Recent Advances in Automatic Continuous Online Monitoring of Polymerization Reactions (ACOMP)

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Summary: ACOMP allows comprehensive, model-independent, near realtime monitoring of many different types of polymerization reactions. It provides conversion kinetics, and the evolution of average molar mass, intrinsic viscosity and average composition distributions (for copolymers). Here, recent advances in ACOMP will be summarized, dealing with continuous reactors, copolymerization, 'living' type reactions (NMP, RAFT, ATRP, ROMP), polyelectrolytes, heterogeneous phase reactions, including free radical reactions in emulsions, and predictive control. In the case of emulsion polymerization, a new approach will be presented in which the evolution of the characteristics of both the soluble phase – monomer conversion, polymer molar mass and intrinsic viscosity- and the dispersed phase – particle size – are simultaneously monitored. NSF CBET 0623531, BOR ITRS 019B, NASA NCC3-946, TIMES, PolyRMC (Tulane Center for Polymer Reaction Monitoring and Characterization).

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Introduction

ACOMP is a rapidly maturing, versatile platform for monitoring polymerization reactions. It furnishes in a largely modelindependent fashion reaction characteristics, such as weight average molar mass M_w , weight average intrinsic viscosity $[\eta]_w$, monomer and comonomer conversion kinetics, average composition drift and distribution, and also alerts to unexpected events, such as microgelation.

Since 1998 ACOMP has been adapted to new types of reactions and reactors. This report focuses on some recent advances in ACOMP: Continuous reactors, 'living' type polymerization, copolymerization, polymer modifications, polyelectrolytes, predictive control, and heterogeneous phase polymerization, emphasizing emulsion polymerization.

There is a large body of literature that deals with models that can make predic-

tions about the final properties of polymeric endproducts, such as molecular weight distributions (MWD), and rheological properties. These models often proceed from the data available from simple sensors, such as temperature and pressure, although there is a growing use of spectroscopic measurements, such as Raman,^[1,2] near infra-red (NIR),^[3] and mid infra red (MIR).^[4,5] ACOMP is now at a mature enough stage that the quantities it furnishes can serve as direct tests of models, in addition to forming the basis for both predictive and feedback control for polymerization processes.

ACOMP Principle and Instrumentation

There have been many different configurations used for ACOMP over the years, but the basic operating principle is the same. The principle is to extract continuously a small stream of reactor liquid (usually 0.010 to 0.200 ml/minute) and dilute this to a level where absolute light scattering and other measurements can be made such that the measurements are dominated by the properties of the polymer chains themselves, not





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their interactions. This allows M_w , $[\eta]_w$, kinetics, and average composition distributions to be directly computed without recourse to empirical or inferential models. After dilution, or between dilution stages, different conditioning steps can be made, such as debubbling (many exothermic reactions will produce frothy reactor contents), filtration, phase inversion, volatilization of monomers, etc. The diluted, conditioned stream then flows through any desired combination of detectors, depending on the goal of the monitoring.

Some of the guiding principles of ACOMP include: 1) Monitoring is adapted to the chemistry. The chemistry is never changed in order to suit the monitoring. 2) Proper online sample conditioning leads to the optimum raw data quality. 3) Measurements are made at the most fundamental level possible (single scattering, dilute regime viscosity and spectroscopy, etc.) to obtain model-free primary quantities, such as conversion, M_w, etc. 4) Obtaining high quality data with model-free primary quantities allows the richness of the ACOMP results to be used for building chemical, physical, and mechanistic models to any degree of elaboration desired, and for potential control of reactions.

The ACOMP 'Front End'

The ACOMP 'front-end' is the set of pumps, mixing chambers, and conditioning elements needed to produce the diluted stream that continuously flows through the detectors. The simplest operation was with a gradient pump^[6] extracting alternately from the reactor and a solvent reservoir with a proportioning valve. This system could not maintain a constant extraction rate and was quickly supplanted by a dual HPLC pump scheme with a single high pressure mixing chamber.^[7] For dealing with higher viscosities and higher dilutions a dual low-pressure/high-pressure mixing scheme was introduced, which utilizes five pumps, including a powerful gear pump for extraction from the reactor.

