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Coupling of near infrared spectroscopy to automatic continuous online monitoring of polymerization reactions

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Abstract

In situ near infrared (NIR) spectroscopy is performed simultaneously with automatic continuous online monitoring of polymerization reactions (ACOMP) during methyl methacrylate polymerization. ACOMP is an absolute technique that furnishes weight average molecular mass M_w , intrinsic viscosity, monomer conversion, and other characteristics, whereas NIR furnishes monomer conversion data via an empirical calibration. An advantage of in situ NIR is that it furnishes immediate information on the conversion in the reactor, whereas ACOMP relies on continuous withdrawal and dilution of a small stream of reactor fluid, so that there is a lag time of several minutes between what ACOMP reports and what is occurring in the reactor. Simultaneous monomer conversion data from in situ NIR and ACOMP, the latter derived from both refractive index and UV absorption, are compared and found to be in good agreement. The evolution of conversion kinetics and M_w generally conform to the predictions of the Quasi-Steady State Approximation. Having established the agreement between the methods, the path is now open for combining NIR with ACOMP to characterize increasingly complex systems, such as copolymerization with two or more monomeric species, that are not feasible by either technique separately.

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1. Introduction

Monitoring polymerization reactions has three areas of application. At the fundamental level it can provide information on kinetics and mechanisms necessary for the development of new materials, while at the bench or pilot plant level it can be used to optimize reaction conditions. Finally, when used in a complete feedback control loop at the industrial reactor level, significant improvement in product quality can be expected, as well as savings of non-renewable resources, energy, reactor and personnel time.

In situ monitoring includes techniques such as rheometry [1-3], ultra-violet [4,5], infrared and mid- and near infrared (NIR) [6], and Raman spectroscopy. One advantage of in situ techniques is that the detector is within the reactor so that there is no delay between what

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is occurring in the reactor and the detector signal. On the other hand, the probe must still be intrusively introduced into the reactor and withstand a harsh environment, with possible plugging, opacity, etc. Furthermore, because the reactor contents are normally quite concentrated detector signals are often dominated by inter-polymer chain effects, rather than the intrinsic properties of the polymers themselves. The response of some of the spectroscopic techniques mentioned remains linear up to fairly high solute concentrations, but all the methods, including these latter ones, rely on some sort of empirical or inferential model for interpreting the detector data. Finally, each of these techniques usually provide a direct estimate of only one characteristic, such as monomer conversion, or bulk viscosity, although correlative models can often be made to other characteristics, such as polymer molar mass.

NIR spectroscopy is well suited to provide real-time structural and kinetic data of polymers [7,8] because a fiber optic probe can be placed directly into the reactor system. This eliminates the need for sampling, and consequently, reduces time and experimental error associated with the sampling process [9]. Additionally, remote monitoring and data collection of in situ NIR spectroscopy can be achieved due to the fact that the optical fibers, connecting the probe with the spectrophotometer and the computer, can be very long and still present up to standard signal-to-noise ratios. Disadvantages associated with the NIR region are that the monomers of interest must have absorbances in the NIR region and it is also preferable if the absorbance bands of the monomers do not overlap.

NIR radiation spans from 700 to 2500 nm. Absorbances of NIR are weaker harmonic overtones and combination bands of the fundamental stretching vibrational bands associated with hydrogen in the mid-infrared (MIR) region [10]. These NIR bands are broad and overlapping. However, one can account for the overlapping bands in the NIR region by using multivariate methods such as partial least squares. The combination of multi-variate techniques and NIR spectroscopy led to the increasing applicability of NIR spectroscopy for in-line monitoring of chemical and physical properties of chemical reactions [3,11].

During solution polymerization of methyl methacrylate in toluene, fiber optic NIR spectroscopy was used to monitor the monomer conversion and the weight average molecular weight of the resulting polymer [12]. In order to relate NIR spectra to conversion and the weight average molecular weight a statistical model was generated using partial least squares (PLS) regression. Santos et al. [13,14] also successfully used the combination of NIRS and the PLS regression for real-time monitoring of average particle sizes in suspension styrene polymerization reactors and close the loop for particle size control. NIR has also been used to investigate polymer rheological properties. Hansen and Vedula [15] presented a methodology in which fiber optic NIR spectroscopy was used to make simultaneous, real-time measurements of melt flow index (MI), the composition of molten poly(ethylene vinyl acetate), and the complex viscosity responses of the copolymers.

Using NIR spectroscopy in conjunction with other analysis techniques can be useful to supplement insufficient information contained in a single spectrum or to investigate which technique is best for particular analyses [16]. Several studies have been done using both Raman spectroscopy and NIR spectroscopy because each is associated with a different spectral region as well as a different collection of vibrational modes in a molecule. The two techniques are particularly complimentary when investigating emulsion polymerizations where droplets of monomer are dispersed in water. However, a very important variation between the two techniques is the way they interact with the water molecule. In Raman scattering, the water molecule has a weak scattering effect whereas it has a very strong absorption in NIR. Reis et al. assessed Raman and NIR spectroscopies for the monitoring of various semicontinuous emulsion homo- and copolymerization reactions [17]. Both techniques yielded good results when estimating the monomer conversion. They concluded that neither Raman nor NIR is better in monitoring the emulsion polymerization, but it is important to investigate which situations are more appropriate for their use.

