Online Monitoring of Composition, Sequence Length, and Molecular Weight Distributions during Free Radical Copolymerization, and Subsequent Determination of Reactivity Ratios

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ABSTRACT: Exploiting differences in refractivity and ultraviolet absorption between pairs of monomers and their associated polymers, automatic, continuous, online monitoring of polymerization reactions (ACOMP) was extended to copolymerization. ACOMP uses no chromatographic separation columns. Copolymerization of methyl methacrylate and styrene was chosen for developing the method. Both the instantaneous concentrations of comonomers and their incorporation rates into copolymer are obtained, which allows model-independent evolution of the average copolymer composition to be followed. Using the compositional information and simultaneous light-scattering data permits monitoring model-independent Mₕ (cumulative weight-average molecular weight), without requiring measurements in different solvents. Simultaneous use of a viscometer allows a cross check on the light-scattering data. Molecular weight and composition data are used to obtain the copolymer bivariate mass and composition distribution. Monomer reactivity ratios are found by an errors in variables method. The reactivity ratios and composition distribution allow sequence length distributions to be computed.

Introduction

There is an extensive literature on theoretical, experimental, and applied aspects of copolymerization reactions. Early work on kinetic models includes reports by Mayo and Lewis1 and Alfred and Goldfinger.2 It has long been recognized that the overall composition of the resulting copolymer depends on the ratios of the propagation rate constants known as the reactivity ratios. Other important copolymer characteristics include molecular weight, composition, and sequence length distributions.

The so-called bivariate distribution, in terms of copolymer composition and mass, was first treated theoretically in the 1940s1–5 and has since been revisited for systems containing multiple comonomers.6 To determine the bivariate composition and mass distributions from an existing polymer usually requires an involved process of cross-fractionation. Techniques used to determine molar mass and/or composition distributions include HPLC,7 thermal field-flow fractionation,8 Fourier transform infrared spectroscopy (FTIR),12 and other types of elution gradient chromatography13,14 for determining chemical composition, and size exclusion chromatography (SEC) and related techniques for mass distribution determination,15,16 including combinations of the above into integrated instruments.17 Furthermore, the sequence length distribution of a copolymer and associated averages are often important in determining the “blockiness” of the copolymer, microscopic morphology,18 and macroscopic properties, including solubility, blending and other thermodynamic behavior.19–22 Knowledge of the reactivity ratios and feed composition is often used to compute sequence length distributions on theoretical grounds.23 Sequence lengths have also been determined by dynamic scanning calorimetry24 and NMR,25,26 as well as chemical degradation of the copolymer and a subsequent analytical technique, such as gel permeation chromatography (GPC).27–30

The goal of this work is to extend a recently introduced technique for automatic, continuous, online monitoring of polymerization reactions (ACOMP) to the simultaneous, model-independent determination of the average composition, and mass distributions during free radical copolymerization reactions. Reactivity ratios can be computed as well as model-dependent sequence length distributions. To accomplish this, the differences in differential refractive index and ultraviolet absorption of comonomers A and B, in their monomeric and polymeric forms, are exploited to obtain the monomer and polymer composition as a function of time and, simultaneously, total monomer conversion. With this compositional information it is possible to develop a method for the meaningful analysis of light-scattering data, to determine the absolute weight-average mass Mₕ as a function of conversion, and hence also to determine the average Mₕ distribution.

ACOMP methods have been previously introduced and described.31 They have been extended to include continuous reactors,32 and have been applied to the detailed determination of acrylamide polymerization kinetics,33 chain transfer constants,34 monitoring of polydispersity evolution,35 and controlled radical polymerization.36 The aim of ACOMP is 3-fold: (1) to provide polymer scientists with a tool to study fundamental aspects of kinetics and mechanisms in new polymer synthesis, (2) to provide the means for optimizing reactions at the bench and pilot plant levels, and (3) to ultimately allow online monitoring and control of polymer production at the full industrial scale reactor level. A further benefit in the latter case is that, in
addition to helping control properties of the copolymer during the reaction, the final product emerges well characterized.

**Experimental Section**

**ACOMP Instrumentation.** The ACOMP technique itself has been adequately described but is undergoing constant improvement. Briefly, a small amount of reactor material is continuously removed from the reactor and mixed with a much larger volume of pure solvent. The continuously diluted polymer solution passes through a train of detectors comprising a home-built multianalyte light-scattering chamber, a home-built single capillary viscometer, a Shimadzu SPD-10AV ultraviolet spectrophotometer (UV), and a Waters 2410 differential refractometer (RI). No chromatographic columns are used, and no injections of discrete amounts of sample are made; i.e., this is not a flow injection method.

Significant modification of the automatic continuous dilution process was developed for this work, where it was necessary to ensure that the pump extracting from the reactor maintained a precisely known flow rate and that the abundant bubbles produced during the reaction did not enter the pump, since this would cause it to send a gas-laden sample stream to the detectors, destroying their monitoring capabilities. The problem of maintaining a precise volume withdrawal rate was solved by using two Hewlett-Packard 1100 isocratic pumps and attaching their outputs to a high-pressure micromixing chamber. The constant flow rate of the pump withdrawing from the reactor is maintained at the expense of increasing backpressure as the reaction liquid becomes more viscous as conversion proceeds. The problem of bubbles was solved by interposing an ISCO gradient programmer between the reactor and the input of the isocratic pump withdrawing from it. The mixing chamber of the gradient programmer has a debubbling feature, which allows all bubbles entering the chamber to be exhaled through the purge outlet. Still, because of the increase of viscosity of the reactor solution as polymerization proceeds, there came a point in each reaction in which either the pump pressure exceeded a preset safety level of 50 bar or cavitation caused the reactor-side pump to deprime. Hence, 100% conversion was not achieved in the reactions but typically ranged from 50% to 75%. Meanwhile, efforts are underway to develop a more robust automatic extraction/dilution system that will be effective to much higher reactor viscosities.

**Data gathering and analysis software.** Data gathering and analysis software was written by the authors. The response time of the system, due to mixing effects, was determined to be about 200 s, which means that reactions going to complete conversion on this time scale are at the limit of resolution. Since this response time is just a function of "plumbing", it can be reduced much further by appropriate design, if desired.

**Monomer Preparation and Polymerization Reactions.** Methyl methacrylate (MMA) and styrene (Sty), both from Aldrich, were freed from inhibitor by washing with 5% sodium hydroxide solution two times and then with water several times, until the water had a neutral pH. Monomers were dried over calcium sulfate and fractionally distilled and stored at 4 °C. Initiator, azobisobutyronitrile (AIBN), and the carrier solvent butyl acetate (BuAc) were used as received (Aldrich).

Before beginning the polymerization reaction, pure BuAc was pumped through the detector train to obtain the baseline of each instrument. After stabilization, Sty, in the desired initial concentration, was pumped at a rate of 0.16 mL/min from the reactor and continuously diluted with a flow of 1.84 mL/min of BuAc from the solvent reservoir. These same flow rates from the reactor and reservoir were maintained throughout the entire experiment. The diluted solution always reached the detector train at T = 25 °C, regardless of the reactor temperature. The Sty stabilization step was taken to ensure good UV detector calibration for the starting concentration of Sty. The reaction vessel, containing a total of 25% total monomer and 75% BuAc by mass, with a total reaction liquid mass of about 150 g, which had been previously purged for 15 min with N₂, was then lowered into a temperature-controlled bath at 65 °C. ACOMP withdrawal and dilution continued at the fixed ratio stated, and the reaction mixture was allowed to flow until stabilization of the detectors occurred.

