Fundamental Measurements in Online Polymerization Reaction Monitoring and Control with a Focus on ACOMP

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Fundamental measurements in online polymerization reaction monitoring and control seek to avoid empirical and inferential models in data interpretation. One such approach making use of multiple detectors is automatic continuous online monitoring of polymerization reactions (ACOMP), wherein a continuous reactor stream is automatically, continuously diluted and conditioned to where measurements reflect intrinsic particle properties and not the interactions that can dominate measurements in concentrated media. Examples where dilute regime measurements are needed include static and dynamic light scattering, and reduced viscosity. This review focuses on ACOMP to illustrate a number of reaction contexts where fundamental measurements are used to gain a comprehensive picture of reaction characteristics.

Review

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Introduction

The ability to monitor polymerization reactions as they occur has a number of advantages: it allows quantitative determination of reaction kinetics and the evolution of polymer molar mass, intrinsic viscosity, and other characteristics such as copolymeric composition drift and distribution. This allows for critical assessment of physico-chemical theories and hypotheses that drive advances in polymer science and engineering. The monitoring approach also allows for optimization of reaction conditions that can be useful for scale-up from the bench to industrial levels.

As an important long-term goal, online polymerization reaction monitoring is expected to lead to significant savings of energy, petroleum and other non-renewable resources, and plant and labor time, and lead to more sophisticated and higher quality polymeric materials, while reducing the amount of environmental impact per kilo of product.

Most methods for realtime or near realtime monitoring of polymerization reactions use in situ sensors, of which a wide variety are now available: Raman scattering, near- and mid-infrared, ultrasound, turbidity, rheological probes, dielectric sensors, density, temperature, pressure, etc. Each of these has its own virtues and drawbacks. Advantages of in situ probes can include zero or near zero delay time between sensing and measurement output, and simplicity in the sense of inserting a single device into a single access point in a reactor. Drawbacks include exposure to concentrated reactor contents that can lead to fouling of optical sensors and plugging of mechanical...
ones, the need for empirically established calibration and interpretation models, and the fact that such probes typically provide only one type of signal, yielding a limited number of characteristics of the reaction, such as conversion and co-conversion, bulk viscosity, etc. For some of the spectroscopic methods it is possible to avoid in situ contamination of the probe by providing a window in the reactor that is transparent to the probe radiation, provided the inside of the window itself does not foul.[1–3]

The focus of this review is to outline several of the fundamental types of characterizing measurements that can be made on polymers, and how they are used in the polymerization reaction monitoring context. The main feature of these approaches is that they connect the raw data from their detection means with basic physical properties without the use of fitting procedures or empirical or inferential models.

Automatic continuous online monitoring of polymerization reactions (ACOMP) uses a variety of detection methods on an automatically withdrawn, diluted, and conditioned sample stream, and likewise has advantages and disadvantages. Advantages include its versatility as a generalized approach, its ability to make fundamental measurements without recourse to empirical models and calibration, its capacity for providing a data-rich stream of complementary information from multiple independent detectors, yielding multi-faceted characteristics of polymerization reactions, and its use of a “front-end” to extract, dilute, and condition a sample stream that allows sensitive detectors to provide reliable data without exposing them to harsh reactor or sample conditions. Disadvantages include the mechanical complexity of the “front-end,” the delay time between a continuous fluid element’s extraction from the reactor and downstream measurement by the detector train, and a small but continuous waste stream, that typically extracts a few tenths of a milliliter to several milliliters per hour from the reactor. Delay times are typically tens to hundreds of seconds. ACOMP is more “invasive” than probes that can be placed at an outside reactor window, but are no more invasive than in situ probes, in that in either case access to the reactor contents is required.

It is also important to note that in situ reactor probes, such as conductivity, near IR, pH, and stirring reactor torque have frequently been used in a very complementary fashion with ACOMP to provide extra detail and multifaceted analyses of polymerization reactions. Entirely omitted from this review is the vast literature involving very simple but effective sensors, such as temperature, pressure, stirring torque, etc. Calorimetric and other models associated with these methods can themselves range from fundamental to purely inferential.

**Measurement of Monomer and Polymer Characteristics During Polymerization Reactions**

**Light Scattering**

Most, but not all of light scattering theory used in polymer analysis is based on the assumption of single scattering; i.e., each photon received at the detector has undergone only one scattering event. This places limitations on the concentration of any solution that is to be analyzed by typical theories, such as those for static light scattering by Rayleigh, Debye, Zimm, and Mie.

There is, nonetheless a growing literature on light scattering used directly for concentrated solutions in which multiple scattering occurs. Turbidity measurements are probably the simplest example of the latter. For both...
forward and backscattered light more sophisticated approaches to analyzing multiply scattered light exist.\(^\text{[6-7]}\) For example, in diffusing wave spectroscopy (DWS), light scatters so many times that photons essentially undergo a random walk (diffusion) in the sample medium before reaching the detector, in which case DWS measurements can yield the mean free photon path length as well as self-diffusion coefficients, and hence average particulate concentration and estimates of particle sizes.\(^\text{[8,9]}\) in addition to micro rheological characteristics.\(^\text{[10-12]}\)

The simplest analysis of single event scattering in dilute media is due to Lord Rayleigh\(^\text{[13]}\) and deals with scatterers, e.g., atmospheric molecules, whose characteristic linear dimension, \(a\), is much smaller than the incident wavelength of light \(\lambda\). When scatterers begin to interact, e.g., through excluded volume mechanisms, and when their size grows to the order of magnitude of \(\lambda\), what is sometimes termed Rayleigh-Debye theory is used, with its very useful extensions due to Zimm. The underlying assumption for this theory to be applicable is that the optical path length of light

\[
\text{when } n_{\text{poly}} - n_{\text{sol}} (n_{\text{poly}}, n_{\text{sol}} \text{ are the real part of the indices of refraction of the particle and supporting medium, respectively}) \text{ and } \lambda \text{ is the vacuum wavelength of the incident light. When this condition is met one of Zimm’s most useful expressions is:}\]

\[
Kc = \frac{1}{MP(p)} + 2A_2c + [3A_3Q(p) - 4A_3^2MP(p)(1 - P(q))]c^2 + O(c^3)
\]