The delay time between sample extraction and measurement by the detector train depends on the configuration used, and typically runs from 20 seconds to five minutes. The response time is typically in this same range, and is defined as the halftime for the detectors to equilibrate to a sudden step function change in the reactor (e.g. addition of a detectable reagent, such as an initiator).

The ACOMP Detector Train

A widely used detector train includes a multi-angle light scattering (MALS) detector (BI-MwA, Brookhaven Instruments Corp.), a Shimadzu P-20 full UV/visible diode array spectrophotometer, a Shimadzu differential refractometer (RI), and a single capillary viscometer. Complementary *in-situ* probes include conductivity, pH, and near infra-red detectors.^[8] Recently, Mie scattering, using the Malvern Mastersizer has been incorporated into a particle detection stream for emulsion polymerization, discussed below.

While there are often many advantages to obtaining the continuous records of conversion, M_w , etc. afforded by ACOMP, there are instances where full molecular weight distributions (MWD) may be desired. In this case, the continuous, conditioned stream feeding the detectors can be periodically and automatically diverted in pulses into a standard Size Exclusion Chromatography (SEC) system. Hence, ACOMP can be used with continous non-chromatographic detection, or periodic chromatographic detection, or both approaches simultaneously.

First Commercially Available ACOMP System

In 2004 Polymer Laboratories (PL, Shrophsire, England, now a part of Varian Inc.) licensed ACOMP and related technologies from Tulane University. PL has developed a fully modular ACOMP platform, now available for as the PL Process Monitoring and Control platform, PCM (http:// www.polymerlabs.com/pdfs/pmc.pdf) The PL system, a working prototype of which is shown in Figure 1, includes many improvements over the Tulane research



Figure 1.

The first commercial prototype ACOMP unit by Polymer Laboratories Ltd. (now a part of Varian, Inc.).

versions: The standard configuration includes dual low and high pressure mixing stages, with a heavy duty Zenith gear pump providing reactor extraction and fast recirculation through a temperature controlled loop from which the desired extraction rate is provided via a state-of-the-art microfluidic controller (Bronkhorst, Inc.). Pressure and temperature sensors provide automatic feedback to the system to monitor its own performance, and an automatic clean cycle will make operation simpler and increase throughput. The software platform provides complete instrument control and analysis functions, including authentication, appropriate levels of security, over-the-Net operating and monitoring capabilities, and databasing for advanced storage and 'data mining'. The National Instruments interface is openended and allows PL to easily adapt new

instruments and sensors into the platform. The stock configuration is compatible with a variety of PL instruments (RI and viscometer), the Brookhaven BI-MwA MALS unit, and Shimadzu UV/visible detectors. The BI-MwA light scattering unit (http://www.bic.com/BI-MwAmw.html) is based on the original prototype first described by Florenzano, Strelitzki, and Reed in 1998.^[6] Figure 2 shows a recent model BI-MwA, including the flow cell and fiber optic mutli-angle detection.

Results

Continuous Reactor

Continuous reactors are frequently used in industrial applications because they can run at a steady state, with constant flows of reagents and output products. ACOMP was



Figure 2.

The seven angle BI-MwA light scattering photometer from Brookhaven Instruments Corp., based on the original ACOMP prototype. The flow cell is seen to the left, with fiber optics emanating from it and led to a CCD detector in the rear. A vertically polarized, temperature stabilized laser diode(center) is used as the incident source.

applied to a continuously stirred tank reactor, and proved capable of monitoring both the steady state, once reached, as well as the approach to the steady state.^[9] Monitoring the approach to steady state can be quite important when switching from one product grade to another, allowing the most efficient use of reagents and time.

Figure 3 shows typical ACOMP data for a continuous reactor when it is fed with a constant concentration of monomer (acrylamide in water), but the amount of initiator (potassium persulfate) is changed. The fractional monomer conversion f, and M_w are monitored. In the steps shown the amount of initiator is increased in increments, causing a new steady state of higher conversion and lower M_w each time.