The traditional use of mid-infrared (MIR) spectra is to identify organic compounds. The MIR region has many sharp peaks that are the result of fundamental vibrational bands [18]. Olinga et al. showed that there is equivalence in the results from Fourier transform MIR (FT-MIR) and Fourier transform NIR (FT-NIR) spectroscopy in the attenuated total reflection (ATR) mode to monitor solution polymerization of methyl methacrylate [19]. MIR spectroscopy has also been used to supplement the NIR spectroscopy of bulk curing reaction of multi-component unsaturated polymer (UPE) resins [20]. NIR spectroscopy has been used to analyze the curing process of epoxy resins [21]. Kortaberria et al. [22] simultaneously used dielectric and NIR measurements to monitor in situ and real-time cure of poly(methyl methacrylate)-modified epoxy thermosets.

Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP), in contrast, is not an in situ technique, but rather relies on the continuous withdrawal and high dilution of a small stream of reactor fluid, provided by a 'front end' of pumps and mixing devices, and a string of detectors, most frequently comprising multi-angle light scattering, viscometry, refractive index and visible/ultra-violet absorption [23]. ACOMP involves no chromatographic columns. Because the fluid reaching the detector is very dilute it is possible to make simultaneous, continuous, absolute measures of several characteristics, such as $M_{\rm w}$, $[\eta]_{\rm w}$, monomer conversion, measures of polydispersity, and copolymer composition information, without recourse to empirical models. A disadvantage of ACOMP is that there is typically a delay time of several minutes between extraction/dilution and measurement. For reactions lasting on the order of at least tens of minutes, however, this is often acceptable. Results from the first ACOMP experiments and details of the instrumentation were first reported in 1998 [23]. Since then, ACOMP has been applied to free radical copolymerization, including determination of composition, mass and sequence length distributions, and reactivity ratios [24], and nitroxide mediated controlled radical homo- and copolymerization [25,26]. In the latter case, a means for determining the composition profile along 'living' gradient copolymers was developed. ACOMP has also been applied to determination of chain transfer kinetics [27], and to the monitoring of the approach to the steady state and steady state characteristics in continuous reactors [28].

The object of this work is to bring together in situ NIR with ACOMP and to make a critical comparison of the results on monomer conversion provided by each method. These data are also used in conjunction with the other ACOMP detectors to provide M_w , $[\eta]_w$ and the instantaneous weight average molecular mass $M_{w,inst}$. The ensemble of data can be compared with kinetic and hydrodynamic theories. This work hence sets the stage for the coupled use of NIR and ACOMP for more complex systems, such as those involving polymerization of two or more monomeric species, where neither technique alone would be capable of making the type of comprehensive characterization desired.

2. Materials and methods

2.1. The reactor and connection to ACOMP 'front end'

The reactor consisted of a round bottom three neck flask, placed in a silicon oil bath atop a feedback controlled, temperature regulating hot plate, combined with a magnetic stirrer. A column inserted into one of the flask necks allowed cooling water to flow during the experiment. A needle inserted through a septum on another neck allowed continuous nitrogen purging of the reactor. This neck also contained a withdrawal tube that pumps solution out of the reacting chamber to the dilution stage. The Brimrose NIR- AOTF spectrometer with a Luminar AOTF 2000-300 probe, fiber optically coupled to the spectrum analyzer, was inserted through the third flask neck as an in situ probe during the reactions. The NIR spectrometer was programmed to deliver the absorbance at 1623 and 1631 nm to the ACOMP data gathering software, although only the 1623 nm wavelength is used in the analysis here.

A Knauer K-20 HPLC pump was used to withdraw a small stream of the reaction mixture (0.2 ml/min). An ISCO 2350 pump was used to pump the carrier solvent (butyl acetate) at 1.8 ml/min (for experiments I and II), providing a dilution ratio of 1:10. Both streams were combined in an Upchurch microbore high pressure mixing chamber to obtain the diluted, continuous sample stream measured by the detector train.

2.2. The detector train

The diluted sample stream was fed through a Brookhaven Instrument BI-MwA multi-angle scattering photometer, a home-made single capillary viscometer, a Shimadzu SPD-10AV Vp dual wavelength UV/visible spectrophotometer, and a Waters 2410 differential refractometer. The signal from each instrument, in addition to the two NIR wavelengths from the Brimrose, and the output of the reactor thermocouple were all digitized by A/D inputs on the BI-MwA input module, which contained 20 input channels working at 24 bit resolution. The UV wavelengths used were 245 nm and 266 nm. The viscometer used a capillary of length 20 cm and internal diameter of 0.02 in.