where \(R(c, q)\) is the excess Rayleigh scattering ratio, that is, the scattering from the polymer solution at concentration \(c\) (g cm\(^{-3}\)) measured at \(q\), minus the scattering from the pure solvent \(R_s\). \(R(c, q)\) is obtained by dividing the scattered intensity per unit volume occupied by scatterers by the incident intensity, and multiplying by \(r^2\) (\(r\) = distance from scatterer to detector) to eliminate the dependence on the detector’s distance from the scattering volume. \(R(c, q)\), which has units of cm\(^{-1}\), can be interpreted as the fraction of the incident intensity scattered per steradian of solid angle per centimeter of scattering media traversed. The Rayleigh scattering ratio \(R\), for several pure liquids at a variety of wavelengths and temperature is known to high precision; i.e., \(R\) and hence calibration of light scattering detectors with such liquids is “absolute,” not empirical. For example, \(R = 1.069 \times 10^{-8} \text{ cm}^{-1}\) for toluene at \(T = 25^\circ \text{C}\) when light of \(\lambda = 677 \text{ nm}\) is incident. This means, in practical terms, that \(R\) for any polymer solution can be determined simply by comparing the ratio of the scattering detector voltage from the polymer solution to the voltage found by scattering from pure toluene, and making any geometrical optical corrections that might be required due to cell geometry and refractive effects. Hence, a solvent such as toluene firmly anchors light scattering measurements to absolute values of \(R\). In turn \(R\) is related to fundamental polymer properties.

In Equation (2), \(M\) is the scatterer’s molar mass, \(P(q)\) is the particle form factor, which sums the phase differences over all scattering centers of the particle, \(A_2\) and \(A_3\) are the second and third virial coefficients, respectively, which measure two and three body excluded volume effects, respectively, and the magnitude of the scattering vector, \(q\), is given by

\[
q = \frac{4\pi n_s}{\lambda} \sin(\theta/2)
\]

where \(\theta\) is the detection angle. \(K\) is an optical constant, given for vertically polarized incident light by

\[
K = \frac{4\pi^2 n_s^2 (\partial n / \partial c)^2}{N\lambda^4}
\]

\(\lambda\) is the vacuum wavelength of the incident light, \(N\) is Avogadro’s number, and \(Q(q)\) involves a sum of Fourier transforms of the segment interactions that define \(A_2\).\(^\text{[16]}\) \(\partial n / \partial c\) is the differential refractive index for the polymer in the solvent and embodies the Clausius-Mossotti equation for a dilute solution of particle density \(N\), which relates \(\alpha\), the molecular polarizability, to the index of refraction \(n\) of the polymer solution,

\[
n^2 - n_s^2 = 4\pi N\alpha
\]

Most water soluble polymers have a positive value of \(\partial n / \partial c\), chiefly because \(n_s = 1.33\) for water is low compared to most organic substances, whereas organosoluble polymers in organic solvents frequently have negative values of
\(\frac{\partial n}{\partial c}\). When \(\frac{\partial n}{\partial c} = 0\) the polymer/solvent pair is termed “iso-refractive,” and there is no excess scattering due to the polymer. \(\frac{\partial n}{\partial c}\) also allows computation of the polymer concentration, \(c\), in Equation (2) using a differential refractometer (RI).

Equilibrium characterization of polymers usually takes place in dilute solution where \(1 \gg 2A_2 c \bar{M}_w \gg 3A_2 c^2 \bar{M}_w\) and over an angular range such that \(q^2 (S^2) \ll 1\). In this case, the Zimm Equation reduces to one of its most frequently used forms:

\[
\frac{Kc}{R(c, q)} = \frac{1}{\bar{M}_w} \left( 1 + \frac{q^2 (S^2)}{3} \right) + 2A_2 c
\]  

(6)

A typical batch experiment involves measuring \(R(c, q)\) over a series of angles for several polymer solutions at different concentration. If for each concentration the angular data is extrapolated to \(q = 0\), and these points are then fit, the slope will yield \(2A_2\), and the \(y\)-intercept will be \(1/\bar{M}_w\). Similarly, if the concentration points at each angle are extrapolated to \(c = 0\) and these are then fit, the slope will be \((S^2)/3\bar{M}_w\) and the intercept again \(1/\bar{M}_w\). Hence, the ‘Zimm technique’ allows determination of \(\bar{M}_w\), \(A_2\), and \(\langle S^2 \rangle\). The root mean square radius of gyration is often simply called the “radius of gyration” and abbreviated as \(R_g = \langle S^2 \rangle^{1/2}\). Nothing impedes the use of the Zimm approach in time-dependent situations, as long as one is still operating within the range of validity of the approximations.

When Equation (1) no longer applies, as is often the case for many emulsions, latex particles, and other colloids (e.g., a typical latex particle in water 100 nm or larger), the difference in index of refraction of a particle and the surrounding medium can contribute significantly to optical path lengths of scattered light. In this case exact solutions of the scattered waves are found using Maxwell’s Equations and associated boundary conditions for specified particle morphologies. Such solutions were first obtained for dielectric spheres by Mie,[15,16] and other solutions by Lord Rayleigh,[17] and this approach to scattering analysis is complementary to Mie scattering which usually has poor resolution below 100 nm, but is robust up to hundreds of \(\mu\)m. The autocorrelation function is fundamentally very sensitive to flow and attempts to adapt DLS to flow cells have had mixed results. A recent innovation by Brookhaven Instruments Corporation, the Nano-DLS uses an automatic stop-flow device with a bypass valve to ensure that the DLS measurements are made periodically on non-flowing solutions, thus avoiding the serious effects of flow on the results.

Whether DLS, DWS, Mie scattering, or other applications in which unfractonated samples are analyzed, the resulting “distributions” produced by modern instruments, while frequently facile to obtain and neat in appearance, must be treated with caution, as there is usually a large amount of data smoothing, fitting, and assumptions applied in using inverse Laplace transform and several other commonly employed methods. The best means of finding distributions of size and mass continue to be fractionation methods, such as size exclusion chromatography (SEC),[20–22] field flow fractionation (FFF),[23–25] capillary electrophoresis,[26] capillary hydrodynamic fractionation,[27] etc.

**Viscosity Measurements**

A fluid is said to be viscous when there is spatial inhomogeneity in the fluid’s velocity field. Such inhomogeneity can arise both from differential momentum transport of fluid, and the presence of particles within the fluid that alter the velocity field, which contribute additional dissipative internal friction to the fluid. The amount of viscosity that a macromolecule contributes to a fluid is easy to measure, and can be related to conformational and other properties of the macromolecule, making viscosity measurements a valuable characterization tool.