Copolymerization

There are several challenges in monitoring copolymerization, among them the simultaneous determination of the concentration of comonomers of similar spectral characteristics, and the use of light scattering to determine M_w .

A recent advance involves the incorporation of a full UV/visible spectrophotometer into the ACOMP train, and the development of an associated numerical algorithm for determining comonomer concentration with no *a priori* assumptions about spectral shapes, empirical models or calibrations.^[10] The single assumption is that the absorption spectrum is the linear superposition of spectra of all absorbing species. The extinction coefficient spectra for each of these species is determined, often at the outset of a reaction during sequential addition of the monomers to the reactor, or read from a library, since, in any given solvent the extinction coefficient spectra are constant properties of the comonomers. Spectra are then collected during the reaction, typically each second, and a numerical procedure is applied to minimize the error between each measured spectrum and the computed spectrum that involves the extinction coefficient spectra and optimized concentrations of each absorbing species. Taken over several dozens of wavelengths, this procedure has been found to be quite robust, even for



Figure 3.

ACOMP monitoring of a continuous reactor. Fractional monomer conversion f, and M_w are shown for each step in which a new steady state is reached with increasing increments of initiator.

comonomers of similar spectral characteristics, such as butyl acrylate (BA) and methyl methacrylate (MMA).

Figure 4 shows an example of the copolymerization of BA and MMA. The

starting mass percentage ratios (g/g) was $25_{BA}/75_{MMA}$. The solid lines are the concentrations determined from the UV spectral treatment described above, and the discrete points are from SEC determinations of



Figure 4.

Detector concentrations of butyl acrylate (BA) and methyl methacrylate (MMA) during copolymerization, obtained by multi-wavelength UV spectral analysis. Large circles and diamonds are SEC values from manually withdrawn reaction aliquots.

conversion from aliquots manually withdrawn from the reactor during the reaction. The agreement is excellent.

Figure 5 shows the average composition drift of BA, $F_{inst,BA}$, for several different copolymerization reactions. $F_{inst,BA}$ was determined by the derivative $F_{inst,BA} = dc_{BA}/d(c_{BA} + c_{MMA})$, where c_{BA} and c_{MMa} are the mass concentrations (g/cm³) of BA and MMA, respectively.

ACOMP provides an excellent means of obtaining reactivity ratios^[11] and the UV method was subsequently applied to copolymerization of a more 'exotic' methacrylate, N-methacryloxysuccinimide (MASI), with MMA and BA, and it was found that the reactivity ratios of the methacrylate pair MASI/MMA were much closer than the methacrylate/acrylate pairs MASI/BA and MMA/BA.^[12] This showed that the presence of the methyl group near the vinylic bond dominates the reactivity compared to the nature of the pendant groups.

Obtaining M_w for copolymers by light scattering has been traditionally a difficult task. If the Zimm^[13] homopolymer approximation is used for analyzing copolymer scattering data, only an apparent weight average weight M_{ap} is found. Stockmayer et al.,^[14] and Bushuk and Benoit developed a method for obtaining the true M_w by making measurements in 3 different solvents.^[15] Kambe et al. later extended this to terpolymers, which requires 6 solvents.^[16] In fact, for N different comonomers it requires separate scattering measurements in N(N+1)/2 different solvents, and $N(N+1)^2/2$ different values of dn/dc for the different copolymeric components in the various solvents must be known.

This nearly untenable approach to determining M_w has recently been circumvented by ACOMP which furnishes the average cumulative and instantaneous compositions as well as angular dependent scattering data in each moment. It was demonstrated how these data can be integrated efficiently and numerically at every instant to obtain true M_w during copolymer synthesis, using only one solvent, no matter how large N.^[17]

Polymer Modifications and Copolymer Polyelectrolytes

A frequently used strategy for producing polymers with desired characteristics is to first produce a relatively simple polymer, and then modify it by some subsequent chemical treatment. Such modifications can include hydrolysis, quaternization, sulfonation, etc. A modification reaction of particular current interest is the Huisgen



Figure 5.