2.3. Polymerization reactions

The monomer, methyl methacrylate (MMA), the initiator, azobisizobutyronitrile (AIBN), and the carrier solvent butyl acetate (BA) were used as received from Aldrich. Reactions were carried out at either 9% or 15% by volume of MMA, and hence the correction in concentrations due to the increase in reactor liquid density as polymerization proceeds is negligible. The reactor containing the solvent (BA) was placed in a temperature regulated oil bath and was heated to the desired temperature (75 °C or 85 °C). Before beginning the reaction pure BA was pumped at 2.0ml/min through the entire detector train to obtain the baseline for each instrument. The solvent in the reactor was purged with nitrogen at least 30 min prior to beginning the reaction.

After stabilization of the detector baselines by pure BA, and after the reactor solution reached the desired temperature, the MMA baseline was established by withdrawing from the reactor at 0.2 ml/min, and mixing with solvent at 1.8 ml/min. The flow rates of both the pure solvent from reservoir and that of the solution in the reactor, as well as the total solute concentration (monomer plus polymer) in the detector train for each experiment are given in Table 1. These flow rates were maintained throughout the entire experiment. In all of the experiments, the total flow rate was set at 2.0 ml/min and the diluted solution always reached the detector train at a temperature of $25 \,^{\circ}\text{C}$.

After baseline stabilization for MMA the AIBN was added to initiate the reaction. The amount of AIBN

Table 1 Conditions for and some results of different experiments

	Experiment I	Experiment II	Experiment III
MMA, by volume	15%	15%	9%
Butyl acetate, by volume	85%	85%	91%
AIBN, by total mass	2.4%	1.2%	0.17%
Temperature (°C)	75°C	75°C	85°C
Flow rate reactor (pure solvent) (ml/min)	0.2(1.8)	0.2(1.8)	0.08(2.5)
Conc. reactor (g/cm^3)	0.14145	0.14145	0.0896
Conc. det. (g/cm ³)	0.014145	0.014145	0.0028
Final $[\eta]_{\rm w}$ (cm ³ /g)	5.7	6.8	9.1
Final $M_{\rm w}$ (g/mol) by ACOMP	8372	9100	11,197
Final $M_{\rm w}$ (by SEC)	8266	8636	12,282
$\langle S^2 \rangle_n^{1/2}$ (nm)	2.33	2.50	3.08
Experimental $r_{\rm H,z}$ (nm)/0.7 ^a	2.43	2.79	3.07
α (s ⁻¹)—RI	2.3×10^{-4}	1.57×10^{-4}	4.73×10^{-4}
α (s ⁻¹)—NIR	2.14×10^{-4}	1.62×10^{-4}	4.78×10^{-4}
α (s ⁻¹)—UV1 (UV2)	2.46×10^{-4}	1.89e-4	4.80e-4
	(2.45×10^{-4})	(1.84e - 4)	(4.2e-4)
$\langle \alpha \rangle \pm \%$ error	$2.34 \times 10^{-4} \pm 6\%$	$1.73 imes 10^{-4} \pm 9\%$	$4.63 \times 10^{-4} \pm 5\%$
Final conversion	0.90	0.94	0.48

^a The theoretical non-free draining value is $r_{\rm H,z} = 0.7 \langle S^2 \rangle_n^{1/2}$.

used for each experiment is given in Table 1. The temperature in the reactor was constantly monitored to make sure that no unusual exothermicity or other thermal processes were occurring.

2.4. Multi-detector GPC and DLS instrumentation

Cross-checks on the ACOMP M_w results were made using traditional multi-detector Gel Permeation Chromatography. THF was the eluent, pumped at 0.8 ml/ min by a Shimadzu LC 10AD-VP pump, through a PL gel 10 μ mixed B column. The detector train comprised a Shimadzu RID-10A RI detector, Shimadzu SPD-10AV VP UV detector, homebuilt single capillary viscometer, and a Brookhaven Instruments BI-MwA multi-angle light scattering photometer.

Cross-checks on the ACOMP $[\eta]_w$ results were made using a Brookhaven Instruments BI-90 Plus Dynamic Light Scattering (DLS) instrument, operating with a diode laser beam at 660 nm vacuum wavelength.

2.5. Determination of monomer concentration

One of the main goals of this work is to compare the monomer concentration measured by the NIR and the ACOMP detectors. The method of computation in each case is given below.