Spatial variations in the velocity field are specified locally by the tensorial gradient terms \(\partial \psi / \partial x_j\), where \(\psi\) is the velocity component in the \(i\)-direction of a three component space and \(x_j\) is the \(j\)th directional component of the space. The gradient terms have dimensions of \(s^{-1}\), and are referred to as shear rates \(\dot{\gamma}\).

Stokes and Einstein[28] made the initial, arduous computations of the frictional factors of spherical particles in a fluid, and found the additional viscosity they contribute to be proportional to the fluid’s own viscosity and a factor which is characteristic of the particle’s own geometry and mass distribution, the intrinsic viscosity \([\eta]\). The total viscosity of a fluid, whose pure viscosity is \(\eta_s\), and which

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\[^{18,19}\] The so-called overlap concentration \(c^*\), which marks the passage from dilute to semi-dilute solution is often approximated by \(v I_0\), where \(v\) is the intrinsic polymer viscosity.
contains particles of concentration \( c \) and having an intrinsic viscosity \([\eta]\) is given by
\[
\eta = \eta_r \left\{ 1 + [c + k_p [\eta]^2 c^2 + O(c^3)] \right\}
\]
(7)

where \( k_p \) is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers, and \( O(c^2) \) represents terms of order \( c^3 \) and higher. It is customary to define the reduced viscosity \( \eta_r \) as
\[
\eta_r \equiv \frac{\eta - \eta_s}{\eta_s c} = \eta + k_p [\eta]^2 c + O(c^2)
\]
(8)

\([\eta]\) is the extrapolation to zero concentration and zero shear rate of the reduced viscosity \( \eta_r \). Determination of \([\eta]\) hence requires that \( \eta_s \) of the sample solvent and the total viscosity of the fluid containing the macromolecules \( \eta \) be measured. In both SEC and ACOMP the concentration is usually low enough that to a good approximation \([\eta] \approx \eta_r \), where \( \eta_r \) is measured by combining viscometer and concentration detector data. Importantly, \([\eta]\) is a direct measure of the ratio of a polymer's hydrodynamic volume \( V_H \) to its molar mass \( M \). For example, \([\eta]\) for an ideal random coil in \( \Theta \)-solvent conditions is \([30]\)
\[
[\eta] = \frac{\Phi_v}{M} \left( \sqrt{6} \langle S^2 \rangle_0^{1/2} \right)^3
\]
(9)

where \( \Phi_v = 2.56 \times 10^{23} \) and \( \langle S^2 \rangle_0 \) is the unperturbed (\( \Theta \)-condition) mean square radius of gyration. The value of \( \Phi_v \) changes with chain architecture and the perturbing effects of hydrodynamic interactions \([26,31]\).

As for \( \langle S^2 \rangle \), in general, there is often a scaling law between \([\eta]\) and \( M \), of the form
\[
[\eta] = GM^\gamma
\]
(10)

where \( \gamma \) is sometimes termed the Mark-Houwink exponent and \( G \) is a scaling constant. \( \langle S^2 \rangle \) often also has a relationship to \( M \) of the form
\[
\langle S^2 \rangle^{1/2} = AM^\beta
\]
(11)

and viscosity exponents are expected to bear a relationship close to
\[
\gamma = 3\beta - 1
\]
(12)

For example, a random coil in \( \Theta \) conditions has \( \beta = \gamma = 0.5 \), whereas a random coil with excluded volume has \( \beta = 0.6 \) and \( \gamma = 0.8 \). Knowledge of \( G \) and \( \gamma \) also allows computation of the viscosity-averaged mass \( \overline{M}_n \), which lies between \( \overline{M}_r \) and \( \overline{M}_w \) for \( \gamma < 1 \). Viscosity measurements can also be useful for assessing branching, since branched polymers will have smaller values of \([\eta]\) than their unbranched analogs of the same molar mass.

Several geometries can be used to create velocity gradients in fluids for the computation of \( \eta \). The Navier-Stokes Equation provides the basis for finding the relationship between \( \eta \), the geometry, and applied forces. One of the most common arrangements is the capillary viscometer, for which the Poiseuille solution to the Navier-Stokes equation, which has a parabolic flow profile, is used:
\[
\eta = \frac{\pi R^4 \Delta P}{8 L Q}
\]
(13)

where \( Q \) is the flow rate of solution through the capillary (in \( \text{cm}^3 \cdot \text{s}^{-1} \)) of radius \( R \), across whose length \( L \) there is a pressure drop \( \Delta P \). If \( z \) is taken as the direction of fluid flow in the capillary and \( r \) is the distance from the center of the capillary then the shear rate is
\[
\dot{\gamma}(r) = \frac{d \nu_z}{dr} = -\frac{4 Q r}{\pi R^2}
\]
(14)

The average shear rate in the capillary is found by integration over the capillary cross-section to be
\[
|\dot{\gamma}_{ave}| = \frac{8 Q}{3\pi R^3}
\]
(15)

for which a typical value is 860 s\(^{-1}\), given \( Q = 1 \text{ mL} \cdot \text{min}^{-1} \), and \( R = 0.0254 \text{ cm} \).

Single capillary viscometers are remarkably easy and inexpensive to construct using a modern differential pressure transducer with a double T-network and capillary of desired \( L \) and \( R \). Capillary bridge viscometers, based on the Wheatstone bridge principle of null measurement are inherently more sensitive than single capillary viscometers, and can largely eliminate temperature and pump pressure fluctuations. The latter are most useful for SEC but are normally not suitable for long-term flow measurements, however, since a hold-up volume is used in one or more bridge arms, which leads to zeroing out of the differential signal with time. Single and bridge capillary viscometer results have been exhaustively compared \([32]\).

Refractometry

In traditional SEC applications, the difference in the index of refraction between a polymeric solute and the pure solvent in which it is dissolved provides as a measure of the solute’s concentration, if \( \Delta n/\Delta c \) is known. If the refractometer yields a net voltage above the solvent baseline of \( V \), and its calibration factor is \( \text{CF (} \Delta n/\text{volt}) \), then the solute’s
concentration is given by

$$c = \frac{V \times CF}{\frac{dn}{dc}}$$ (16)

In the reaction monitoring context, typically, the refractive index of a polymer is greater in a given solvent than that of its corresponding monomer. This allows the use of refractometry to follow conversion, as some examples below will demonstrate.