The reactions were initiated by adding AIBN in powder form. The solution was magnetically stirred during the reaction. The reactor temperature was monitored with a thermocouple whose signal was integrated into the data acquisition software. Conversion of monomer to polymer was followed with the decrease of UV absorption of the monomer during polymerization reactions at 282 nm and with RI measurements. The value of $\text{in/}i_{c}$ (differential refractive index increment) of monomers, polymers, and initiator are given in Table 1, along with the labeling scheme for the various experiments, which were carried out at varying initial mass ratios of Sty and MMA. The differential refractive indices of poly(methyl methacrylate) (PMMA) and polystyrene (PS) were determined during ACOMP measurements of homopolymerization reactions according to the method recently developed by Broussau et al.

As mentioned above, reactions were terminated when the pump pressure reached a preset limit, or if the reactor draw pump deprimed. The contents of the reactor were added to methanol immediately after termination, and the polymer was precipitated for subsequent characterization.

**Determination of Comonomer and Polymer Concentrations from ACOMP.** The concentrations of the two comonomers in their monomeric form must be computed from the raw RI and UV data, as well as the concentrations of each incorporated into polymer. In this work $c_n$ refers to the mass concentration of species $A$ in g/cm³, whereas $[A]$ is the molar concentration. Throughout this work Sty will be taken as monomer A and MMA as B. The UV voltage $V_{UV}$ at a specific wavelength is composed of the signals from each of the four species:

$$V_{UV} = \frac{i_{UV}}{i_{cA}} c_{nA} + \frac{i_{UV}}{i_{cB}} c_{nB}$$

- Table 1. Monomer, Solvent, and Polymer Characteristics

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Solvent</th>
<th>Polymer</th>
<th>density (g/cm³)</th>
<th>$\beta$ (cm²/g)</th>
<th>$\lambda$ (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sty</td>
<td>BuAc</td>
<td>0.162</td>
<td>104.15</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>MMA</td>
<td>BuAc</td>
<td>0.019</td>
<td>100.12</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>AIBN</td>
<td>BuAc</td>
<td>0.043</td>
<td>xx</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>Sty, 100%</td>
<td>BuAc</td>
<td>0.0203</td>
<td>xx</td>
<td>1.04</td>
<td>0.000045</td>
</tr>
<tr>
<td>Sty/MMA 3/1</td>
<td>BuAc</td>
<td>0.166</td>
<td>xx</td>
<td>xx</td>
<td>0.00046</td>
</tr>
<tr>
<td>Sty/MMA 1/1</td>
<td>BuAc</td>
<td>0.149</td>
<td>xx</td>
<td>xxx</td>
<td>0.00045</td>
</tr>
<tr>
<td>Sty/MMA 1/3</td>
<td>BuAc</td>
<td>0.114</td>
<td>xx</td>
<td>xx</td>
<td>0.00008</td>
</tr>
<tr>
<td>MMA 100%</td>
<td>BuAc</td>
<td>0.099</td>
<td>xx</td>
<td>1.18</td>
<td>0.00013</td>
</tr>
</tbody>
</table>
where \(c_{mA}\) and \(c_{pa}\) are the monomer and polymer concentrations in the reactor of species A, and likewise for \(c_{mB}\) and \(c_{pb}\), and \(s\) is the fraction of the volume flow to the detector train coming from the reactor. Throughout this work \(s = 0.08\). In principle, all four species could each have useful and distinct UV absorption spectra, so that four equations could be generated by monitoring four separate wavelengths, which would fully determine the system, without additional signals or use of mass conservation equations. In this work, however, only styrene has significant UV absorption, so that at least one more data signal that yields an additional equation, coupled with two mass conservation equations, is needed.

The second signal comes from the RI. The refractive index detector voltage \(V_{RI}\) is given by

\[
V_{RI} = \left(\frac{dn}{dc_{mA}} c_{mA} + \frac{dn}{dc_{pa}} c_{pa} + \frac{dn}{dc_{mB}} c_{mB} + \frac{dn}{dc_{pb}} c_{pb}\right) dV\dn (2)
\]

where \(dV/dn\) is the calibration factor of the RI: i.e., the RI voltage output per index of refraction unit. Here, it is assumed that the refractivity of the solution is simply the sum of the refractivities of the component monomers and corresponding homopolymers. The summation of refractivities of the monomers in dilute solution should be nearly exact, whereas the assumption that the refractivity of a copolymer of given composition is the same as that of a mixture of homopolymers of the same concentration composition of A and B is less obvious. This approximation has been used extensively, however, since the first treatments of light scattering by copolymers were made and has been borne out through the years by experimental measurements.

Using conservation of mass of A and B in the reactor, together with the density differences existing among the monomers, polymers and solvent, allows the volume of fluid in the reactor to be expressed, ideally, as

\[
V_{reactor} = V_{solvent}(1 + R_A + R_B - \delta_A R_A p_A - \delta_B R_B p_B) (3)
\]

and conversion of monomer \(A, p:\)

\[
p_A = \frac{1 - \frac{c_{mA}(1 + R_A + R_B - \delta_B R_B p_B)}{c_{mA,0}(1 + R_A + R_B)}}{1 - \frac{c_{mB} \delta_A R_A}{c_{mA,0}(1 + R_A + R_B)}} (4)
\]

where \(p_A\) is the conversion of monomer B, \(R_A\) is the initial volume of monomer A to solvent volume, and likewise for \(R_B, c_{mA,0}\) is the initial concentration of monomer A, and

\[
\delta_A = 1 - \frac{p_A}{p_{mA}} (5)
\]

where \(p_{mA}\) and \(p_{pa}\) are the densities of monomer A and homopolymer A, respectively. Ideality of mixing is assumed in these derivations, \(p_{a}\) is obtained by simply interchanging subscripts A and B in each equation.

In the absence of density corrections \(p_A\) recovers the more familiar form

\[
p_A = 1 - \frac{c_{mA}}{c_{mA,0}} (6)
\]

The relationship between the polymer concentration and conversion is determined through conservation of mass to be

\[
c_{mA} = \frac{p_A m_{A,0}}{V_S(1 + R_A + R_B - \delta_A R_A p_A - \delta_B R_B p_B)} (7)
\]

where \(m_{A,0}\) is the initial mass of monomer A in the solvent volume \(V_S\).

Hence, analysis of the RI and UV data according to the above scheme yields a continuous record of the monomer concentrations \(c_{mA}(t)\) and \(c_{mB}(t)\), as well as the concentration of A and B involved in copolymer \(c_{A}(t)\) and \(c_{B}(t)\). Knowledge of these concentrations yields extraordinary analytical power for characterizing instantaneous average and integrated average properties of the copolymer, while it is being produced.

Most of the expressions involving concentrations in this work involve ratios, in which case the concentrations in the reactor and detector train can be used interchangeably, since the dilution factor, \(s\), will cancel in the numerator and denominator. Concentrations in the detector train must be used, however, when interpreting the detector signals. In those cases, an explicit statement will be made.

**Viscosity Determination.** The viscometer was a single capillary mounted via T-connectors to a Validyne Engineering differential pressure transducer, and has been discussed in detail. \(^{38}\) Total solution viscosity is

\[
\eta = \eta_s [1 + (\eta) c_p + k_p (\eta)^2 c_p^2] (8)
\]

where \(\eta_s\) is the pure solvent viscosity, \([\eta]\) is the intrinsic viscosity of the polymer, \(c_p\) is here the total copolymer concentration in the detector, and \(k_p\) is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers. \(^{42}\) The intrinsic viscosity is the extrapolation to zero concentration and zero shear rate of the reduced viscosity \(\eta_r\).

**Size Exclusion Chromatography (SEC).** Results of terminal \(M_w\) and \([\eta]\) from ACOMP were compared with SEC results, both because SEC continues to be the analytical method of choice for many polymer scientists determining \(M_w\), and because SEC gives a complete mass distribution. The SEC system used an Agilent 1100 isocratic pump, Polymer Laboratories PL gel 10 mixed B columns, an Anspec refractometer, a home-built light-scattering instrument previously described in detail, and a home-built light-scattering instrument identical to the one used for the ACOMP measurements. This instrument has been described previously, \(^{39}\) and its use for SEC has been demonstrated. \(^{40}\) The light-scattering analysis is different than that used for homopolymers, and this is discussed below.

