Determination of Molecular Mass during Online Monitoring of Copolymerization Reactions

Pascal Enohnyaket, Tomasz Kreft, Alina M. Alb, Michael F. Drenski, and Wayne F. Reed*

Physics Department, Tulane University, New Orleans, Louisiana 70118

Received August 1, 2007; Revised Manuscript Received August 22, 2007

ABSTRACT: Light scattering determination of weight-average molecular mass M_w of a copolymer has historically required that measurements be made in at least three separate solvents of different index of refraction. Recently, however, it was demonstrated that, in principle, the evolution of M_w of a copolymer can be followed during copolymerization reactions using automatic continuous online monitoring of polymerization reactions (ACOMP). The continuous measurement of M_w by ACOMP is made possible by the fact that ACOMP provides the comonomer concentrations and absolute light scattering intensity at each instant of time during conversion and, hence, also yields the evolution of the average and instantaneous composition distribution. In this work, a workable and practical formalism for determination of M_w during reactions, using a single solvent, is developed for the case of N comonomers. The traditional method quickly becomes intractable since the number of solvents required grows as $N(N+1)/2$, and the number of auxiliary measurements of differential index of refraction of polymers in the solvents is $N(N+1)^2/2$. The formalism is applied to experimental cases involving copolymerization of styrene and methyl methacrylate, and M_w and apparent mass M_{ap} are compared. Results are correlated with traditional multisolvent determinations on endproducts and gel permeation chromatography approaches.

Introduction

Copolymers are becoming increasingly important for adhesives, high performance coatings, drug encapsulation and delivery, and many new materials with specific mechanical, optical, and electrical properties. The bivariate composition and mass distribution controls many aspects of the materials behavior, such as tensile strength, processability, surface, and phase stability aspects, etc. Determining the bivariate distribution can be very time-consuming and expensive, and it usually requires complementary techniques, such as thermal field-flow fractionation,[1] temperature rising elution fractionation (TREF),[2−4] Fourier transform infrared spectroscopy (FTIR),[5] and other types of elution gradient chromatography[6,7] for determining chemical composition and size exclusion chromatography (SEC) and related techniques for mass distribution determination,[8,9] including combinations of the above into integrated instruments.[10]

The growing ability of automatic continuous online monitoring of polymerization reactions (ACOMP) to monitor the evolution of the average bivariate distribution, in principle, not only means that the copolymer is “born” characterized but it should also be possible to control and tailor the distribution, thus leading to polymers of desired properties “on command” .

Light scattering is one of the standard methods for the determination of molecular weights of macromolecules. Its use is straightforward in the case of homopolymers,[11] but becomes considerably more complicated for copolymers. Stockmayer et al.[12] and Bushuk et al.[13] elaborated a formalism for finding the true weight-average molar mass M_w of a copolymer by making light scattering measurements of the copolymer in at least three different solvents of varying index of refraction. This approach was later expanded to the case of terpolymerization, and examples of measurements requiring a minimum of six solvents were presented.[14] Berry[15] has given a detailed compendium of scattering expressions in many different contexts, including general forms for the optically diverse scattering elements that occur in copolymers. Other specific copolymer examples have been published elsewhere.[16]

This work first generalizes the traditional scattering approach to the case of N comonomers, and then derives a compact form for determining copolymer M_w that is readily and practically usable, given a stream of continuous composition and light scattering data during copolymer synthesis, such as is provided by ACOMP.[17,18] Experimental data for copolymer synthesis (with $N = 2$) is analyzed by this formalism, and results are compared to the traditional multiple solvent approach and to results from gel permeation chromatography (GPC) using polymer standards.

Theoretical Section

Background. It has long been known that obtaining weight-average copolymer molecular mass M_w using light scattering is not nearly as straightforward as for homopolymers. In the following, N is the number of comonomers involved in the polymerization reaction. The previous literature cases for $N = 2$ (copolymer)[12,13] and $N = 3$ (terpolymer)[14] are generalized to arbitrary N. Throughout this work all concentrations are mass concentrations in g/cm^3, and use the symbol “c” . All molecular masses are in g/mol.

Following the homopolymer approach of extrapolating scattering data to zero concentration and zero scattering angle, one obtains an apparent mass M_{ap} that is related to the true weight-average mass M_w of the copolymer via the differential refractive increments $\nu_j = \partial n/\partial c_j$, of each comonomeric component $j = 1, 2, ..., N$, where c_j is the mass concentration (g/cm^3) of monomer j, and the respective weight-average of each comonomer in copolymeric form, M_{w1}, M_{w2}, ..., M_{wN}. Traditionally, measurements must be made in several different solvents where $\partial n/\partial c$ for each copolymeric component is different, so that the unknowns M_w, $M_{w,1}$, $M_{w,2}$, ..., $M_{w,N}$ can be found.