Most flow-type refractometers use a balanced, split photodiode design to measure the angular deflection of a light ray passing through a split cell, one half of which contains the pure solvent and the other half contains the solvent with polymer.

**UV/Visible Absorption**

This widespread method is used for concentration detection, since, for a given chemical species in a given solvent there is normally a well-defined, repeatable UV/Visible absorption spectrum, characterized by an absorption cross-section at each wavelength, usually termed an “extinction coefficient,” \( \varepsilon(\lambda) \) (which can be expressed in either molar or mass concentration terms), related to solute concentration \( c \), via

$$A(\lambda) = \varepsilon(\lambda) c l$$ (17)

where \( l \) is the path length of the cell, and \( A(\lambda) \) is the absorption, related to the intensity of light emerging from the cell \( I(\lambda) \), for an incident intensity of \( I_0(\lambda) \).

$$I(\lambda) = I_0(\lambda) 10^{-A(\lambda)}$$ (18)

Most common monomers have little or no visible absorption, but frequently have measurable absorbance in the 190–300 nm UV range. It should be noted that since the transmitted intensity is measured, \( \varepsilon(\lambda) \) contains all terms that remove photons from the beam traversing the sample, including both absorption per se and scattering. This can lead to necessary corrections in UV-based concentration measurements during polymerization, since, although \( \varepsilon(\lambda) \) for the converting monomer is a constant, the total \( \varepsilon(\lambda) \), due to monomer and polymer contributions can be increasing as more polymer is produced and scatters more light. This effect is generally small but can be significant.

Modern UV/Visible spectrophotometers at moderate prices are available with diode array detection that offer rapid sampling and readout (>1 Hz) of the entire 190–800 nm spectrum using flow equipped cells.

**Infrared (IR) Spectroscopy and Raman Scattering**

Whereas in Rayleigh scattering there is essentially no frequency shift in the scattered light, Raman scattering differs in that excitation or de-excitation of molecular vibrational energy states during the scattering event can either add to (anti-Stokes shift) or subtract from (Stokes shift) the incident photon’s energy, so that the scattered light has a different frequency than the incident light. This allows different types of monochromator and cut-off optical filter schemes for measuring this relatively weak type of scattering.

Similarly, IR spectroscopy has great analytical power because the photon energies in this spectral range correspond to the quantized vibrational energy levels of covalent and ionic bonds between atoms in molecules. These levels arise from the binding energy “well” between atoms that leads to quantized (harmonic and anharmonic) oscillations. Raman scattering and IR absorption follow different quantum mechanical selection rules, making them very complementary analytical methods.

In the context of monitoring polymerization reactions, IR spectroscopy has a long history, with early reports of its use related to polymerization reaction monitoring stretching back to at least the 1950s with a subsequent report of continuous IR measurements at 805 cm\(^{-1}\) to monitor ethacrylate polymerization in toluene. IR methods have been extended to offline copolymer sequence length analysis, curing reactions, picosecond time-resolved studies of initiation events, and other aspects of polymer characterization.

In the past twenty years, IR monitoring has become increasingly common for polymerization reaction monitoring and a variety of near and mid-IR in situ probes are now commercially available. While IR is often well suited to homopolymerization, copolymerization monitoring, while often quite feasible, can present particular challenges due to broad overlapping of bands for comonomers and associated copolymer. Near IR monitoring has also been coupled to the ACOMP approach. A notable area for fruitful application of IR monitoring is in the field of polymerization in emulsions.

Likewise, Raman has been used to follow monomer concentrations and it has been shown that Raman spectra are affected by particle size in emulsion polymerization. Many of the foregoing referenced works, and others, combine IR and Raman measurements.

**The Automatic Continuous Online Monitoring of Polymerization Reactions (ACOMP) Platform**

Having described fundamental measurement approaches that have been generally applicable to
polymer characterization in equilibrium contexts for many years—e.g., to batch or SEC analyses on reaction aliquots and end products—the remainder of this presentation focuses on their broad applications within the context of the ACOMP platform.

The ACOMP Front-End

The heart of the ACOMP system is the “front-end,” the ensemble of extraction devices, pumps, mixing chambers, and conditioning steps, which transform the full strength reactor contents into a dilute, conditioned stream that flows through the sensitive detector train.

Many different configurations have been used for this. Extraction of liquid from the reactor typically ranges from $0.010^{-3}$ to $0.500 \text{ mL} \cdot \text{min}^{-1}$, depending on the application. One system uses two HPLC pumps, one for reactor extraction, the other for dilution, and a high pressure mixing chamber. This arrangement supplies a reliable, diluted, conditioned stream up to reactor viscosities of only about $300 \text{ cP}$.

To deal with very high reactor viscosities, up to $10^6 \text{ cP}$, a two stage mixing system was introduced, which consists of (1) a reactor extraction pump capable of withdrawing high viscosity fluids, such as a gear pump, (2) a mixing stage at atmospheric pressure, which also allows any bubbles created by exothermicity or other processes in the reaction to be exhaled and excluded from the detector stream, (3) a high pressure mixing stage which allows for further dilution after the low pressure stage. This normally involves five pumps. Some configurations use a direct reactor feed to the first mixing chamber, whereas others use a reactor recirculation loop with a feedback controlled pickoff valve.

The ACOMP Detector Train

Any number of detectors can be incorporated into the ACOMP platform, and different types are continuously being added. Also, data from in situ reactor probes, such as conductivity, near IR, temperature, and pH, are frequently combined with data emanating from the dilute stream detector train. Since ACOMP is normally used in a non-chromatographic context, with a continuous flow where reactions take minute to hours, the inter-detector dead volumes, while easy to account for in the analysis, do not have a large effect on data analysis. In contrast, in multi-detector SEC, where a sample “pulse” is injected into the separation columns, polydispersities, and viscosity and radius of gyration scaling laws can be dramatically mis-determined by even a couple hundred μL of error in dead volume determination between detectors. It is also noted that the detector order is not of critical importance in ACOMP. Nonetheless, the RI is usually the last detector since its flow cell is often the most likely to break due to back pressure.