**Determination of Reactivity Ratios, Composition, Mass, and Sequence Length Distributions from ACOMP**

In the simplest paradigm for propagation in free radical reactions, it is assumed that the rate of reaction for a given comonomer depends only on which monomer bears the radical at the chain terminus. For the molar concentrations of monomer \([A]\) and \([B]\), this leads to propagation equations of the form

\[
\frac{d[A]}{dt} = k_{AA}[A][A^*] + k_{BA}[A][B^*] (9a)
\]

\[
\frac{d[B]}{dt} = k_{BA}[B][B^*] + k_{AB}[B][A^*] (9b)
\]

where \(A^*\) and \(B^*\) are the propagating radicals of A and B, respectively. The quasi steady-state approximation assumes that the rate at which \([A^*]\) and \([B^*]\) change is low compared to the other rates in the reaction \((d[A^*]/dt \approx 0, \text{ and similarly for } B^*)\). The instantaneous composition of copolymer is then the Mayo–Lewis copolymer equation

\[
\frac{d[A]}{d[B]} = \left(\frac{[A]}{[B]}\right) = \frac{[A][r_A[A] + [B]]}{[B][r_B[B] + [A]]} (10)
\]
where the reactivity ratios $r_A$ and $r_B$ are defined as
\[ r_A = \frac{k_{BA}}{k_{AB}}, \quad r_B = \frac{k_{BB}}{k_{BA}} \] (11)

The instantaneous mole fraction of $[A]$ incorporated, $F_A$, is given by
\[ F_A = \frac{d[A]}{d[A + B]} \]
\[ = \frac{r_A f_A^2 + f_A (1 - f_A)}{r_A f_A^2 + 2f_A (1 - f_A) + r_B (1 - f_A)^2} \] (12)

where $f_A$ and $f_B$ are the mole fractions of monomer A and B, respectively, at any instant,
\[ f_A = \frac{[A]}{[A] + [B]}, \quad f_B = \frac{[B]}{[A] + [B]} \] (13)

$F_B$ is obtained by interchanging the subscripts A and B. These expressions form the basis for finding composition and sequence length distributions.

Reactivity Ratios from the Online Data. Leaving aside the early single point linear methods, contemporary approaches are based on an analytical solution of the copolymerization equation, such as the one given by Mayo,\(^1\) or the Skeist\(^4\) solution. Experimental errors emanate from measurements of initial monomer composition, final polymer composition and the degree of conversion. Many authors have shown that nonlinear methods minimizing $\chi^2$ and taking error propagation and individual errors on each of the measurements into account are superior in error handling.\(^45\text{--}49\) They avoid much of the distortion of the error structure that is inherent in the linear methods and have smaller and better defined regions for a given percent probability. In traditional experimental methods, to obtain the parameters $r_A$ and $r_B$, one needs the ratios of initial monomer concentrations, final monomer concentrations or the concentrations of the two monomers in the polymer, and the conversion ratio. While earlier nonlinear methods could take into account only one of these sources, more recent errors in variables methods (EVM)\(^30\text{--}34\) take errors emanating from all three of the measurements into account.

In this work a recent EVM developed especially for on-line monitored reactions and based on a numerical, rather than an analytical solution of the copolymerization equation is used to determine the reactivity ratios.\(^55\) As the monomer concentrations, $c_A$ and $c_B$, and therefore $[A]$ and $[B]$ are known throughout the reaction, the evolution of these values are compared with numerical solutions of the copolymerization equation as A and B are depleted. In this method the errors in UV and IR measurements during the reaction and also during the initial plateaus are used to find the variance of $[A]$ in the $\chi^2$ calculations.

\[ \chi^2 = \sum_{j=1}^{n} \sum_{i=1}^{m} (I_i - I_{i,j})^2 / \text{Var}(I_{i,j}) \] (14)

Here the index “$j$” denotes the experiment number and the index “1” the data point of that experiment. The variation $\text{Var}(I_{i,j})$ includes the contributions from fluctuations in the signal and the baseline value as well as the calibration constants of both the UV and RI measurements. The sum runs over all data points in all of the experiments.

Instead of using a minimization procedure, we sweep through the $r_A$, $r_B$ parameter space to obtain $\chi^2$ as a function of the two reactivity ratios generating a map. Although a $\chi^2$ map can be obtained from a single experiment, for a reliable set of reactivity ratios, three experiments with widely differing initial compositions are used.

Note that while in single point methods the composition drift is a problem to be dealt with, here it is actually made use of. Also, data taken during the whole reaction are used, instead of a single datum at the end of the reaction.

It should be noted that since there are calibration errors as well as random experimental errors, the fluctuation in the signal is not the sole source of the variation of the concentration $[A]$. When there are sufficiently enough data points without separate variations, it is permissible to use the data itself to obtain the variations.\(^56\)

The Instantaneous Average Composition Distribution. The remaining mass fraction of monomer A at any point is given by
\[ x = \frac{c_{mA}}{c_{mA} + c_{mB}} \] (15)

The total mass conversion of monomer is defined as
\[ p = 1 - \left( \frac{c_{mA} + c_{mB}}{c_{mA,0} + c_{mB,0}} \right) \frac{1 - \frac{1}{R_A} + \frac{1}{R_B}}{1 + \frac{1}{R_B}} \] (16)

The instantaneous average value of $A$ incorporated into polymer, in terms of mass, at any instant or degree of conversion is $z(p)$,
\[ z(p) = \frac{\text{d}c_{mA}(p)}{\text{d}c_{mA}(p) + \text{d}c_{mB}(p)} \] (17)

$p$ and $z$ can be computed from the online values of $c_{mA}$ and $c_{mB}$, so that a fractional population distribution, $ip/iz$ can be determined at each point during the reaction. The dependence on the instantaneous weight-average mass, $M_{w,\text{inst}}$, is discussed below. It is cautioned that taking derivatives of data with noise usually presents technical challenges if meaningful derivatives are to be found. (ip/iz) dz is the fraction of the copolymer population that has a fractional styrene mass content between $z$ and $z + dz$. Its computation requires taking a derivative of $p$ with respect to $z$, which is already built on derivatives of the data. Unless the data have exceptionally low noise, it will be more profitable to fit $c_{mA}$ and $c_{mB}$ to functional forms, from which analytical expressions for $ip/iz$ can be found online. An alternative is to build histogram representations of $ip/iz$, by building up concentrations in specified intervals of $z$.

Because ip/iz is built on the average instantaneous values, $z$, there is no knowledge of the width of the instantaneous value. The current methodology does not provide a means of experimentally determining this. Widths, based on theory, can be assumed and convoluted with $ip/iz$, to provide an approximation to the full bivariate distribution $w(l,u)$, discussed below.
The Sequence Length Distribution (SLD).

Whereas the average composition distribution is model independent, use of the Mayo–Lewis theory allows a model-dependent SLD to be computed.

Let \( W_{AA} \) be the probability that \( A^* \) adds to \( A \). Using the reactivity ratios, this can be expressed, at any conversion point \( p \), during the reaction as

\[
W_{AA}(p) = \frac{r_A f_A(p)}{f_A(p)(r_A - 1) + 1} \tag{18}
\]

The probability of having a sequence of \( k \) monomers in a row of type \( A \), followed by a monomer \( B \), \( P_{A,k} \), then follows the well-known geometric distribution

\[
P_{A,k}(p) = (1 - W_{AA}) W_{AA}^{k-1} \tag{19}
\]

\( P_{A,k}(p) \) from ACOMP measurements at each point \( p \) is hence the instantaneous sequence length distribution. The moments of this distribution are well-known. The instantaneous number-average sequence length of monomer \( A \), \( \langle N_A \rangle_n \), at conversion point \( p \), is

\[
\langle N_A \rangle_n(p) = \frac{1}{1 - W_{AA}(p)} \tag{20}
\]

while the instantaneous weight-average sequence length of \( A \), \( \langle N_A \rangle_w \) is

\[
\langle N_A \rangle_w(p) = \frac{1 + W_{AA}(p)}{1 - W_{AA}(p)} \tag{21}
\]

The cumulative values of the number and weight averages, \( \langle N_A \rangle_{n,cumu} \) and \( \langle N_A \rangle_{w,cumu} \), can be found by simply summing, or integrating, over all conversion points

\[
\langle N_A \rangle_{cumu}(p) = \int_0^p \langle N_A \rangle(p') dp' \tag{22}
\]

where the cumulative averages of any moment (e.g., \( n \) or \( w \)) is obtained by using the corresponding instantaneous average in the integrand.