NIR

Fig. 1 shows spectra for MMA, taken at different concentrations in butyl acetate. This leads to the relation

$$A_{1623} = \varepsilon_{\rm MMA} c_{\rm MMA} + \varepsilon_{\rm BA} c_{\rm BA} \tag{1}$$



Fig. 1. NIR spectra for MMA at different concentrations in butyl acetate, with the absorption of the latter subtracted. The inset shows the NIR spectra without subtraction of butyl acetate contribution.

where A_{1623} is the absorbance of the NIR detector at the 1623 nm wavelength, $\varepsilon_{\lambda,MMA}$, $\varepsilon_{\lambda,BA}$ are the extinction coefficients of MMA, and butyl acetate respectively, and their values are given in Table 2. $\varepsilon_{\lambda,BA}$ was deter-

Table 2
Properties of the monomer and polymer

	MMA	PMMA	BA
dn/dc in THF ^a (cm ³ /g)	NA	0.089	NA
dn/dc in BuAc (cm ³ /g)	0.019	0.096	NA
A_2 in BuAc ^b (cm ³ mol/g ²)	NA	1.3×10^{-4}	NA
$\varepsilon_{\text{UV}} = 245 \text{nm} (\text{cm}^2/\text{g})$	9.04×10^{3}	0.601×10^{3}	0.123×10^{3}
$\varepsilon_{\rm UV} = 266 \rm nm (cm^2/g)$	3.17×10^{3}	0.30×10^{3}	0.07×10^{3}
$\varepsilon_{\text{NIR},\lambda} = 1623 \text{nm} (\text{cm}^2/\text{g})$	2.64	0.22	According to baseline
ρ (g/cm ³)	0.943	1.188	0.881

^a Used for GPC only, value from Ref. [24].

^b The concentrations of PMMA in GPC were so low that the A_2 correction term in THF was entirely negligible.

mined by the baseline NIR value during each ACOMP experiment. Similarly, the value for $\varepsilon_{\lambda,PMMA}$ was found by measuring varying concentrations of PMMA in BA. This allows determination of c_{MMA} during an ACOMP experiment by

$$A_{1623} = \varepsilon_{1623,\text{MMA}} c_{\text{MMA}} + \varepsilon_{1623,\text{PMMA}} c_{\text{PMMA}} + \varepsilon_{1623,\text{BA}} c_{\text{BA}}$$

$$(2)$$

where c_{BA} is known and remains constant throughout the reaction (ignoring a slight density change of reactor contents). The concentration of PMMA, by mass conservation is given as $c_{PMMA} = c_{MMA,0} - c_{MMA}$, where $c_{MMA,0}$ is the initial concentration of MMA in the reactor before polymerization begins.

UV

Table 2 also shows the UV extinction coefficients at each wavelength for butyl acetate, MMA, AIBN and polymethyl methacrylate (PMMA). This allows determination of the concentration of MMA in the detector train according to Eq. (2), where the corresponding UV wavelength is substituted for 1623 nm. Since the UV is blanked against BA, the c_{BA} term in Eq. (2) is equal to zero.

RI

The voltage provided by the RI, V_{RI} , is related, via its calibration factor CF ($\Delta n/V$) to c_{MMA}

$$V_{\rm RI} = \frac{1}{\rm CF} \left\{ c_{\rm MMA} \frac{{\rm d}n}{{\rm d}c} \bigg|_{\rm MMA} + c_{\rm PMMA} \frac{{\rm d}n}{{\rm d}c} \bigg|_{\rm PMMA} \right\}$$
(3)

where $(dn/dc)_{\rm MMA}$ and $(dn/dc)_{\rm PMMA}$ are the values of dn/dc of the monomer and polymer, respectively. These values were determined as discussed below, and are given in Table 2. Again, mass balance relates $c_{\rm PMMA}$ to $c_{\rm MMA}$ via $c_{\rm MMA,0}$, the initial concentration of MMA in the detector train. The effect of the small amount of added AIBN on $V_{\rm RI}$ was determined to be negligible.

2.6. Light scattering data analysis

The well known Zimm approximation [29] allows determination of weight average molecular mass M_{w} ,

second and third virial coefficients A_2 and A_3 , respectively, and particle shape factor P(q). Zimm has shown, that to 2nd order in polymer concentration c (g/cm³), the quantity $Kc/I_R(q,c)$, where $I_R(q,c)$ is the excess Rayleigh scattering ratio, can be approximated by

$$\frac{Kc}{I_{\rm R}(q,c)} = \frac{1}{MP(q)} + 2A_2c + [3A_3Q(q) - 4A_2^2MP(q)(1-P(q))]c^2$$
(4)

This equation forms the basis of the well known Zimm plot, which, at low concentrations and for $q^2 \langle S^2 \rangle \ll 1$ can be written, for a polydisperse polymer population as

$$\frac{Kc}{I_{\rm R}(q,c)} = \frac{1}{M_{\rm w}} \left(1 + \frac{q^2 \langle S^2 \rangle_z}{3} \right) + 2A_2c \tag{5}$$

which directly permits determination of M_w , A_2 and the *z*-averaged mean square radius of gyration $\langle S^2 \rangle_z$. *K* is an optical constant, given for vertically polarized incident light by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4}$$
(6)

where *n* is the solvent index of refraction, λ is the vacuum wavelength of the incident light, dn/dc is the differential refractive index for the polymer in the chosen solvent, and *q* is the usual scattering wave-vector $q = (4\pi n/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The means of obtaining $I_{\rm R}(q,c)$ from raw scattering voltages via comparison to the well known $I_{\rm R}$ for toluene have been well documented [23–28,30].