Selected ACOMP Results

ACOMP has been applied to a wide variety of reactions, including step growth reactions, free radical and controlled radical homo- and copolymerization, to gradient and block copolymers, grafting and cross-linking reactions, postpolymerization modifications, and in homogeneous and heterogeneous phases, including in emulsions and inverse emulsions and in batch, semibatch, and continuous reactors. ACOMP has also been coupled with various in situ probes, and to discrete, automatic SEC detection.

Current work in progress on “2nd generation ACOMP” and adaptation of the ACOMP platform to natural product processing are briefly described in the last section below. A selection of results in different areas is presented next.

Free-Radical Copolymerization

These reactions are still of basic and applied interest, and there is a significant industrial production based on them, both for organosoluble and water soluble polymers. Important features of these reactions include the composition drift and resulting composition distribution, in addition to the molar mass and intrinsic viscosity distributions. These can be determined in model-independent fashion using ACOMP.

On the other hand, some model-dependent characteristics are often desirable to obtain, including reactivity ratios and sequence length distributions. Primary model-independent ACOMP data can be used for obtaining model parameters.

Figure 1 shows raw data signals from a free radical terpolymerization reaction of methyl methacrylate (MMA), butyl acrylate (BA), and styrene in butyl acetate at 66 °C. After the first 30 min of pure solvent baseline, as each successive monomer was added, there is an increase in both the ultraviolet (UV) absorption and the refractometer (RI) signals, according to the absorption, refractivity, and concentration. Complete UV spectra were acquired at the detector sampling rate of 2 s between each full detector train reading, and Figure 1 shows only the signal for 265 nm. It is noted that during the monomer addition phase the

4In multi-detector GPC $\overline{M}_w$ and $[\eta]$ are spared dead volume errors, since they are computed from the sum of the MALS points and sum of the viscometer points, respectively, divided by the summed concentration detector points.
viscosity and light scattering (the 90° signal is shown of the seven angles collected) signals do not change, since they are not sensitive to the dilute solution of monomer. The total concentration of monomer plus polymer in the detector train throughout the reaction was 0.01 g/C1 cm/C0 3.

At about 9000s the initiator, azoisobutyronitrile (AIBN), was added and the polymerization reaction began. The drop in the UV signal follows composite conversion due to the loss of the double bonds in each monomer type, whereas the increase in RI reflects the fact that dn/dc for each monomer in polymeric form is greater than in the corresponding monomeric form. The increase in light scattering and viscosity is due to the increasing concentration of high molecular weight polymer.

It is important to note that Stockmayer[70] and Benoit[71] realized the problem of determining copolymer mass by the usual homopolymer approach to light scattering [Equation (6)], which yields only an apparent mass, M_ap, in the copolymer case. The origin of the difference between M_ap and M_w lies in the difference in dn/dc values of the comonomers in polymeric form, which is important only when there is a significant composition drift. They formulated a method requiring light scattering measurements in a minimum of 2N – 1 solvents to find true M_w, where N is the number of comonomer types (i.e., three solvent minimum for two comonomers, five for terpolymers, etc.). This impractical limitation has been circumvented in ACOMP, since it measures the evolution of average composition drift, so that true M_w can be computed at each instant of synthesis, as recently reported.[72]

Various means have been used in ACOMP for determining the concentration of each comonomer. In principle, two monomeric signals are sufficient for determining the two concentrations, such as one UV signal and the RI signal (with dn/dc of each comonomer and corresponding polymer known), or two UV wavelengths, or an entire range of UV wavelengths. This latter method was separately developed for distinguishing comonomers of very similar UV spectra,[73] e.g., MMA and BA. In some cases, where the signals are too close for resolution, or another species overwhelms the monomer signals (e.g., certain RAFT agents), then the continuous detector train has been used in combination with automatic periodic chromatography to separate the monomers.

Figure 2 shows analyzed data concerning conversion and M_w for the interesting case of copolymeric polyelectrolytes (copolyelectrolytes) synthesized by free radical polymerization from acrylamide (Am) and vinyl benzene sulfonic acid in sodium salt form (VB).[74] Strikingly, this reaction ([VB]/[Am] = 10/90 mol-%) inadvertently led to a blend of copolyelectrolyte and acrylamide homopolymer. This is seen in the smooth, first order conversion of VB in the first half of the reaction (f_VB is the fractional VB conversion), while Am also slowly co-converts (see f_Am). When the VB is exhausted at 6000 s the conversion of remaining Am accelerates, producing homopolymer in the last part of the reaction.

Molecular weight is quite affected by the changeover from copolymerization to homopolymerization. M_w shown in Figure 2 is the cumulative weight-average molecular weight of polymer in the reactor, whereas M_w,inst is obtained from

$$M_{w,\text{inst}} = \frac{d(f_{\text{w,\text{inst}}})}{df}$$

where f is the fractional monomer conversion.

Figure 1. Typical ACOMP signals collected during the free radical terpolymerization of methyl MMA/BA/styrene.

Figure 2. Conversion of each comonomer f_VB and f_Am. M_w, and M_w,inst for copolyelectrolytes made during the acrylamide (Am)/ vinyl benzene sulfonic acid in sodium salt form (VB); (10/90 = [VB]/[Am]). The upper panel, left shows the instantaneous fraction of VB in the chains f_{inst,VB}. The charged chains indicate production of copolyelectrolyte in the first phase and neutral homopolymer of Am in the second phase. (Adapted from ref.[40]).
The comonomer conversion data in this particular reaction were obtained by monitoring just two UV wavelengths (206 and 250 nm), where the extinction coefficients of VB and Am were determined from their baseline values, and small residual absorption from the polymer was accounted for at each wavelength. From this, the concentrations, and hence conversion of each species was computed each 2 seconds during the reaction. The concentrations were combined with the multi-angle light scattering data to compute the evolution of absolute $M_w$ and z-average mean square radius of gyration $S_{2z}$.

In Figure 2, $M_w$ is computed from Equation (6), and $R(c,q)$ is determined at each of the multi-angle laser light scattering (MALS) seven scattering angles, and the $2A_2 c$ term of Equation (6) in such experiments is either negligible, or the value of $A_2$ is determined in a separate experiment (e.g., by automatic continuous mixing)\cite{75}, and used in the $M_w$ computation.

