal is affected by the other components of the emulsion, shown by the presence of a second peak in the figure at 11 mL. The last peak at 14 mL corresponds to the monomer, whereas the first peak indicates the polymer build up with conversion. In the inset, UV peak corresponding to monomer is shown. As expected, it decreases as conversion proceeds. As noted, the polymers are too large for efficient separation on the column, so that there is no shift in the RI elution volume, even though ACOMP data below show that polymer molecular mass increases during the reaction.

The fact that the polymerization occurred without the added initiator for SMO A meant that either there was an “intrinsic” initiator among the reagents used in the inverse emulsion formulation, or that the acrylamide was undergoing thermal auto-initiation. This latter possibility was excluded however, when it was observed that no thermal polymerization took place at 53 °C, when a homogeneous reaction was set up with acrylamide/water in the same 1/2 proportion as in the emulsions.

Further evidence against thermal auto-initiation comes from the fact that the monomer conversion displays first-order kinetics, to a good approximation, both with and without added initiator. This holds true in the quasi-steady-state approximation when the thermal decomposition of the initiator(s) is slow compared to the rate of polymerization.

Within the quasi-steady-state approximation (QSSA), the concentration of radicals \([R^*]\) is assumed to vary slowly in time. If multiple initiators and radical scavenging impurities are present, the QSSA can be expressed as

\[
\frac{d[R^*]}{dt} = 2\sum_j F_{jk} [I]_j - k_i [HC]_{imp} [R^*] \approx 0 \tag{4}
\]

where the sum is over all initiator species present, \(k_{ij}\) is the first order thermal decay constant of initiator \(j\), and \(F_j\) is the initiator efficiency that describes what fraction of radicals produced by decomposition of initiator \(j\) go on to initiate propagating radicals. A factor of 2 is included to indicate that two radicals are produced per molecule. \([M]\), \([I]\), and \([HC]_{imp}\) are the monomer, initiator, and hydrocarbon phase impurities concentrations, and \(k_i\) and \(k_i'\) are the radical termination rate constants for radical—radical and radical—impurity mechanisms, respectively. It is frequently reported that SMO acts as a transfer agent, and may hence constitute all or part of \([HC]_{imp}\), if transferred radicals are then terminated. It is also remembered that if the transfer agent goes on to initiate new chains this does not lead to radical termination, and hence does not appear in eq 4.

The termination step is due to both radical/radical and radical/impurity termination. Two limiting cases can be distinguished. The first is where the radical/radical termination predominates

\[
k_i [R^*]^2 \gg k_i' [HC]_{imp} [R^*] \Rightarrow [R^*] = \sqrt{\frac{2\sum F_{jk}[I]_j}{k_i}} \tag{5a}
\]

\[
R_p = -\frac{d[M]}{dt} = k_p [R^*][M] = k_p' [M] \sqrt{\frac{2\sum F_{jk}[I]_j}{k_i}} \tag{5b}
\]

which is the classical free radical polymerization case where the rate of polymerization \(R_p\) is proportional to the square root of the initiator concentration and monomer concentration to the
first order. This behavior has indeed been found for inverse emulsion polymerization of acrylicamide and in general for reactions where water soluble initiators were used. It is routinely found in bulk and solvent-based polymerizations.

The second limiting case is where radical/impurity termination dominates

\[ k_{r}[R^*]^2 \ll k_{r}^i[HC]_{imp}[R^*] \rightarrow [R^*] = \frac{2\sum_j F_j k_{dj}[I]}{k_{r}^i[HC]_{imp}} \]  

(6a)

\[ R_i = -\frac{d[M]}{dr} = k_p[R^*][M] = k_p \frac{2\sum_j F_j k_{dj}[I]}{k_{r}^i[HC]_{imp}}[M] \]  

(6b)

In this case, \( R_i \) is proportional to the initiator and monomer concentration to the first order. The first order dependence of \( R_i \) on \([I]\) is much less frequently found in bulk and solvent-based cases, but is frequently found for inverse emulsion polymerization.10–13,15,33