Average composition drift of butyl acrylate during different copolymerization reactions of BA and MMA.

cyclization reaction, also termed the 'click' reaction.^[18,19] In fact, current work is underway in adapting ACOMP to the monitoring of 'click' reactions.

Recently, ACOMP was used to monitor the base hydrolysis of acrylamide, which forms a random copolymeric polyanion.^[20] By selecting an ACOMP aqueous dilution solvent of low to moderate ionice strength, it was possible to monitor the increasing intrinsic viscosity of the copolymer, whose charge increases as hydrolysis proceeds, as well as increasing electrostatic excluded volume, which leads to a progressive decrease in light scattering intensity. Conductivity was also monitored, which allowed computation of the degree of conversion.

Another recent approach to copolymeric polyelectrolytes involved direct polymerization of styrene sulfonate (SS) and acrylamide (Aam).^[21] Due to large differences in reactivity ratios the SS was rapidly converted in a first order process, producing a relatively low mass copolyelectrolyte with Aam. Then, the residual Aam converted to form a high mass homopolymer. Thus, a blend of polyelectrolyte and neutral polymer was formed. Understanding of such processes through monitoring could lead to the ability to produce 'on-command' blends, avoiding the arduous and costly process of mixing large industrial lots of polymers.

Another area now under study by ACOMP is the chemical and enzymatic modification of natural products, such as galactomannans.^[22] In fact, ACOMP is well suited to monitor the many stages of processing involved in the use and application of natural products; extraction processes, chemical and enzymatic modifications, interactions with other agents, including drug encapsulation, formation of nanostructures, etc.

Living Polymerization

Living type polymerizations can produce highly tailored, low polydispersity materials. Controlled radical polymerization (CRP) includes Atom Transfer Radical Polymerization (ATRP),^[23,24] Reversible Addition Fragmentation chain Transfer (RAFT),^[25,26] and Nitroxide Mediated Polymerization (NMP).^[27,28] ACOMP has included composition profile determination during gradient copolymerization.^[29] Another living type polymerization is Ring Opening Metathesis Polymerization (ROMP).^[30,31]

ACOMP has been successfully applied to ATRP.^[32] NMP^[7,29]. RAFT.^[33] and ROMP.^[34] Figure 6a shows examples of the transition between uncontrolled radical polymerization of BA (reaction #5) and the increasingly controlled living reaction when a RAFT transfer agent, 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic acid (DoPAT), is used in higher concentrations in reactions #1-#4, where #1 has the highest amount and is almost perfectly living. All reaction conditions are identical except for the increasing amount of DoPAT. The DoPAT had no measurable influence on the conversion kinetics, seen in Figure 6b. Conversion closely resembled a first order processe with rates shown in the figure. This is similar to previous findings by Goto et al.,^[35] where the rate is essentially of zeroeth order in [RAFT] and depends almost solely on the initiator (AIBN) concentration. There are examples of RAFT systems, however, in which increasing [RAFT] at fixed initiator concentration leads to increasing retardation (longer induction period and slower conversion).^[36–38]

Current work in the living area includes gradient and block copolymerization, and adaptation to emulsion polymerization.

Emulsion Polymerization

Emulsion polymerization reactions represent complex sets of chemical and physical events wherein colloidal structures, such as emulsions and polymer latex particles, exchange mass in processes driven by chemical reactions and diffusion. There are two distinct aspects to the process; the evolution of the colloidal particles, and the monomer conversion kinetics and characteristics of the polymers produced within the colloidal particles. There is an abundant literature on experiment, theory, and monitoring of emulsion polymerization.^[39–41]



Figure 6.

a. ACOMP results of M_w vs. Monomer conversion f, for RAFT homopolymerization of BA in butyl acetate. All conditions were identical except that a maximum amount of RAFT agent, DoPAT, was used in reaction #1, and decreasing amounts in the succeeding reactions. In #5 no DoPAT was used, and typical uncontrolled free radical behavior for M_w is observed. b. Increasing amount of DOPAT does not affect the conversion kinetics for RAFT polymerization in these reactions.