Data in the section below show how the large composition drift can be controlled by programmed reagent feed to the reactor (semi-batch operation). It is also noted that, because of the exquisite sensitivity of light scattering to even small populations of polymer aggregates, ACOMP provides an immediate notification of microgelation and other association phenomena during reactions.

**Semi-Batch Control of $M_w$ and Composition**

The precise knowledge of reaction kinetics furnished by ACOMP allows predictive control of reactions, via calculable flow rates of reagents into the reactor, to yield desired molecular weight and composition trends, with subsequent online verification of the actual reaction trajectory. In this sense, the predictive approach is a prelude to full feedback control of the reactor, where the predicted trajectory can serve as an Ansatz, and deviations from the desired trajectory can then be corrected by small changes to the feed pumps and other variables.

Figure 3 shows the results of predictive control of $M_w$ for acrylamide polymerization.\cite{76} The lower curve shows the natural tendency of $M_w$ to monotonically decrease during a batch reaction. This is typical of free radical polymerization when chain transfer is negligible and the initiator decomposes slowly compared to the conversion rate. The constant $M_w$ data were achieved by knowledge of the Am conversion rate and setting the Am reactor feed rate to maintain $[\text{Am}]$ constant in the reactor. With a near constant concentration of initiator in the reactor, and very little change in reactor volume (a concentrated Am reservoir was used for reactor feed) the kinetic chain length remains constant. To demonstrate the robustness of the approach the third curve shows $M_w$ increasing versus conversion, achieved by increasing the flow rate of Am into the reactor, and hence producing the opposite trend of $M_w$ from a batch reaction.

As shown in the preceding section, free radical copolymerization of Am and VB leads to very high composition drift, and production of a blend of copolypelectrolyte and pure pAm. With knowledge of the composition drift in batch and the conversion kinetics from separate ACOMP experiments it was possible to largely control the composition drift.

Figure 4 shows composition drift curves $F_{\text{inst,VB}}$ versus conversion for VB/AM copolymerization reactions made under different monomer flow schemes.\cite{77} $F_{\text{inst,VB}}$ is the fraction of VB in chains produced at any instant, and is
given by

\[
F_{\text{inst.VB}} = \frac{d[V\text{B}]}{d([V\text{B}] + [A\text{m}]})
\] (20)

The quasi-isoreactive data show the results of using simultaneous VB and Am feeds. While not perfectly constant, it is much closer than an uncontrolled batch reaction, which depends on the reactivity ratios. The upper curve demonstrates how the natural batch tendency to rapidly deplete VB can be countered by flooding the reactor at a high VB addition rate from an external reservoir.

Free-Radical Emulsion (Co)Polymerization

A large current effort is being devoted to monitoring heterogeneous phase polymerization reactions. The first heterogeneous phase reaction monitored by ACOMP was the inverse emulsion polymerization of acrylamide.

Emulsion polymerization was developed for producing polymers with unique properties and because of environmental considerations. Although the reaction medium in emulsion polymerization remains at low viscosity, factors such as instability of the lattices and other non-equilibrium phenomena, complexity of the materials produced, and multi-faceted properties requiring multiple characterization approaches make the whole process of monitoring the reaction quite challenging.

Characterization of organosoluble component characteristics and colloidal size distributions have typically been carried out using different sampling procedures and disparate instrumentation is tedious and makes it difficult to assess and quantitatively evaluate the characteristics and interrelationships of these complex, non-equilibrium colloidal/polymer systems.

A new advance with regard to the instrumentation and methods available for online monitoring of emulsion polymerization reactions was achieved. Data and an ACOMP embodiment for a typical emulsion polymerization reaction are illustrated in Figure 5. The method developed by the authors allows, for the first time, two different aspects of the emulsion polymerization reaction to be monitored simultaneously without recourse to empirical models: (1) monitoring the polymer and monomer characteristics, achieved by diluting the reactor content continuously and automatically throughout the reaction with an organic solvent miscible with water (in this case, tetrahydrofuran, THF); (2) monitoring the colloidal components, monomer droplets, and polymer particles, achieved by diluting the emulsion with H₂O throughout the reaction. Thus, this approach offered a unified means of monitoring colloid/polymer characteristics and gives information about both the polymer and particle evolution, allowing one to make correlations between key features. Online monitoring of both particle and polymer characteristics should allow for studies of reaction kinetics, predictive, and active reaction control, and also the ability to observe deviations and unexpected phenomena.

The dual stream reactor extraction approach ACOMP platform was applied also to batch copolymerization reactions in emulsion, using BA and methyl methacrylate (MMA) as the comonomers. An extended spectrum UV analysis for discerning concentrations of comonomers with similar spectral characteristics was involved. On the polymer/monomer stream, the average composition drift and distribution, \(M_w\) and reduced viscosity \(\eta_{r,w}\) were measured, and on the colloid stream the particle size distributions were measured. Shown in Figure 6 are curves as functions of total monomer conversion for selected copolymerization reactions in emulsion versus solution copolymerization reactions. The composition drift profiles were roughly similar to those observed in corresponding homogeneous phase copolymerization with notable exceptions during early conversion due to thermal

![Figure 5. Data and ACOMP set-up for simultaneously measuring polymer/monomer (conversion, \(M_w\), \([\eta]_{w}\), etc.) and colloid (latex and droplet size distributions) characteristics during emulsion polymerization reactions.](image-url)
and/or differential solubility effects between BA and MMA. Remarkably, polymer latex particle size distributions were largely independent of copolymer composition.

It is important to mention that the ACOMP approach of liquid-to-liquid sample handling, which avoids any solid intermediate phases, has been thoroughly tested in the context of emulsion (and inverse emulsion) polymerization. In the case of the Figure 5 type emulsions, rapid particle dissolution in THF was verified by continuously recirculating THF from a solvent reservoir through the detector train with a peristaltic pump and adding a few drops of emulsion to the reservoir to make the combined concentration of monomer and polymer similar to that used in the ACOMP dilution stage. The response of the UV, RI, and MALS detectors then monitor the dissolution of the particles into homogeneous solution. It was found that the monomers were homogenized under 20 s. The polymers were solubilized also under 20 s, but it could take up to a few hundred seconds for the MALS signal to reach a stable plateau, possibly indicating a period for the chains to disentangle from each other after the polymer particles are dissolved. The delay time between extraction from the reactor and reaching the detector train was between 2 and 6 min, depending on the details of the dilution stages and flow rates. Likewise, the system response time due to the dual mixing stages was between 2 and 4 min, again depending on mixing details. The response time is defined as the reciprocal of the exponential rate at which a step function applied to the system reaches steady state (e.g., a rapid injection of initiator or other detectable molecule into the reactor can be used to measure this).