Using the method of Automatic Continuous Mixing [30–32], A_2 in butyl acetate was previously determined to be 0.00013 cm³ mol/g². With a maximum concentration in the ACOMP detector train of 0.014 g/cm³ (experiment I in Table 1), the maximum A_2 correction was 3%. The value of $\langle S^2 \rangle_z$ for the PMMA of such small M_w as produced in the reactions in this work were so small (about 2.3 nm), that the $q^2 \langle S^2 \rangle_z/3$ term in Eq. (5) was only about 6×10^{-4} at $\theta = 90^\circ$, so that it could be neglected, and it sufficed to use light scattering data from this angle alone.

2.7. Viscosity data analysis

Total solution viscosity is given by

$$\eta = \eta_{\rm s} [1 + [\eta]c + k_{\rm p} [\eta]^2 c^2] \tag{7}$$

where η_s is the pure solvent viscosity, $[\eta]$ is the intrinsic viscosity of the polymer, and k_p is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers [33]. The intrinsic viscosity is the extrapolation to zero concentration and zero shear rate of the reduced viscosity η_r . η_r can be computed directly from the voltage of a single capillary viscometer (a differential pressure transducer) at every point *i*, without need of an instrumental calibration factor, in terms of the viscometer baseline voltage V_b and the concentration at point *i*, c_i :

$$\eta_{\mathrm{r},i} = \frac{V_i - V_\mathrm{b}}{c_i V_\mathrm{b}} \tag{8}$$

This is so because the output of the viscometer is directly proportional to the pressure drop across the capillary of radius R and length L, which in turn is directly proportional to the total solution viscosity via Poisseuille's equation

$$\eta = \frac{\pi R^4 P}{8LQ} \tag{9}$$

where Q is the flow rate through the capillary (in cm³/s). The average shear rate in the capillary is

$$\dot{\gamma}_{ave} = \frac{8Q}{3\pi R^3} \tag{10}$$

In the method presented here it is possible to extrapolate η_r to c = 0, although the average shear rate will remain finite at about $860 \,\mathrm{s}^{-1}$ for $Q = 1 \,\mathrm{ml/min}$ and $R = 0.0254 \,\mathrm{cm}$. Fortunately, shear effects diminish with diminishing c. It is also noted that it is currently standard practice in SEC coupled to viscometric detectors to approximate $[\eta]$ by the values of η_r determined at finite (but low) c and finite shear rate. In what follows the measured value of η_r will be taken as equal to the (batch) weight average intrinsic viscosity $[\eta]_w$.

3. Results and discussion

Fig. 2a shows typical RI, UV_{245 nm}, UV_{266 nm} and NIR data for an MMA polymerization reaction. The overset shows the temperature profile at each stage. The different steps, stabilization with pure solvent, then with pure monomer, followed by addition of AIBN are all indicated in the figure.

The double bond in the MMA is lost on polymerization leading to a decrease in UV signal at both wavelengths. Because dn/dc of PMMA is greater than dn/dcof MMA, the RI signal *increases* as polymerization pro-



Fig. 2. (a) Raw data from experiment I, with each period labeled. UV wavelengths at 245 nm and 266 nm, NIR at 1623 nm, and RI. Overset shows the temperature at each point. Temperature and NIR signals lead the rest of the data by 300s, since both the thermocouple and NIR probe are in the reactor. (b) Raw viscosity and light scattering (at 90°) signals for the same experiment as (a).

ceeds. The loss of the vinylic bond also leads to the loss of the NIR signal.

Fig. 2b shows light scattering (at $\theta = 90^{\circ}$) and viscosity data for the same experiment. The increase of the two latter signals corresponds to the increase in polymer concentration in the reactor, and once combined with the polymer concentration data yield the time course of $M_{\rm w}$ and $[\eta]_{\rm w}$.

Fig. 3 uses the method of Brousseau et al. [34] to determine simultaneously dn/dc of the monomer and polymer. Let $c_{m,0}$ represent the initial monomer concentration in the detector train. After the initiator is added at time t = 0, the RI voltage can be expressed as



Fig. 3. Use of the ACOMP data to determine dn/dc by the method of Brousseau et al. [34].