Most of the authors have attributed this behavior to the existence of a radical/impurity (emulsifier, solvent phase) termination step. However, it has been reported that a transition from case i to case ii occurs at high conversion, where termination will be diffusion controlled, which can also lead to an increase in polymer molecular mass.12

The general solution to eq 4 is of the form

\[ [R^*] = \frac{k_{r}^i[HC]_{imp}}{2k_{r}} \left( -1 + \sqrt{1 + 4\frac{2k_{j}\sum_j F_j k_{dj}[I]}{(k_{r}^i[HC]_{imp})^2}} \right) \]  

(7)

Thus, the rate constant is

\[ \kappa = \frac{k_p k_{r}^i[HC]_{imp}}{2k_{r}} \left( -1 + \sqrt{1 + 4\frac{2k_{j}\sum_j F_j k_{dj}[I]}{(k_{r}^i[HC]_{imp})^2}} \right) = a(-1 + \sqrt{1 + 4k_{j}\sum_j b_j[I]}) \]  

(8)

where

\[ a = \frac{k_p k_{r}^i[HC]_{imp}}{2k_{r}} \]  

and \( b_j = \frac{2F_j k_{dj}}{(k_{r}^i[HC]_{imp})^2} \)

Figure 10 shows that this behavior is found for both SMO A and SMO B, as seen by the concave downward curvature and the fits to eq 8; that is, both radical/radical and radical/impurity termination mechanisms are important, and one does not predominate.

The monomer conversion data for all the experiments can be fitted with first-order functions. This implies, according to eqs 3 and 8, that both \([I]\) and \([HC]_{imp}\) are approximately constant during the reaction; that is, the initiator decomposes slowly and there is a significant amount of impurity. For SMO B there is only one initiator, the added one, whereas for SMO A there are two initiators in the sum, the added one, and the constant amount of “intrinsic” initiator in SMO A, whose presence is seen in the nonzero intercept in Figure 10.

One can notice the difference between the two cases. In the first case, the positive intercept indicates that the polymerization occurs due to the radicals created by the emulsifier, whereas a zero intercept for the latest set of data proves the absence of adventitious radicals to initiate the polymerization. It is surmised that in SMO A, which had a lighter color, there may have been radical producing impurities that were residuals from the bleaching process used to produce the lighter color.

The fitting parameters together with literature values of \( k_p \) (10^4 L/mol s), \( k_{r}^i \) (10^8 L/mol s) for acrylamide and \( k_{r}^d \) for the V50 initiator (10^-6 L/mol s) allow estimates of the impurity concentration to be made (1.2 \times 10^{-5} M for SMO B and 4 \times 10^{-6} M for SMO A). Although these concentrations appear small, they are significant compared to the typical radical concentration at any point, which is on the order of 10^{-8} M (computed by dividing a typical rate constant, 10^{-4} s^{-1} by \( k_p \approx 10^4 \) L/mol s).

The activation energy for thermal decomposition of the intrinsic initiator is shown in the Arrhenius plot, inset to Figure 10. The activation energy was determined to be 160 kJ/mol. In this determination the values for \( k_p^2/k_{r} \) were computed based on the data listed in Table 1a (experiments C0–C4), and according to the method described in ref 11.

**Figure 11. ACOMP \( \eta_s \) vs conversion for reactions listed in Table 1a. In the inset the average particle diameter is plotted versus conversion for aliquots withdrawn from the reactor during a polymerization reaction (B4, Table 1b) and subsequently diluted in Exxsol oil.**

**Figure 10.** ACOMP \( \eta_s \) vs conversion for reactions listed in Table 1a. In the inset the average particle diameter is plotted versus conversion for aliquots withdrawn from the reactor during a polymerization reaction (B4, Table 1b) and subsequently diluted in Exxsol oil.