Semi-Batch Emulsion Polymerization

Semi-batch emulsion polymerization is a versatile process which allows polymer latexes with special particle morphology and composition to be produced.\(^{[82–87]}\) In this context, a first study of reaction kinetics with ACOMP was made for the semi-batch emulsion polymerization of MMA at 70 °C.\(^{[88]}\) The use of continuous monitoring offered a robust means of determining the characteristic features of the starved and flooded monomer conditions, and identifying them during the experiments. Particular emphasis was given to the method used to follow molecular weight evolution during the reaction monitoring, in an absolute fashion, based on multi-angle light scattering detection.

Figure 7 shows the effect of the monomer feed rate on \(M_w\) reactions in batch versus semi-batch mode (left panel); mass distributions for the same experiments, as determined from SEC (right panel). Both techniques capture distinct \(M_w\) kinetics for a batch reaction and for a reaction in starved conditions. Typical free radical behavior is observed for the \(M_w\) trend for the reaction in batch, where \(M_w\) starts with very large values, on the order of \(10^7\), and decreases with conversion nearly an order of magnitude. In contrast, for the experiment in semi-batch conditions, \(M_w\) reached a plateau at around 20% conversion and has much smaller magnitude (over 20 times smaller than batch molecular mass). The shape and breadth of the molecular weight distribution (MWD) provided by SEC is also affected by the details of monomer addition, e.g., narrower MWD for

![Figure 6. \(F_{\text{rel}}\) curves as functions of total monomer conversion for selected copolymerization reactions in emulsion versus solution copolymerization reactions.](image1)

![Figure 7. The effect of the monomer feed rate on \(M_w\) reactions in batch versus semi-batch mode (left panel); mass distributions of end-products for the same experiments, as determined from SEC (right panel).](image2)
the semi-batch reaction, where almost all monomer is flowed in.

**Living Gradient Copolymerization in Solution**

Living/controlled polymerization methods (CRP)\(^{[89–91]}\) have attracted a lot of interest due to their versatility and robustness, and their compatibility with a large number of monomers and functional groups. CRP allows gradient copolymers to be produced, in which the composition profile changes along the polymer chain, conferring distinctive material properties on the end product. Block copolymers are easily synthesized, as well as more complex architectures such as star, dendritic, and brush/comb/graft (co)polymers. Moreover, chain modifications, control of composition, and, hence, polymer properties become possible.

RAFT is the newest of the major CRP techniques, and arguably the most versatile.\(^{[92–95]}\) The key feature of the reaction mechanism is the reversible transfer of the radical activity to a dormant species, making it active. Rapid equilibrium established between the active and dormant species allow all the chains to grow in a controlled fashion.

ACOMP was used to follow trends in the evolution of conversion, \(M_w\), and \([\eta]_w\) during RAFT block and gradient copolymerization reactions for several monomers, using different trithiocarbonates as catalysts. In the later case, the effects of the initial comonomer composition on the living character of the reactions were studied. Reactivity ratios during RAFT gradient copolymerization reactions were determined and compared to those obtained in traditional free radical copolymerization reactions.

An example is shown in Figure 8 for the case of the BA/MMA (80/20 M/M) copolymerization reaction by RAFT.

**ACOMP with Simultaneous Continuous Detection and Discrete Automatic SEC**

While the most prominent ACOMP approach is non-chromatographic and involves continuous detection of a dilute, un-fractionated sample stream, there are certain applications where chromatographic separation, such as offered by SEC, is advantageous. A serendipitous feature of the ACOMP front-end dilution/conditioning is that it feeds the continuous detector train with the same concentration levels usually used in SEC. Hence, the front-end sample stream can be fed straight to a SEC system equipped with an automatic injector valve that injects samples into the columns periodically, or the sample stream can first pass through a continuous detector train and the waste stream can then be periodically injected into the columns.

Since fractionation by SEC is relatively slow, data points will be delayed from each other usually by 10 min or more, although small, “high speed” SEC columns also exist but usually give less resolution. Living reactions are a good area for ACOMP with SEC detection, since they are usually slow and involve very low polydispersity, so that the determination of the complete MWD and polydispersity offered by SEC can provide verification of this. Another area where SEC detection can be valuable is in the case of copolymerization when other batch methods, such as UV spectroscopy and refractometry fail. It is frequently possible to separate monomers with SEC columns, so that discrete conversion points can be obtained.

A recent demonstration coupled the usual continuous non-chromatographic detection of ACOMP with a multi-detector SEC instrument fed by the continuous ACOMP waste stream.\(^{[96]}\) Figure 9 shows the combination of continuous and discrete SEC data obtained simultaneously. The reaction involved the RAFT polymerization of BA in butyl acetate (20–35% by mass) at 70 °C. Continuous, non-chromatographic raw ACOMP signals from the different detectors are monitored. Thus, the increase of LS 90 and RI voltages follows the growth of the polymer chains, whereas the decrease in UV (the 245 nm data are shown) follows the monomer consumption. Temperature and viscosity evolution during the reaction are also monitored. In the same time, raw SEC signals follow the same reaction; RI, UV, light scattering at 90° (LS90), and differential viscometer pressure (DP). The interval between injections was 10 min. In reference 66 ACOMP with simultaneous continuous detection and discrete SEC was used to follow the appearance of bimodal populations in doubly initiated free radical polymerization, for RAFT homopolymerization, and, separately, for copolymerization by RAFT.