$$V_{\rm RI}(t) = \frac{c_{\rm m,0}}{\rm CF} \left\{ f_{\rm m}(t) \frac{{\rm d}n}{{\rm d}c} \bigg|_{\rm m} + (1 - f_{\rm m}(t)) \frac{{\rm d}n}{{\rm d}c} \bigg|_{\rm p} \right\} + \Delta V_{\rm RI,initiator} H(t - t_0)$$
(11)

where $\Delta V_{\text{RI,initiator}}$ is the increase in RI voltage due to addition of the initiator (which is negligible in this work), $H(t - t_0) = 1$ for $t \ge t_0$, and $H(t - t_0) = 0$ for t < 0 (the Heaviside step function), and $f_m(t)$ is the fraction of initial monomer remaining at time $t. f_m(t)$ is given from the UV voltage $V_{\text{UV}}(t)$ by

$$f_{\rm m}(t) = \frac{V_{\rm UV}(t) - \Delta V_{\rm UV,initiator} H(t - t_0)}{V_{\rm UV}(0)}$$
(12)

where $V_{\rm UV}(0)$ is the UV voltage when pure, unreacted monomer flows, before addition of initiator, and $\Delta V_{\rm UV,initiator}$ is the change in the UV signal when the initiators are added. The following expression then permits for convenient determination of dn/dc for monomer and polymer taken over early conversion intervals:

$$\frac{\operatorname{CF} \times V_{\operatorname{RI}}(t)}{c_{\operatorname{m},0}f_{\operatorname{m}}(t)} = \frac{\mathrm{d}n}{\mathrm{d}c}\Big|_{\operatorname{m}} + \frac{\mathrm{d}n}{\mathrm{d}c}\Big|_{\operatorname{p}} \frac{[1 - f_{\operatorname{m}}(t)]}{f_{\operatorname{m}}(t)}$$
(13)

The results for experiments I and II are shown in Fig. 3, but overlap so closely that they cannot be distinguished. The dn/dc values in Table 2 come from the average of these experiments, as well as independent cross-checks using the RI and steps of monomer concentration, and separately, steps of polymer concentration.

Fig. 4a shows the concentration of MMA in the reactor obtained by averaging the concentrations computed by the NIR, RI and two UV signals for reaction I. The NIR data was shifted by 300s to account for the lagtime between its own in situ measurements and the delayed ACOMP measurements. The inset to the figure shows the unaveraged swath of concentration data from all



Fig. 4. (a) The average concentration of MMA in the reactor for experiment I, averaged over the concentrations as determined by IR, NIR and both UV wavelengths. The inset shows concentrations for all four signals. (b) 'Residual plots' of RMS fractional error, for each detector, with respect to the average signal shown in (a).

four detectors. These are close enough to each other that the result is simply a broadened curve.

A first order fit (exponential) to the average curve is shown by the dashed line, where

$$c_{\rm m}(t) = c_{\rm m,0} \mathrm{e}^{-\alpha t} \tag{14}$$

where α is the kinetic rate constant. The fit is so close to the actual data that it is only seen before and after the data points end. The rate constant found was $2.34 \times 10^{-4} \text{s}^{-1}$. A first order fit for free radical polymerization is expected under the Quasi-Steady State Approximation (QSSA) [35], in the limit where the initiator lifetime is significantly longer than the time it takes for full monomer conversion. The AIBN half-life is close to 10^4 s at 75 °C [36], whereas the half-life of the conversion, given the above rate constant is 0.3×10^4 s.

Table 1 shows the rate constants for each reaction, as determined by each detector. The standard deviations

among the different rate constants lead to the error bars shown in Table 1.

Simple first order kinetics predict that $\alpha = k_p[R]$, where k_p is the propagation rate constant, and [R] the molar concentration of propagating free radical. The QSSA further predicts that $[R] \propto [AIBN]^{1/2}$, so that $\alpha_I = 2^{1/2} \alpha_{II}$, by this theory. Examination of the average rate constants for experiments I and II in Table 1 show that $\alpha_I = 1.36\alpha_{II}$, which is very close to the predicted value (1.41). Also, as seen in Table 1, the rate constant increases when the reaction runs at 85°C, vs. 75°C, even though less initiator was used at 85°C.

Fig. 4b shows the 'residuals', or fractional errors, for each detector, expressed as $(c_{m,i}(t) - \langle c_m \rangle(t)) / \langle c_m \rangle(t)$, where $c_{m,i}(t)$ is the MMA concentration computed by detector j at time t, and $\langle c_m \rangle(t)$ is the average value from Fig. 4a at time t. The root mean square error is also shown in each plot. In all cases the RMS error is less than 5%, indicating that any of the detectors will furnish a reliable concentration within these error bars. This is important, because as the number of components increase in co- and terpolymerization, the number of unknown concentrations could become equal to the number of viable detector signals, so that each one must be independently reliable. It was also found that the residual curves and associated RMS error are fairly insensitive to errors in delay time determination; i.e. even shifting the NIR delay by one hundred seconds had little effect on the errors.

Fig. 5a gives M_w vs. time for experiments I–III in Table 2, using the type of concentration and TDSLS (time dependent static light scattering) data shown in Fig. 1. The values of M_w and conversion used c as computed by UV1. No substantial difference in the results were obtained if instead the average value of c showed in Fig. 2a was used. The solid circles at the end of each curve are the values of M_w obtained by GPC on the final aliquots of each experiment. The agreement is excellent, which puts a good cross-check on ACOMP using a more traditional method. The much larger noise level for experiment III reflects the much higher dilution of solute in the detector train for that experiment (see Table 1).