Evolution of Reduced Viscosity and Observations on \( M_w \). Using the ACM data on PA, and the \( k_{r} \) factor, it is possible to directly extract the weight averaged intrinsic viscosity \( [\eta]_w \) from \( \eta_r \) via

\[ \eta_r = [\eta]_w + k_1 [\eta]_w^2 c \]  

(9)

where \( k_1 \) is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers.

These calculations show that \( [\eta]_w \) is virtually identical to \( \eta_r \). Figure 11 shows the evolution of \( [\eta]_w \) during polymerization for several reactions. Remarkably, \( [\eta]_w \) (and \( M_w \)) increases during these reactions, in contrast to most free radical polymerizations where \( [\eta]_w \) either decreases in time (the usual QSSA result when the initiator lifetime is longer than the period of total monomer conversion), remains constant (e.g., when there is significant transfer to monomer), or increases, as is commonly found when termination rates decreases. A further case is in a so-called “dead-end” reaction, where the initiator is exhausted before full monomer
conversion occurs, leading to an increase in \([\eta]_w\) and \(M_w\).

In the case of a dead-end polymerization, however, the monomer conversion is not a first-order process, but rather an exponential one.

Since the light scattering signal cannot be used to calculate \(M_w\) in the following experimental relationship, obtained from SEC data, was used to obtain a rough estimate of the apparent weight-average molecular mass of the polymer:

\[
M_w,\text{app} = \left( \frac{[\eta]_w}{0.0041} \right)^{1.235}
\]

(10)

It is pointed out that this is only an empirical correlation between weight averaged quantities of broad distribution samples and not the usual Mark–Houwink relationship between narrow distribution samples.

A similar trend in the reduced viscosity behavior and hence in \(M_w\) is found for all of the experiments, a slight increase with conversion. This feature was found by other studies, and it was believed to be caused either by the influence of the gel effect and/or by the transfer to monomer. For example, if transfer leads to SMO or other agents leads to termination rather than propagation, the number of radicals can diminish in time (not part of the QSSA), leading to increasing chain lengths. The fact that acrylamide resides with the amide group in the aqueous phase and the vinyl group oriented toward or into the emulsifier layer would make the labile hydrogens more accessible than the double bond and increases the probability of transfer relative to propagation. In addition, since SMO has an unsaturated carbon in the middle of its hydrophobic tail and five labile hydroxy groups on its surfactant head, these radical active groups could react with primary radicals in the continuous phase and increase the molecular weight.

DLS measurements of emulsion polymerization reactions have been frequently made, but, in fact, they furnish data on the emulsions themselves and not on the polymeric contents. The ACOMP approach focuses on the polymer properties rather than the emulsion properties, and should hence prove more useful in the long run as an online characterization tool. The inset to Figure 11 shows the average particle diameter versus conversion for aliquots withdrawn during a polymerization reaction (B4, Table 1b), and subsequently diluted in Exxsol oil in order to keep the emulsions intact. Not surprisingly, there is very little change in the droplet diameter, in contrast to the monomeric and polymeric contents measured by ACOMP.

The molar mass of the final polymer can presumably be controlled by the amount of initiator. The ACOMP data show that \([\eta]_w \) decreases as the initiator concentration increases. The value of \([\eta]_w @ 40\%\) conversion vs \(1/[I]^{1/2}\) is shown in Figure 12, which follows the expected trend. Also shown is \(M_w,\text{app}\) computed via eq 10, which likewise increases with decreasing \([I]\), and is fairly linear vs \(1/[I]^{1/2}\). The effective diameters from DLS were measured for endproduct emulsions that were diluted with Exxsol D80 (the same way as for the data in the inset in Figure 11). Because the DLS data measure the effective droplet diameters, they are insensitive to small differences in initiator concentration. Figure 12 show no trend as a function of \([I]\).