To obtain the appropriate expressions for monomer \( B \), the subscript \( B \) is substituted for \( A \) in each variable in the above equations.

**Mw and Mass Distributions from ACOMP.**

Whereas differences in \( \delta n/\delta c \) between homopolymers of \( A \) and \( B \) allow ACOMP to follow the instantaneous compositional changes during copolymerization, this very difference leads to well-known complications in the interpretation of light-scattering data, compared to the straightforward situation when scattering from homopolymers is measured. Stockmayer et al. and Bushuk and Benoit derived relatively simple expressions for interpreting copolymer scattering data.

For homopolymers the Zimm single contact approximation is generally used to determine \( M_w \), the z-average mean square radius of gyration \( \langle S^2_z \rangle \), and the second virial coefficient \( A_2 \), via extrapolation to \( c_0 = 0 \) and \( q = 0 \) of the following expression

\[
\frac{K''c^2}{I(q,c_p)} = \frac{1}{M_w} \left( 1 + \frac{q^2 \langle S^2_z \rangle}{3} \right) + 2A_2 c_p + O(c_p^2) \tag{23}
\]

where \( c_p \) is the concentration of the homopolymer in the detector and \( q \) is the scattering vector with the usual definition

\[
q = \frac{4\pi n \sin(\theta/2)}{\lambda} \tag{24}
\]

where \( \theta \) is the angular position of the scattering detector. \( K' \) is an optical constant, given for vertically polarized light as

\[
K' = \frac{4\pi^2 n^2}{N_A \lambda^4} \tag{25}
\]

and

\[
\nu = \frac{\delta n}{\delta c_p} \tag{26}
\]

For the home-built light-scattering detector used in this work a vertically polarized diode laser of vacuum wavelength 677 nm was used. Absolute excess Rayleigh scattering ratios \( I(q,c_0) - \)total polymer solution scattering minus solvent scattering—were determined at each angle by the method reported in detail in refs 31, 33, and 37.

For copolymers in the dilute solution limit, it was realized long ago that the intensity of scattered light is not related to \( M_w \) as directly as in the homopolymer case. In fact, when the quantity \( K''c^2 \) \((q,c_p)\) is extrapolated to \( c_p = 0 \) and \( q = 0 \) for a copolymer, whose \( \langle S^2_z \rangle \) is present in a solution of total copolymer concentration \( c_p \), an apparent molecular weight, \( M_{ap} \), is obtained

\[
\frac{1}{M_{ap}} = \frac{c_p \lim_{q \to 0} 0}{I(q,c_p)} K''c^2 \tag{27}
\]

which is related to the true copolymer \( M_w \) as discussed below. \( M_{ap} \) is composed of the sum over all the compositional elements constituting the copolymer population, that is, each concentration element \( i \) has an assigned pair of values of composition and mass

\[
M_{ap} = \frac{1}{\nu} \sum_i \gamma_i \nu_i^2 M_i = \frac{1}{\nu} \sum_i \gamma_i \nu_i^2 M_i \tag{28}
\]

where \( \gamma_i \) is the weight fraction of the polymer population with a given pair of composition and mass values

\[
\gamma_i = \frac{c_i}{c_p} \tag{29}
\]

and \( \nu \) is the value of \( \delta n/\delta c_p \) measured for the copolymer solution, which is given by

\[
\nu = \frac{\delta n}{\delta (c_{PA} + c_{PB})} = \gamma_A (1 - \gamma) \nu_B + \gamma_B (1 - \gamma) \nu_A \tag{30}
\]

and \( y \) is the mass fraction of accumulated polymer composed of \( A \)

\[
y = \frac{c_{PA}}{c_{PA} + c_{PB}} \tag{31}
\]
Similarly, \( v_i \) is the incremental refractive index of the sub-population of copolymer of fraction \( \gamma_i \)

\[
v_i = z_i v_A + (1 - z_i) v_B
\]  

(32)

where \( z_i \) is the mass fraction of copolymer of mass \( M_i \) composed of A

\[
z_i = \frac{c_{pA,i}}{c_{pA,i} + c_{pB,i}}
\]  

(33)

using these definitions of \( \gamma_i, v_i, \) and \( z_i \) in eq 28 leads to Benoit’s expression

\[
M_{ap} v_i^2 = v_A v_B M_w + \nu_A (v_A - v_B) y M_A + \nu_B (v_B - v_A) (1 - y) M_B
\]  

(34)

where \( M_A \) and \( M_B \) are the weight averages of the portion of copolymer constituted by A and B, respectively, that is

\[
M_A = \frac{\sum z_i^2 c_{pA}}{c_p}
\]  

(35)

and

\[
M_B = \frac{\sum (1 - z)^2 c_{pB}}{(1 - y) c_p}
\]  

(36)

where \( c_{pA} \) is the concentration of polymers of weight fraction \( z_i \) with a mass \( M_i \). \( M_w \) has the usual definition

\[
M_w = \frac{\sum c_{p} M_i}{c_p}
\]  

(37)

To obtain the correct \( M_w \) traditionally, for a copolymer of unknown composition, it was hence necessary to perform light-scattering experiments in three different solvents (i.e., three different values each for \( v_A \) and \( v_B \)) to determine the three unknowns \( M_w, M_A, \) and \( M_B \). Only in the case of a homogeneous composition distribution is \( M_{ap} = M_w \).

Because \( M_{ap}, c_{pA} \) and \( c_{pB} \) are known at each sampling point \( i \) in the online experiments, however, it is possible to obtain the correct value of \( M_w \) for the copolymer at each instant of the ACOMP experiment. In fact, Benoit’s numbering over the index \( i \) lends itself naturally in an ACOMP experiment to finite intervals of conversion, as \( p \) goes from 0 to 1; i.e., ACOMP follows the incremental buildup of the final copolymer composition and mass distribution until the reaction is stopped or completed. As pointed out by Benoit,\(^{41}\) the use of a double sum over both composition and mass in eq 28 is avoided by introducing the single index \( i \), and bearing in mind that for a given composition there can be more than one corresponding mass: if the instantaneous width of the composition distribution is considered and/or if \( M_w(p) \) is not monotonic. In this latter case, ACOMP can follow the possible multivalued nature of the function \( \gamma_i(M) \), since composition and mass measurements are made simultaneously during the polymerization.

Over each conversion interval, \( i \), in the reaction the new increment to the polymer distribution has its own value of \( z_i \) over the interval given by

\[
z_i = \frac{\Delta c_{mA,i}}{\Delta c_{mA,i} + \Delta c_{mB,i}}
\]  

(38)

where \( \Delta c_{mA,i} = c_{mA,i} - c_{mA,i-1} \), and likewise for \( \Delta c_{mB,i} \).