**Polymer Modification**

Postpolymerization modification of polymers represents an important alternative route to obtaining desired final
endproduct properties. There are many types of reactions used, such as acid and base hydrolysis, enzymatic treatments, quaternization, sulfation, grafting, PEGylation, peptidization, etc. The Huisgen reaction, often termed “click chemistry,” is a popular means of adding functionality to a polymer using an azide and alkyne reaction.[97–100]

ACOMP is ideally suited to monitoring such modifications by homing in on the physical or chemical changes that accompany the modifications. Figure 10 shows a recent example involving the base hydrolysis of polyacrylamide (PAAM), which turns it into a polyelectrolyte of increasing charge density as hydrolysis proceeds.[101]

By selecting an ACOMP diluent of low to moderate ionic strength, 0.01M in this case, the evolution of the polyelectrolyte properties, in terms of polymer coil expansion, increased intrinsic viscosity, and strong interparticle correlations are clearly monitored. The increasing viscosity signals shows the effect of the neutral pAm chains becoming increasingly charged and expanding due to the electrostatic charge, which increases their intrinsic viscosity. The increase in chain dimensions and the increasing interparticle electrostatic fields leads to electrostatically enhanced excluded volume between chains, which increases $A_2$ and $A_3$ in Equation (2) above, leading to a decrease in light scattering.

These experiments also made use of a complementary in situ conductivity probe. The solution conductivity decreased as small, free mobile charges were taken from the solution and incorporated in the increasingly charged polyelectrolyte chain, which has much smaller electrophoretic mobility than the free ions. In fact, this method was subsequently used to monitor quantitative trends in counterion condensation during copolyelectrolyte synthesis, where the decreasing conductivity was directly related to the monitored composition drift, and hence to the degree of free counterions “condensing” on the chains.

Conclusion and Outlook

Commercialization

ACOMP is now firmly established as a valuable instrument in the R&D setting. Several laboratories on different continents have built or are building their own ACOMP units. Transfer to the industrial sector is at this point a purely engineering challenge, but will require a different focus; instead of high level, multi-faceted instruments providing a massive data stream of intricately related characteristics to skilled and knowledgeable users as in the R&D setting, the industrial reactor implementation will require the simplest possible configuration and a reduced set of detectors to provide the minimum necessary amount
of information for the monitoring application. An industrial implementation will require several levels of fail-safe operation, extra pressure, temperature and flow sensors together with redundant and alternate flowpaths and electronic checks, and an overall ruggedness and simplified and ritualized maintenance program. PolyRMC at Tulane University, a non-profit university R&D center, is currently piloting non-profit R&D and industrial technology transfer programs to participating industries, and expects to form a capital venture to provide customized ACOMP platforms in the near future.

2nd Generation ACOMP (SGA)

Whereas ACOMP discussed herein is of the “first generation” (FGA) sort, SGA will have the added feature of providing immediate data on how the stimuli responsiveness of polymers evolves during synthesis. There is much current work in stimuli responsive polymers, sometimes also termed “smart” materials, with potential for use in drug delivery, electronics and optics, high performance coatings, self-healing materials, etc. Stimuli responsiveness includes conformational and thermodynamic phase transitions (e.g., lower critical solution temperature, LCST), aggregation, ability to encapsulate and release other agents (e.g., drugs), ability to interact with surfactants, other polymers, etc. Stimuli producing these responses include temperature, light, pH, ionic strength, specific small molecules, surfactants, solvent type, and mixtures, etc.[102–108]

The goal of SGA is not only to monitor important characteristics of the reactions, but also to monitor the onset and evolution of stimuli responsiveness of the polymers during synthesis. This will allow determination of what conditions are needed to produce specific stimuli responsive behavior, which will both help in the fundamental understanding of these phenomena and materials, and in the practical task of optimizing their synthesis conditions.

The SGA approach involves simultaneous use of multiple sample detectors, including banks of flow cell equipped static light scattering cells with and without polarized detection, fluorescence cells, and viscometers (each being a differential transducer), either coupled to the FGA output or with separate reactor extraction and dilution stages. These detectors build on the simultaneous multiple sample light scattering (SMSLS) platform recently introduced by the authors and their colleagues,[109,110] aimed at economically screening many independent samples simultaneously and continuously. Groups of cells can also be toggled between parallel and serial operation with millifluidic valves, together with multi-head peristaltic pumps for simultaneous mixing and continuous detection. For example, in parallel mode polymer behavior can be monitored under different solvent conditions by separate automatic dilution with the chosen solvents, using the multi-head pump.

An example of serial operation is determination of LCST for a polymer during synthesis by passing the diluted stream through a series of scattering detectors, each at a different temperature. N-Isopropylacrylamide (NIPAM) and its copolymers are a well-studied example of polymers yielding LCST behavior.[111–114] Polarized scattering detection can help detect morphological changes; e.g., from isotropic to anisotropic structures, whereas fluorescence detection can be used for monitoring micellization properties, encapsulation of agents, etc. Viscosity measurements have wide applicability to particle morphology, polyelectrolyte response to pH, and ionic strength, etc.

Natural Products

A vast array of materials are derived from plant, animal, and bacterial sources. In terms of polymeric materials there are particularly large sectors involving polysaccharides and proteins derived from natural products. Xanthans, gum arabic, alginates, pectins, starches, proteinaceous gels, glycosaminoglycans, galactomannans, etc. are each large industries unto themselves, and support markets in the agricultural, biomedical, drug, personal care, papermaking, oil field, water treatment, and other fields. Additionally, plant sources will be increasingly important as the development and use of biofuels increases, and as the need for renewable sources of monomers for the polymer industry grows.

ACOMP is ideally poised to monitor, and hence control and optimize, each step in the usual natural product processing cycle. Typical process steps involve extraction, microbial production, chemical, enzymatic, or radiolytic modification, purification, interaction with other agents, etc. There are many ways that the ACOMP approach can be adapted to monitoring these processes, and additional detectors, such as dichroism and birefringence can be added. Enzymatic activation and deactivation processes can be monitored, degradation, hydrolysis and other modification rates of polymers quantified, and, SGA can be impressed into service to monitor the evolution of desirable polymer properties (e.g., viscosifying and emulsifying power, ability to interact with surfactants, etc.). Such adaptations can be of especial importance in the natural product sector, since R&D and production in this field is chronically hampered by the wide variability of raw starting products.

Monitoring polymerization reactions with detectors that make fundamental measurements of polymer properties allows a virtually model-free set of primary data concerning conversion, composition drift, and evolution of molecular
weight and intrinsic viscosity. Unusual or unexpected events, such as microgelation or phase separation can also be monitored directly. The primary data furnished by such detection then allows interpretation of kinetics and mechanisms and can serve as the basis for building specific quantitative, mechanistic models, as well as for controlling polymerization reactions. The ACOMP platform is one means of embodying and employing any chosen set of such detectors, and these can also be complemented by widely used in situ detectors.

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