The inset to Fig. 5a shows the random fractional error in $M_{\rm w}$ for experiment I, due solely to the noise levels in each of the detectors (not to systematic errors, such as possible long term detector drift, error in any calibration constants, etc.). This was computed by first taking the standard deviations of the light scattering baseline to get a variance $\langle (\Delta I)^2 \rangle$ and of the average concentration data to get a variance $\langle (\Delta c)^2 \rangle$. Because the RI and LS detectors are independent, their fluctuations are also independent, so that $\langle \Delta I \Delta c \rangle = 0$, and the fractional error in $M_{\rm w}$, $\sigma_{M_{\rm w}}/M_{\rm w}$, at each sampling point can be *estimated* as



Fig. 5. (a) M_w vs. time for experiments I, II and II in Table 1. The large, solid circles at the end of each trace correspond to the GPC value of M_w as determined by GPC on endproducts of each reaction. The inset shows the RMS fractional random error for experiment I, as discussed in the text. (b) M_w vs. conversion for each experiment. The inset shows $M_{w,inst}$ and a linear fit over the QSSA regime.

$$\frac{\sigma_{M_{w}}}{M_{w}}\Big|_{i} = \frac{\sqrt{(\Delta M_{w,i}^{2})}}{M_{w,i}}$$
$$= \frac{1}{M_{w,i}} \sqrt{\left(\frac{\partial M_{w}}{\partial I}\Big|_{i}\right)^{2} \langle (\Delta I)^{2} \rangle + \left(\frac{\partial M_{w}}{\partial c}\Big|_{i}\right)^{2} \langle (\Delta c)^{2} \rangle}$$
(15)

or

$$\frac{\sigma_{M_{w}}}{M_{w}}\Big|_{i} = M_{w,i}$$

$$\times \sqrt{\left(\frac{c_{i}k}{I_{i}^{2}}\right)^{2} \langle (\Delta I)^{2} \rangle + \left(\frac{k}{I_{i}} - 2A_{2}\right)^{2} \langle (\Delta c)^{2} \rangle} \quad (16)$$

The inset to Fig. 5a also shows the component of the error which arises from just the light scattering random error. It is much smaller than that due to concentration random error. At any rate the total random error at t = 1000s is only about 8% and remains between 1% and 2% for the rest of the reaction.

Fig. 5b gives M_w vs. monomer conversion f, for experiments I and II. The trend in both cases is for M_w to increase quickly initially, reach a maximum and then decrease linearly until near-final conversion. Remarkably, the linear portion conforms well to the QSSA in the limit mentioned above. Namely, when the initiator concentration varies little during the time of monomer conversion f, it is easily demonstrated that the cumulative M_w measured by TDSLS is

$$M_{\rm w}(f) = M_{\rm w,0}(1 - f/2) \tag{17}$$

where $M_{w,0}$ is the initial value. The straight lines drawn into the linear portions in Fig. 5b, show that in both cases $M_{w,0} = 14,500 \text{ g/mol}$, and in experiment I decreases at f = 1-7400, and in experiment II to 8300. Considering that M_w deviates significantly from the QSSA for the first 25% of conversion in each case, both of these values are quite close to the ideal QSSA prediction in Eq. (17) of 7250. The final M_w for experiment I is lower than for experiment II, as expected, since I uses more AIBN. The reason for the dependence of M_w on [AIBN] between experiments I and II being less than expected (1/ [AIBN]^{1/2}), is probably related to the initial period of deviation from the QSSA.

The $M_{\rm w}$ provided by LS in ACOMP is the cumulative average of the polymer in the reactor. The instantaneous value of $M_{\rm w}$, termed $M_{\rm w,inst}$ can be computed according to [37]

$$M_{\rm w,inst}(f) = M_{\rm w}(f) + f \frac{\mathrm{d}M_{\rm w}}{\mathrm{d}f}$$
(18)

The inset to Fig. 5b shows $M_{w,inst}$ made from M_w for experiment I made by taking successive M_w values at finite conversion intervals and making the numerical computation according to Eq. (18). This shows that there are values of $M_{w,inst}$ of 16,000 that exceed the maximum value of M_w of 12,000. Making a linear fit over the QSSA regime (f > 0.25) gives the same value of $M_{w,0}$ as the linear fit over M_w yields. Furthermore, the f = 1intercept very close to $M_{w,inst} = 0$ agrees with the QSSA prediction that

$$M_{\rm w,inst}(f) = M_{\rm w,0}(1-f) \tag{19}$$

These data together give strong support to the existence of the QSSA regime over the majority of conversion. It is possible to take $M_{w,inst}$ and construct polydispersity histograms as a function of f, according to the methods of Ref. [37]. This analysis is not pursued here.