The authors proposed an original means of monitoring both the colloidal and monomer/polymer characteristics by expanding ACOMP to a dual extraction/dilution/ conditioning platform.^[42] In this, one extraction stream is diluted with a suitable organic solvent that is miscible with water to produce a dilute, homogeneous solution containing solubilized monomers and polymers (the polymer side), and the second extraction stream is diluted with aqueous solvent, to preserve the colloidal structures (the colloid side). The detectors for the polymer side can be those typically used for ACOMP; MALS, viscometer, RI, and UV/ Visible spectrophotometer, whereas the colloid side uses particle characterizing detectors such as Mie scattering (here, a



Figure 7.

Schematic of the instrumentation used for simultaneous monitoring of colloid and soluble component characteristics during emulsion polymerization reactions.

Malvern Mastersizer 2000), dynamic light scattering, turbidity, or heterogeneous time dependent static light scattering (HTDSLS).^[43] The ensemble is depicted in Figure 7.

The recently enhanced ACOMP that allows simultaneous online measurements of both the colloidal aspects of the emulsion polymerization (particle size distribution) and the soluble components (polymer/ monomer) is a powerful tool for correlating the relationship between the micelles and droplets and the polymers being formed in them, and allows testing specific hypotheses concerning the proposed emulsion mechanisms. 23

An example of the comprehensive information obtainable by this method is shown in Figure 8, for free radical emulsion polymerization of methyl methacrylate at





Emulsion polymerization of MMA at 70 °C. Raw data and analysis.

70 °C. The left side (below) shows raw light scattering, UV, refractometer, and viscosity data signals used to compute M_w and $[\eta]_w$. These latter are shown vs. fractional monomer conversion f (above) from the sample stream diluted by THF, containing the soluble polymer/monomer components. The right side (lower) shows particle distributions from Mie scattering on the colloidal aspects obtained by dilution of the reactor contents with water. Distributions #1-3 are from progressive points of monomer conversion, and show the initial large monomer droplet populations (>1 micron) are consumed and transformed into nucleated polymer particles (~150 nm); the upper panel shows the evolution of large and small particle modes from Mie scattering data, and the specific particle surface area. Final particle sizes were crosschecked by dynamic light scattering and cryogenic transmission electronmicroscopy, and found to be in excellent agreement.

On-Command Polymers

Ultimately, the sophisticated monitoring capabilities of ACOMP can be extended to control of poymerization processes. While a complete ACOMP-driven system of full feedback control has not yet been developed, initial steps are being taken in terms of 'predictive control'. In predictive control, the details of polymer kinetics and molecular weight evolution furnished by ACOMP are harnessed to give a predictive set of equations that can be used for control of processes. For example, reagents can be selectively fed into the reactor (often termed 'semi-batch') to achieve desired endproducts.

Initial efforts in predictive control currently underway involve feed of initiator and/or monitor to produce desired trends in molecular weight and composition. For example, in the case where free radical homopolymerization is involved, and an initiator with a decomposition lifetime long compared to the complete reaction is used, the molecular weight in the semi-batch reactor can be kept constant by keeping the monomer concentration constant. This latter requires adjusting the flow rate of monomer to the reactor to compensate for monomer conversion to polymer in the reactor. Of course, other feed schemes can be used to provide desired distributions; increasing monomer concentration by proper feed can lead to progressively increasing M_w , whereas discrete additions of intitiator at intervals can lead to multimodal molecular weight distributions.

Conclusions

ACOMP is a versatile platform that has been adapted to the continuous monitoring of M_w , $[\eta]_w$, monomer conversion kinetics, average composition drift and distributions, and more. The current work highlights some of the recent advances into continuous reactors, 'living-type' controlled radical and ROMP polymerization, copolymerization, post-polymerization modifications, polyelectrolytes, emulsion polymerization reactions, and predictive control.

ACOMP should become progressively used in controlling polymerization processes, and should also prove to be an excellent means of verifying and testing many different types of reaction models and control strategies.

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