Now, only in the case where \( z_i \) is constant—i.e., for a copolymer of homogeneous comonomer composition (ignoring the natural width of the composition distribution)—is there a simple relationship between \( M_w \) and \( M_A \) and \( M_B \)

\[
M_w = M_A + M_B
\]  

(for homogeneous composition only) \(^{39}\)

Here, we present an approach to finding \( M_w(p) \) from the measured values of absolute scattering I(\( q_c, c_p \)) and the continuous knowledge of \( c_{pa}(p), c_{pa}(p), c_{pa}(p), \) and \( c_{pa}(p) \) afforded by ACOMP. These latter concentrations allow immediate computation of \( y(p) \) by eq 31 and \( v_i(p) \) by eq 30. To aid in the solution \( M_w(p) \), it is advantageous to use a continuous representation of \( y(p) \), according to eq 17. If \( M_{w,inst}(p) \) is the instantaneous weight-average polymer mass produced in the conversion interval \( p \) to \( p + dp \) then \( M_A(p) \) can be written as

\[
M_A(p) = \frac{\int [z(p')^2 M_{w,inst}(p') dp']}{yp}
\]  

(40)

where \( M_{w,inst}(p) \) is given by\(^{35}\)

\[
M_{w,inst}(p) = \frac{\partial (p M_w)}{\partial p} = M_w(p) + \frac{p M_w}{\partial p}
\]  

(41)

Likewise, \( M_B(p) \) is found according to

\[
M_B(p) = \frac{\int [z(p')^2 M_{w,inst}(p') dp']}{yp}
\]  

(42)

The instantaneous apparent mass, \( M_{ap,inst}(p) \), is given by

\[
M_{ap,inst}(p) = \frac{\partial (p M_{ap})}{\partial p} = M_{ap}(p) + \frac{p M_{ap}}{\partial p}
\]  

(43)

With these substitutions, eq 34 becomes

\[
\nu_i^2 M_{ap} = \frac{a M_w + b \int z^2 m \ dp'}{p} + \frac{c \int (1 - z)^2 m \ dp'}{p}
\]  

(44)

where for economy of notation

\[
a = v_A v_B
\]  

(45a)

\[
b = v_A (v_A - v_B)
\]  

(45b)

\[
c = v_B (v_B - v_A)
\]  

(45c)

\[
m = M_{w,inst}(p)
\]  

(45d)

\[
m_{ap} = M_{ap,inst}(p)
\]  

(45e)
and the explicit dependence of each variable on \( p \) has been dropped. Multiplying both sides of eq 44 by \( p \) and taking the derivative of each side with respect to \( p \) yields

\[
\frac{\partial (p^2 M_{ap})}{\partial p} = a \frac{\partial (pM_w)}{\partial p} + b z^2 m + c(1 - z)^2 m \tag{46}
\]

Using eqs 41 and 43 we get

\[
\nu^2 m_{ap} + pM_{ap} \frac{dp}{dp} = m[a + bz^2 + c(1 - z)^2] \tag{47}
\]

using the integral form of eq 37

\[
M_w(p) = \int \frac{m \ dp'}{p} \tag{48}
\]

allows \( M_w(p) \) to be found by integrating the factored \( m \) in eq 47 to yield

\[
M_w(p) = \frac{1}{p} \int \left[ \frac{\nu^2 m_{ap} + pM_{ap} \frac{dp}{dp}}{a + bz^2 + c(1 - z)^2} \right] dp' \tag{49}
\]

Operationally, the numerical values of \( y(p), z(p), M_{ap}(p), \) and \( M_w(p) \), the latter computed from the derivative of \( M_{ap}(p) \) according to eq 43, can be inserted into eq 49 and integrated numerically, or forms resulting from fits to \( c_{na}(p), c_{nb}(p), \) and \( M_{ap}(p) \) can be inserted.

These computations lead to the important conclusion that, given the ability to monitor the light scattered by a dilute copolymer solution as the copolymer is produced, together with simultaneous measurements of \( c_{pa} \) and \( c_{ob} \), the true \( M_w \) of the evolving copolymer population can be monitored by ACOMP.

Equation 49 shows that the relationship between \( M_{ap} \) (p) and \( M_w(p) \) can evolve in a complex fashion. In the special case where \( \nu = 0; i.e., \) where \( \nu_A \) and \( \nu_B \) have opposite signs and \( y \) is such that the contributions in eq 30 cancel; \( M_{ap} \) can diverge to infinity since, due to a heterogeneous composition, the intensity scattered will not be zero. In the case of low composition drift and like sign values of \( \nu_A \) and \( \nu_B \) that do not differ greatly, the correction between \( M_{ap} \) and \( M_w \) will, in general, be small. This is the case in the current work.

For example, if \( c_{na}(t) \) and \( c_{nb}(t) \) follow ideal first-order kinetics (simple exponential decay), then \( p, y, \) and \( z \) can be parameterized in time. In the limit where density corrections to \( p \) are negligible, \( p(t), z(t), \) and \( y(t) \) are given by

\[
\begin{align*}
p(t) &= c_{na}(0) [1 - e^{-\alpha_A t}] + c_{nb}(0) [1 - e^{-\alpha_B t}] \tag{50}
y(t) &= \frac{1}{1 + c_{nb}(0) [1 - e^{-\alpha_B t}]} \tag{51} 
z(t) &= \frac{1}{1 + \frac{c_{na}(0) \ e^{-\alpha_A t}}{\alpha_A c_{na}(0)}} \tag{52}
\end{align*}
\]

In the current work \( M_{ap}(p) \) showed little change (see Results), for reasons to be discussed. Taking \( M_{ap} \) as constant in eq 49, with eqs 50–52, and using \( c_{na}(0) = c_{mb}(0) \) and \( \alpha_A \) and \( \alpha_B \) for experiment IV in Table 2 yields the ratio \( M_w/M_{ap} \) shown in Figure 1. The value is virtually unity throughout, reflecting the fact that this experiment and the others were never very far from azoetropy. Also shown in Figure 1 is a hypothetical case where \( M_{ap} \) is again constant, \( \alpha_A = 0.2 \), and \( \alpha_B = 0.2 \). In this case the correction factor changes modestly during conversion.

In the monitoring experiment the scattering, \( c_{pa} \), and \( c_{ob} \) are all determined as functions of time. Furthermore, total monomer conversion, defined in eq 16, can be simultaneously constructed from the measured values of the comonomer concentrations, so that \( M_w \) can be given at any instant of monitoring in terms of the time point \( t \), or the conversion point \( p \). The latter representation allows online approximations to the evolution of polydispersity to be made from a straightforward adaptation of the method recently described.
This allows the fractional mass distribution, \( \frac{\partial p}{\partial M_{\text{w,inst}}} \) at any point to be determined, either by the derivative or histogram methods. \( \frac{\partial p}{\partial M_{\text{w,inst}}} \) represents the fraction of the copolymer population with mass between \( M_{\text{w,inst}} \) and \( M_{\text{w,inst}} + \Delta M_{\text{w,inst}} \). This distribution can also be represented by histogram methods. \( p(z,M_{\text{w,inst}}) \) represents a curve in the space composed of \( z \) and \( M_{\text{w,inst}} \). To convert this into a surface vs \( z \) and \( M_{\text{w,inst}} \), it requires assumptions about the instantaneous widths of both \( z \) and \( M_{\text{w,inst}} \). This is considered in the next section.

**Model-Dependent Instantaneous and Cumulative Composition and Mass Distributions.** The instantaneous average composition and mass distributions treated up to this point are not dependent on any specific models. ACOMP will yield these average distributions based solely on the experimental data. The instantaneous averages can be fleshed out by invoking plausible models for the accompanying instantaneous distributions. These can be applied to each point, and integrated over conversion to yield the complete composition and mass distributions at each point in conversion, including for the final product.