The behavior of $M_{w,inst}$ (and hence also M_w) can be understood in terms of the kinetic chain length v, which is the instantaneous degree of polymerization and is given by

$$v = \frac{k_{\rm p}[\rm MMA]}{k_{\rm t}[\rm R]} \tag{20}$$

where $k_{\rm p}$ and $k_{\rm t}$ are the propagation and termination rate constants, respectively, and [R] is the concentration of propagating radical. It is recalled that in free radical polymerization each chain is initiated, propagates, and terminates on a time scale (typically much less than one second) much smaller than the total time for conversion. Hence, if [R] remains essentially constant during the reaction (long-lived initiator), v decreases as [MMA] decreases during conversion, which is the experimentally observed trend of $M_{w,inst}$ (and M_w) decreasing in time. At the outset of the reaction, however, where $M_{\rm w,inst}$ and $M_{\rm w}$ actually increase, contrary to the simple QSSA prediction, the most likely explanation is the presence of small amounts of impurity/inhibitors that compete with MMA for free radicals and which kill free radicals upon encounter, hence shortening the chains. After an initial period these impurities are eliminated and the reaction then follows the idealized QSSA model. This interpretation in terms of impurities has been recently explored quantitatively [38].

Fig. 6 shows $[\eta]_w$ vs. time for experiments I and II. DLS measurements were made on the end-point products of the reactions for comparison with the viscometric results. For a coil polymer at the Θ -point, the intrinsic viscosity is given by the Flory–Fox relation [39]

$$[\eta] = \frac{\Phi_{\rm v}}{M} (\sqrt{6} \langle S^2 \rangle_{\eta}^{1/2})^3 \tag{21}$$

where $\Phi_v = 2.56 \times 10^{23}$. Using the experimental values of $[\eta]_w$ and M_w from ACOMP, and substituting them in for $[\eta]$ and M in Eq. (21), yields the values of the 'viscometric root mean square radius of gyration' $\langle S^2 \rangle_{\eta}^{1/2}$ shown in Table 1. The DLS scattered intensity autocorrelation

Fig. 6. Reduced viscosity vs. time for experiments I and II.



functions were analyzed using the standard method of moments [40] within the Gaussian scattering approximation relating the intensity autocorrelation function to the scattered electric field autocorrelation function [41]. This yields the z-average self-diffusion coefficient $\langle D \rangle_z$ in the very low polymer concentration limit. The usual Stokes–Einstein relation is used to relate $\langle D \rangle_z$ to the z-average reciprocal hydrodynamic radius $\langle 1/R_H \rangle_z$

$$\left\langle D\right\rangle_{z} = \frac{k_{\rm B}T}{6\pi\eta} \left\langle \frac{1}{R_{\rm H}} \right\rangle_{z} \tag{22}$$

Defining the equivalent reciprocal of $\langle 1/R_{\rm H} \rangle_z$ as $r_{{\rm H},z} \equiv 1/2$ $\langle 1/R_{\rm H} \rangle_z$ allows the DLS and viscometric result to be compared. $\langle S^2 \rangle_{\eta}^{1/2}$ is a measure of the static dimensions of the polymer coil, whereas $r_{\rm H,z}$ is a measure of the polymer's equivalent hydrodynamic radius. In the nondraining limit it is expected [42] that $r_{\rm H} = 0.7 \langle S^2 \rangle$. The agreement of $\langle S^2 \rangle_{\eta}^{1/2}$ and $r_{\mathrm{H},z}$ in Table 1 are surprisingly close, reflecting relatively low polydispersity, and an excellent cross-check between ACOMP viscometry and batch DLS. This also suggests that addition of DLS to ACOMP would not add significant extra information, at least in a case such as this, and that the use of the viscometer in ACOMP is a simple and inexpensive alternative to DLS. Nonetheless, DLS might furnish an additional ACOMP measure of polydispersity in highly polydisperse of multi-modal populations, and so might find utility in the future.

4. Conclusions

It has been demonstrated that NIR can be usefully combined with ACOMP to provide another means of obtaining monomer concentrations during a polymerization reaction. Evaluation of the concentrations obtained by NIR and three other signals (RI and two UV wavelengths) yields concentrations in good agreement with, and within an RMS error of 5% of the average value. The corresponding $M_{\rm w}$ data conform well to the theoretical predictions of the QSSA for free radical polymerization in the limit where initiator decomposition time is long compared to the time for total monomer conversion. There is, nonetheless, a significant deviation from the QSSA over the first 25% of conversion, which may be due to impurities/inhibitors terminating early propagating radicals. The final $M_{\rm w}$ values were cross-checked by GPC and found to be in excellent agreement. Analysis in terms of $M_{w,inst}$ lends further strong support to the QSSA interpretation of the data.

This work sets the stage for application of the coupled NIR/ACOMP system to more complex systems, including co- and terpolymerization. Although this demonstration was made using only a single NIR wavelength, it will be possible in future work to use a larger number of wavelengths for full multi-variate analysis.

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