Table 1b, for SMO B, shows there is a trend for \([\eta]_w\) obtained for PA measured directly in the inverted emulsion (whether measured by ACOMP or ACM) to be less than \([\eta]_w\) for PA


Figure 12. Polyacrylamide \(\eta_0\) (from ACOMP) vs \(1/[I]^{1/2}\), and the corresponding effective hydrodynamic diameters from DLS. Whereas ACOMP measures the properties of the polymers produced, DLS reports data on the inverse emulsions and is not sensitive to the large changes in the polymer properties. Shown are also \(M_w,\text{app}\) values based on eq 10.

Figure 13. HTDSLS spike spectrum for the diluted, phase inverted, polymer containing emulsion flowing through the ACOMP detector train. Sampling frequency was increased from 0.5 to 4 Hz to capture the spikes. Spikes are due to oil droplets in the inverted phase. The baseline scattering due to the polymer is clearly recoverable from this spectrum which has been precipitated in acetone/2-propanol, dried, and redissolved. Although it was shown that N-95 does not interact with PA and that the viscometer signal is sensitive only to polymer in the inverted solution, the data in Tables 1b show an interaction between PA and the “debris” in the inverted emulsion may occur for the case of SMO B. A possible interpretation for this is that the association between the emulsion debris and PA lowers the hydrodynamic volume without significantly changing the mass. The exact origins of the effect, however, require an independent study beyond the scope of the current work.

\(M_w\) obtained by ACM for PA which has been precipitated, dried and redissolved were measurably larger than the values obtained by SEC (data not shown) on the same samples. Furthermore, it was found that if the same PA samples were filtered through 0.45 micron membranes prior to SEC roughly 50% less material eluted from the column than when a 10 micron membrane is used. It seems that, since the SEC column does not provide any useful separation of the large molar mass PA and...
that it may degrade and/or further reduce the amount eluted, it is again concluded that ACM is a preferable technique for characterizing \(M_w\).

Possible Future Use of Heterogeneous Time Dependent Static Light Scattering (HTDSLS). It was recently demonstrated that HTDSLS could be used to usefully measure properties of coexisting colloidal and polymer populations.\(^{37}\) This was accomplished by separating out the spectrum of spikes produced each time a massive colloid particle passed through the tiny scattering volume in the LS detector and recovering the baseline scattering from the polymer population. Figure 13 shows an initial attempt at using HTDSLS for the current ACOMP application to inverse emulsion polymerization. The sampling rate was increased from 0.5 to 4 Hz in order to capture the spikes, which are presumed to be due to the colloids of micro-droplets of oil in the inverted emulsion. The baseline between spikes corresponds to the PA. Because of the many issues that needed to be resolved in this work, development of HTDSLS was not pursued here, but is left for possible future research.

Conclusions

It has been demonstrated that monomer conversion and polymer intrinsic viscosity can be monitored continuously using ACOMP during inverse emulsion polymerization of acrylamide. A series of fundamental and technical challenges were met in order to produce and usefully measure a continuously monitorable stream of dilute, phase inverted emulsion containing monomer, polymer, oil droplets, and other debris.

As a preliminary application of the method, some of the kinetic features of inverse emulsion reactions have been investigated. It was found that monomer conversion closely resembles a first order process, but that there was strong evidence that there was a radical scavenging impurity in the complex emulsion solution. It was also shown that in nominally identical lots of stabilizer surfactant (SMO A and SMO B) there was an “intrinsic” initiator in one of the lots but not the other. The temperature dependence and activation energy of the intrinsic initiator was determined.

It was also verified that \([\eta]_w\) and \(M_{w,app}\) increase monotonically during conversion, which may be related to chain transfer to the stabilizer surfactant or other emulsion component and/or the radical scavenger which appeared to be present in both SMO A and SMO B. In both cases, \([\eta]_w\) of PA was often significantly less when measured together with the inversion “debris” than when measured from precipitated, dried, and redissolved PA. This suggests a possible interaction between inversion debris and PA that can lower \([\eta]_w\), and may have consequences in how the PA is prepared and used in practice.

It is believed that the type of methodology established here will be applicable to other emulsion polymerization reactions, and, more broadly, to other types of heterogeneous reactions.\(^{37}\)