Here, we consider the bivariate distribution proposed by Stockmayer.\(^5\) He proposed that when the monomer feed composition and the mean molecular weight and composition of the fraction polymerized are known, both the composition and chain length distributions can be obtained. In his theoretical model, the weight fraction of the part, with chain length \( L \) and composition deviation \( u = (\Phi - F_A), w(L,u) \) is given by

\[
w(L,u) \, dL \, du = \left[ \exp(-L/\lambda^*)/(1 - \beta_{\text{com}} + \beta_{\text{com}} L/\lambda^*) L \, dL \, \lambda^*/[\sqrt{2\pi F_{A} F_{B} Q}] \times \exp(-Lu^2/2F_{A} F_{B} Q) \right] \, du
\]

where

\[
Q = (1 - 4F_{A} F_{B} (1 - r_{A} r_{B}))^{1/2}
\]

\( \Phi_A \) is the molar fraction of \( A \) monomer units in a chain and \( \beta_{\text{com}} \) is the fraction of chains terminating by combination. The variable \( L \) is the length of a chain in monomer units, \( \lambda^* \) is the average number of living radical chains. When \( \beta_{\text{com}} = 0, \lambda^* = (M_{\text{w,inst}}/m_{\text{mon}})/2 \) and when it is 1, \( \lambda^* = (M_{\text{w,inst}}/m_{\text{mon}})/3. \) For the general case, it can be written as

\[
\lambda^* = \frac{(4 - \beta_{\text{com}})}{(B + \beta_{\text{com}})} \frac{M_{\text{w,inst}}}{m_{\text{mon}}}
\]

Here \( (M_{\text{w,inst}}/m_{\text{mon}}) \) is the ratio of the \( M_w \) of the fraction polymerized at a specific instant to the average molecular weight of the comonomers, \( m_{\text{mon}}. \)

In an actual polymerization reaction, all concentrations are functions of time or, equivalently, of the degree of conversion. For this reason, Stockmayer's formula is valid only for the instantaneous values during a reaction. To find the bivariate distribution of the resulting polymer, Stockmayer's \( w \) function must be integrated over the conversion.

**Results and Discussion**

Figure 2 shows raw data for a typical experiment (experiment IV in Tables 1 and 2). The increase in the RI is due chiefly to the conversion of MMA. These two signals yield the concentrations of the comonomers, the polymer, and the monomer conversions, according to the expressions above. The monotonic increase of both the light scattering and viscosity also show the effect of an increasing concentration of polymer. The temperature of the reaction is also shown in the graph over the principal one. The average was 64.8 °C with an rms temperature fluctuation of 0.29 °C.

Figure 3 shows concentrations in the detector train of Sty and MMA for several experiments (III, IV, and V in Table 1). The monomer decays are very well described by first-order fits, whose rate constants appear in Table 2. Data for a repeat of experiment V is also shown.
Monomer decay rates, final conversion, M_w, [η], and final weight-average sequence length values are given in Table 2. Also shown are SEC results for M_w and polydispersity indices M_n/M_w and M_w/M_n. The values appear somewhere between the 3:2:1 ratios for M_n/M_w: M_w expected for termination by disproportionation and 4:3:2 ratios expected for termination by recombination.

O’Driscoll and co-workers have done considerable work on copolymerization kinetics and their conclusion is that while the Mayo–Lewis equation is often adequate for determining composition it fails to account for the kinetics. That failure to account for the kinetics was noted by other authors and resulted in the cross termination constant φ. This was attributed to penultimate effects rather than to termination effects. Two more reactivity speed ratios s1 and s2 were introduced to account for this. If the kinetic data from Table 1 are plotted (not shown), there is also deviation from Mayo–Lewis kinetics, as far as polymerization rate as a function of initial feed composition is concerned.

Figure 4 shows the evolution of styrene monomer fraction x according to eq 15) vs total monomer conversion p. When the initial styrene fraction is 50% and 75% it increases throughout the reaction and when the initial fraction is 25% and 10% it monotonically decreases. This behavior is typical of systems with both reactivity ratios less than 1. Here it is clear that the azeotropic point is between Sty/MMA = 1/3 and 1/1, that 1 > r_MMA > r_Sty, and that the composition drift is not very significant in these experiments.

Use of Initial Monomer Decay Rates To Determine r_A and r_B. If the composition drift and initiator decomposition rate are slow, the concentrations of A* and B* can be assumed almost constant throughout the reaction, so that [A] and [B], at least at early values of conversion, will yield first-order decay kinetics of the form

\[ [A] = [A]_0 e^{-\alpha_A t} \]  \quad \text{and} \quad \[ [B] = [B]_0 e^{-\alpha_B t} \]  

where \( \alpha_A = k_{AA}[A^*] + k_{BA}[B^*] \)  \quad \text{(57)}  
\( \alpha_B = k_{BB}[B^*] + k_{AB}[A^*] \)  \quad \text{(58)}

Relative insensitivity of the right side of this equation to composition drift has been noted by Walling and Briggs, and Kelen and Tudos have used this fact in developing their extended method. using the ratio of Sty and MMA rate constants from eq 59. The values of r_Sty and r_MMA are 0.21 and 0.62, respectively. Even in the case of high drift, the initial decay rates—i.e., the initial slopes of semilog plots of monomer concentration vs time—should still yield a good approximation for the reactivity ratios.

Figure 5 shows the determination of r_Sty and r_MMA using the ratio of Sty and MMA rate constants from eq 59. The values of r_Sty and r_MMA are 0.21 and 0.62, respectively. Relative insensitivity of the right side of this equation to composition drift has been noted by Walling and Briggs, and Kelen and Tudos have used this fact in developing their extended method. Using the ratio of Sty and MMA rate constants from eq 59. The values of r_Sty and r_MMA are 0.21 and 0.62, respectively. Even in the case of high drift, the initial decay rates—i.e., the initial slopes of semilog plots of monomer concentration vs time—should still yield a good approximation for the reactivity ratios.

Parts a–c of Figure 6 show the \( \chi^2 \) contours of the EVM analysis obtained by comparing the monitored monomer depletion with the copolymerization equation described in the section “Reactivity Ratios from Online Data.” Figure 6a shows the \( \chi^2 \) contours for the statistically acceptable parts of the parameter space for the four experiments. Each experiment gives a long narrow valley as its region of confidence. The valleys are in the clockwise direction (from the steepest), for the experiments with 75%, 50%, 25%, and 10% Sty. The acceptable regions of each experiment intersect in the same area. Note that the regions of confidence corresponding to the acceptable
regions of experiments with 25% and 10% Sty are almost parallel.

In Figure 6b, the best fit values given by pairs of experiments are plotted. Five of the regions are closely packed, and the only outlying region is the long and narrow one for the joint confidence interval of the experiment pair with close initial compositions of 25% and 10% Sty. The five experiment pairs with widely differing initial compositions give small confidence regions and they are closely grouped. This close grouping indirectly validates the terminal model assumption in this work.

Figure 6c shows the joint confidence intervals for all four experiments. Each contour corresponds to one standard deviation. The best fit values $r_{Sty} = 0.225 \pm 0.01$ and $r_{MMA} = 0.621 \pm 0.01$ are very close to the $r_{Sty} = 0.21$ and $r_{MMA} = 0.62$ (shown by the crossed circle in Figure 6c) values, given by the approximate method based on monomer depletion rates.

While the method of using rate constants is convenient and follows immediately from the online data, the parameter search method is more rigorous, accounts quantitatively for error in the data, and, perhaps most significantly, applies to time-independent data. Hence, in principle, the polymerization reactions at a given temperature and starting ratios of monomer can be run at arbitrary and different concentrations of initiator and still be used for determining the reactivity ratios, whereas in the rate constant method of Figure 5 the same initiator concentration must be used in each experiment. The termination reaction and the cross-termination ratio effects can influence the simpler rate constant method but not the time-independent EVM.

Table 3 shows a compilation of reactivity ratios for a variety of solvents and initiator conditions.

Figure 6c shows the joint confidence intervals of the parameter space searches for the individual experiments: in clockwise order, starting from the steepest, V, IV, III, and II. (b) $\chi^2$ contours for combined data for experiment pairs. (c) $\chi^2$ joint confidence contours for the data in all four experiments (II, III, IV, V). The crossed circle represents $r_{Sty}$ and $r_{MMA}$ from the kinetic approach (Figure 5).

Table 3 shows a compilation of reactivity ratios for MMA/Sty from the literature and this work.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$r_{Sty}$</th>
<th>$r_{MMA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dioxane$^{65}$</td>
<td>0.56</td>
<td>0.53</td>
</tr>
<tr>
<td>acetone$^{65}$</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>DMF$^{65}$</td>
<td>0.38</td>
<td>0.45</td>
</tr>
<tr>
<td>cyclohexane$^{66}$</td>
<td>0.35</td>
<td>0.56</td>
</tr>
<tr>
<td>cyclohexanone$^{66}$</td>
<td>0.38</td>
<td>0.57</td>
</tr>
<tr>
<td>toluene$^{67}$</td>
<td>0.534</td>
<td>0.393</td>
</tr>
<tr>
<td>bulk$^{68}$</td>
<td>0.523</td>
<td>0.46</td>
</tr>
<tr>
<td>bulk UV irradiated$^{69}$</td>
<td>0.39</td>
<td>0.22</td>
</tr>
<tr>
<td>bulk$^{70}$</td>
<td>0.472</td>
<td>0.454</td>
</tr>
<tr>
<td>bulk$^{71}$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>bulk$^{71}$</td>
<td>0.37</td>
<td>0.61</td>
</tr>
<tr>
<td>bulk$^{71}$</td>
<td>0.57</td>
<td>0.41</td>
</tr>
<tr>
<td>bulk$^{71}$</td>
<td>0.275</td>
<td>0.314</td>
</tr>
<tr>
<td>bulk$^{71}$</td>
<td>0.225</td>
<td>0.621</td>
</tr>
</tbody>
</table>

* This work.

Figure 7 shows $z(p)$ and $y(p)$, for the 1/1 reaction (IV in Table 1). $y(p)$ is computed directly from the monomer concentrations for Sty and MMA, whereas $z(p)$ is computed directly from the first-order fits to the monomer concentrations, which can be obtained from Figure 3. Direct differentiation of the monomer concentration data to obtain $z(p)$ leads to considerable noise.

Figure 8a shows the average composition distributions for each experiment. Using the expressions for the experimentally found first-order decays of MMA and Sty allows the copolymer composition distribution $\pi(p)$ to be found analytically. These are shown, normalized to total polymer concentration in the detector, in Figure 8a. Because $r_{Sty}$ and $r_{MMA}$ are not widely different from each other, the compositional drift in the experiments is relatively small. As expected, the experiment closest to the azeotropic line gives the narrowest distribution.

Figure 8b shows the curves from Figure 8a integrated at each point with the Stockmayer distribution function given in eq 53.
Figure 7. z(p) and y(p), for the 1/1 reaction. y(p) is computed directly from the monomer concentrations for Sty and MMA, whereas z(p) is computed directly from the first-order fits to the monomer concentrations, which can be obtained from Figure 3.

Figure 8. (a) Normalized composition distributions. As expected, the experiment closest to the azeotropic line gives the narrowest distribution. (b) Composition distribution curves obtained from Figure 8a integrated at each point over the composition portion of the Stockmayer distribution function given in eq 60.

Figure 9a shows the instantaneous number and weight-average Sty sequence lengths, \( \langle N_{\text{Sty}} \rangle_n \) and \( \langle N_{\text{Sty}} \rangle_w \), respectively, vs conversion, for experiment V. These values are computed from eqs 19–21, using the best value of \( r_{\text{Sty}}(0) = 0.225 \). The cumulative averages are shown in the figure to be \( \langle N_{\text{Sty}} \rangle_{n,\text{cumu}} = 2.21 \) and \( \langle N_{\text{Sty}} \rangle_{w,\text{cumu}} = 3.40 \). The inset to the figure shows the actual instantaneous Sty sequence length distributions, \( P_{\text{Sty,k}} \), obtained when the conversion was equal to 0, 0.3, and 0.5.

Figure 9b shows the instantaneous number and weight-average MMA sequence lengths. The values were computed from eqs 19–21, substituting B (MMA) subscripts for all A subscripted variables, and using the best fit value, \( r_{\text{MMA}}(0) = 0.621 \). Table 2 gives the cumulative values of the weight-average sequence length for Sty, \( \langle N_{\text{Sty}} \rangle_{w,\text{cumu}} \), integrated over the entire conversion range, according to eq 22, and similarly for MMA.

Figure 10 shows \( M_w \) vs total monomer conversion, p, from the light-scattering data. The circles show SEC results for the end product of each reaction.

Figure 9b shows the instantaneous number and weight-average MMA sequence lengths. The values were computed from eqs 19–21, substituting B (MMA) subscripts for all A subscripted variables, and using the best fit value, \( r_{\text{MMA}}(0) = 0.621 \). Table 2 gives the cumulative values of the weight-average sequence length for Sty, \( \langle N_{\text{Sty}} \rangle_{w,\text{cumu}} \), integrated over the entire conversion range, according to eq 22, and similarly for MMA.

Figure 10 shows \( M_w \) vs total monomer conversion, p, from the light-scattering data. The circles show SEC results for the end product of each reaction.
above was applied to the ACOMP data. Namely, \( z(p)^2 \)
was fit to a polynomial of 3rd order, and eq 49 was
applied in order to arrive at the ratio \( M_w/M_n \). Because of
the quasi-azeotropy of the reactions, the light-
scattering correction factor due to compositional het-
erogeneity never exceeded 2%.

Since the measurements were made at small, but
finite concentration, however, there was a small cor-
rection due to the \( A_2 \) effect included in the data of Figure
10. Table 2 shows that \( A_2 \) varies monotonically between
its value for pure PMMA (0.00013) and pure PS (0.00045)
as the fractional content of Sty increases in the copoly-
mer. The values of \( A_2 \) in the table were found from
continuous dilution experiments performed on the end-
products of each of the reactions.

In principle, the complex average of \( A_2 \) found by light
scattering, which involves variable excluded volume
interactions for both a polydisperse population, as
detailed by Cassassa and others, and a chemically
heterogeneous population could be built from the knowl-
gedge of both composition and mass obtained in ACOMP,
as first treated by Stockmayer, Fixman, and Epstein. Because the \( A_2 \) correction in these experiments is small,
and composition drift minimal, the correction was made
simply by using the \( A_2 \) values from Table 2 obtained
from separate experiments on the endproducts.

The fractional error introduced by an uncertainty of
\( \Delta A_2 \) leads to an uncertainty in \( M_w \) given by

\[
\frac{\Delta M_w}{M_w} = 2\Delta A_2 M_w c_p
\]  
(60)

where \( c_p \) is the polymer concentration in the detector.
Under the conditions of the current experiments the
quantity \( 2A_2 c_p M_w \) is itself generally well below 10%, and
further error introduced by \( \Delta A_2 \) from varying composi-
tion will be much smaller than this. In general, it is
possible to arrange ACOMP conditions so that \( A_2 \) effects
are negligible, or at least minimized.

The circles in Figure 10 show that the SEC values
obtained on the reaction endproducts are virtually
identical to the ACOMP results.

Interestingly, \( M_w \) does not change significantly during
conversion in any of the experiments, except III, where
there is a measurable increase in \( M_w \). For this reason
we do not proceed to compute mass distributions based
on \( M_w,inst \). For ideal radical polymerization in the
absence of chain transfer, due to decreasing monomer to
initiator concentration ratio, \( M_w \) should decrease
linearly with conversion according to

\[
M_w(f) = M_w(0)\left[1 - \frac{f}{2}\right]
\]  
(61)

and the instantaneous value decreases as

\[
M_{w,inst}(f) = M_w(0)[1 - f]
\]  
(62)

There are two immediate possibilities for the near
constancy of \( M_w(f) \): (1) chain transfer to monomer and
(2) decreasing initiator concentration. For conceptual
simplicity, consider the homopolymeric case. In the case
of chain transfer to an agent \( S \), the reaction

\[
R + S \rightarrow S^* + P
\]

applies, where \( R \) is the propagating macroradical and
\( P \) is the dead polymer chain. \( S^* \) can subsequently
transfer to monomer to initiate a new chain, with rate
constant \( k_3 \). When \( k_3 < k_4 \), the initial transfer to \( R \) is
rate controlling, and it is well-known (e.g., ref 57) that the
instantaneous number-average degree of polymer-
ization \( N_{n,inst} \) is given by

\[
N_{n,inst} = \frac{k_p[m]}{Yk[R] + k_3[S]}
\]  
(63)

where \( Y = 1 \) for termination by recombination and \( Y = 2 \)
for termination by disproportionation. Hence, if the
transfer agent is the monomer itself, and \( k_3[m] > Yk[R] \),
then \( N_{n,inst} \) will remain constant.

Under the second possibility, if the initiator decay rate
is faster than or comparable to the conversion rate, then
\( [R] \) will decrease. If \( [R] \) decreases at a rate comparable
to the decrease in \([m]\), then \( N_{n,inst} \) can also remain
constant, even in the absence of any chain transfer. In
this case, however, \([m](t) \) would show a “stretched exponen-
tial” decay. The decays in Figure 2 appear too
well fit by a simple exponential to fit with this argu-
ment. A similar constancy in \( M_w \) vs conversion was also
found in ref 31, although no definitive reason for it was
found.

Figure 11 shows viscosity vs conversion and the
trends are similar to those for \( M_w \), i.e., no strong change
during the reactions, and both terminal viscosity and
\( M_w \) decrease as the initial fraction of Sty increases.
The viscosity measurements provide a good cross-check
on the light-scattering measurements insofar as they re-
quire no correction factors. On the other hand they do
do not directly furnish \( M_w \). The magnitudes of the viscosity
are such that the ACOMP measurements were made
far below the overlap concentration threshold, which is
roughly the reciprocal of \([η]\): i.e., on the order of 0.1
g/cm³. Viscosities were measured at more than 10 times
less than this value, so that the reduced viscosities
should be very close to \([η]\). An early treatment of how
\([η]\) varies with copolymerization was given by Stock-
mayer et al. Figure 12 shows raw SEC chromatograms for
the final products of both the copolymer and homopoly-
mer reactions. In SEC higher masses elute at lower elution
volumes, so that these chromatograms confirm the
trends revealed by \( M_w \) and viscosity, that average mass
decreases as the fraction of initial Sty increases. Table
1 shows the SEC values of \( M_w \) and \([η]\), which are in
excellent agreement with the ACOMP values. Addition-
ally, SEC provides the polydispersity indices, $M_w/M_n$ and $M_z/M_w$, which are also shown in Table 2.

With the $M_w$ and composition data available, the procedure outline above for computing the Stockmayer bivariate distribution was applied. An example of this is shown in Figure 13, for which the procedure was applied to the results of experiment V.

**Summary**

ACOMP instrumentation, procedures, and analyses have been adapted to monitoring free radical copolymerization reactions. The differences in comonomer and copolymer values of UV absorption and differential refractive index increments make it possible to obtain a continuous record of comonomer and copolymer concentrations.

From this, model-independent average instantaneous and cumulative composition distributions were computed. Use of simultaneous light-scattering data, together with the detailed composition data mean that, not only can the traditional method of making scattering measurements in three different solvents be avoided, but the evolution of $M_w$ can be followed, again, in model-independent fashion. Derivative techniques can also be used to follow the evolution of the polydispersity of the copolymer population, but were not applied here since $M_w$ was fairly constant throughout each reaction.

Well-accepted model-dependent assumptions about the nature of instantaneous composition and mass distributions allow the average data to be integrated to produce realistic representations of the full bivariate distribution. Further use of the differential viscometer yields both valuable information on the copolymer intrinsic viscosity and a cross-check on the masses derived from light-scattering behavior.

Reactivity ratios were computed using two distinct methods; initial kinetics, and a parameter space search. Furthermore, it is possible to determine the instantaneous and cumulative sequence length distributions and averages, based on the Mayo–Lewis model. In further work, combining the viscosity and light-scattering may provide information on branching. Deductions about kinetics and mechanisms can also be made from these combined measurements.

Table 4 summarizes which copolymer characteristics are model independent and which are model dependent.

Since the reactivity ratios of MMA and Sty are not widely different, there were not large composition drifts during the reactions. Hence, future work involving comonomers with widely different reactivity ratios could be used to assess the robustness of the entire technique for both broad composition and mass distributions.

Extending ACOMP to graft and block copolymerization should be possible, although there will certainly be both experimental and computational problems to resolve statistical and block copolymerization using "living" techniques, such as controlled radical polymerization and atom transfer radical polymerization, should provide fertile extension of ACOMP.

Finally, it is hoped that ACOMP for copolymerization will ultimately prove useful in controlling the quality of copolymers during industrial scale production.

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<table>
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<tr>
<th>Table 4. Model Independence and Dependence of the Copolymer Characteristics Determined by ACOMP</th>
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<td>av instantaneous composition</td>
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<td>inst. composition distribution</td>
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<tr>
<td>composition distribution</td>
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<td>reactivity ratios</td>
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</table>
Glossary of Terms

A: monomer A (and likewise for B)
A*: propagating radical A
[A]: molar concentration of monomer A
[A*]: molar concentration of propagating radical A
A,2: second virial coefficient
Cm: mass concentration of monomer A
CpA: mass concentration of A in polymeric form
fA: mole fraction of A left in solution (eq 16)
FA: instantaneous mole fraction of A incorporated into copolymer (eq 12)
I(q;Cp): total copolymer solution excess Rayleigh scattering minus that of the solvent (eq 23)
kAA: propagation rate for A adding to A*
kAB: propagation rate for B adding to A*
kP: second-order viscosity constant (eq 8)
K: light scattering optical constant (eq 29)
L: length of a chain in monomer units
L*: number-average length of live radical chains (eq 55)
Mm: average monomer mass of the comonomers
MA: cumulative weight-average of A portion of polymer (eq 35)
Mpq: mass obtained from
Mw: cumulative weight-average molecular weight (eq 37)
Mw,inst: instantaneous weight-average molecular weight (eq 41)
NA: Avogadro’s number
(NA)1/n: instantaneous number-average sequence length of A (eq 20)
(NA)w: instantaneous weight-average sequence length of A (eq 21)
(NA)cum: cumulative number-average sequence length of A (eq 22)
(NA)w,cum: cumulative weight-average sequence length of A (eq 22)
p: total monomer mass conversion (eq 16)
PA: conversion of monomer A
PA,k: sequence length distribution: probability of occurrence of a sequence of k monomers of type A, terminated by a monomer of type B
q: scattering vector amplitude (eq 24)
ρA: reactivity ratio of A (eq 11)
ρA,R: initial volume of monomer A/solvent volume, in the reactor.
(S2)z: 2-average mean square radius of gyration
u: composition deviation
w(l,u): weight fraction of polymers of degree of polymerization of l and composition deviation u (eq 53)
WpA: probability that A* adds to A (eq 22)
x: average mass fraction of monomer A left in solution (eq 15)
y: average mass fraction of A in copolymer form (eq 31)
z: instantaneous fraction of A incorporated into copolymer (eq 17)
αA: first-order decay constant of A
βcum: the fraction of chains terminating by combination
δA: 1 - ρm/ρA

[η]: weight-average intrinsic viscosity
[η]0: weight-average reduced viscosity
ΦA: fraction of A monomer units in a particular chain
λ: laser vacuum wavelength
ν: differential index of refraction of the copolymer solution is a given solvent (eqs 26, 30)
νA: differential index of refraction of homopolymer A in a given solvent
ρmA: density of monomer A
ρPA: density of polymer A
θ: light scattering measurement angle
χ2: mean square deviation between data and data fit (eq 14)

References and Notes