For *homopolymers* the Zimm[11] single contact approximation is generally used to determine M_w, z-average mean square radius

10.1021/ma0717338 CCC: \$37.00

of gyration $\langle S^2\rangle_z$ and the second virial coefficient A_2, via extrapolation to $c = 0$ and $q = 0$ of the following expression:

$$\frac{K'\nu^2 c}{I_R(q,c)} = \frac{1}{M_w}\left(1 + \frac{q^2\langle S^2\rangle_z}{3}\right) + 2A_2 c + O(c^2) \qquad (1)$$

where I_R is the absolute Rayleigh scattering ratio (cm^{-1}), c is the mass concentration ($\mathrm{g/cm}^3$) of the homopolymer in the detector, q is the scattering vector defined as

$$q = \frac{4\pi n}{\lambda}\sin(\theta/2) \qquad (2)$$

λ is the vacuum wavelength of the incident light, n is the solvent index of refraction, and θ is the angular position of the scattering detector. The approximation applies when $q^2\langle S^2\rangle_z \ll 1$. K' is an optical constant, which for vertically polarized incident light is given by

$$K' = \frac{4\pi^2 n^2}{N_A\lambda^4} \qquad (3)$$

In eq 1 ν is the $\partial n/\partial c$ of the copolymer, which can be measured directly. For copolymers, ν is simply the mass weighted sum of the refractivities of the corresponding homopolymer of each comonomer constituent. According to Stockmayer, this is especially true for block copolymers, and the error is not very large when applied to statistical copolymers. Over many decades, this approximation has proved to be robust.

The quantity $K'\nu^2 c/I_R(q,c)$ extrapolated to $c = 0$, and to $q = 0$ yields only an apparent molecular weight, M_{ap}:

$$\frac{1}{M_{ap}} = \lim_{\substack{c\to 0\\ q\to 0}} \frac{K'\nu^2 c}{I_R(q,c)} \qquad (4)$$

M_{ap} 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. One numbering scheme for this is to assign each concentration element i a pair of values of composition and mass

$$M_{ap} = \frac{1}{\nu^2}\sum \gamma_i \nu_i'^2 M_i \qquad (5)$$

where M_i is the molar mass of element i, ν_i' is the incremental index of refraction of element i, and γ_i is the weight fraction of element i, $\gamma_i = c_i/c$, c is the total copolymer concentration, and c_i is the concentration of element i. ν is the value of $\partial n/\partial c$ for the copolymer solution, which is given according to the above mass weighting by

$$\nu = \frac{\partial n}{\partial c} = \sum_{j=1}^{N} y_j \nu_j \qquad (6)$$

and y_j is the mass fraction of copolymer composed of comonomer j, $y_j = c_j/c$.

ACOMP provides a natural numbering scheme for the copolymer population by taking the concentration elements to be those produced sequentially in time during the synthesis reaction. In the ACOMP approach γ_i will be replaced by $\Delta c_i/c$, where Δc_i is the amount of copolymer concentration formed over sampling interval i ($\Delta c_i = c_i - c_{i-1}$, where c_i is the concentration of copolymer at the end of interval i, and M_i and ν_i are the average values over the interval. This usage is consistent with all continuous ACOMP approaches, where cumulative averages and average values of instantaneous quantities (e.g., average instantaneous weight-average molar mass $M_{w,inst}$) are measured.

In this work the subscript j refers to the monomer type, $j = 1$ to N, whereas i refers to a concentration element. ν_i' in eq 5 is given by

$$\nu_i' = \sum_{j=1}^{N} F_{j,i}\nu_j \qquad (7)$$

where $F_{j,i}$ is the mass fraction of copolymer of mass M_i composed of comonomer j for the element i[19]

$$F_{j,i} = \frac{\Delta c_{j,i}}{\sum_j \Delta c_{j,i}} = \frac{\Delta c_{m,j,i}}{\sum_j \Delta c_{m,j,i}} \qquad (8)$$

where $c_{m,j,i}$ is the concentration of comonomer j at interval i, and $\Delta c_{j,i} = c_{j,i} - c_{j,i-1}$and $\Delta c_{m,j,i} = c_{m,j,i} - c_{m,j,i-1}$. $F_{j,i}$ has been termed $F_{inst,j,i}$ in other publications from this group[20,21] to reflect the fact that $F_{j,i}$ is the instantaneous fraction of comonomer j incorporated into chains formed over interval i. Using these definitions leads to Benoit's expression for the $N = 2$ case,

$$M_{ap}\nu^2 = \nu_1\nu_2 M_w + \nu_1(\nu_1 - \nu_2)y_1 M_{w,1} + \nu_2(\nu_2 - \nu_1)(1 - y_1)M_{w,2} \qquad (9)$$

where $M_{w,j}$ is the weight-average of the portion of copolymer constituted by comonomer j, defined with the ACOMP Δc_i notation as

$$M_{w,j} = \frac{\sum F_{j,i}{}^2 \Delta c_i M_i}{y_j c} \qquad (10)$$

M_w has the usual definition

$$M_w = \frac{\sum \Delta c_i M_i}{c} \qquad (11)$$

In order 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, with three different values each for ν_1 and ν_2, to determine the three unknowns M_w, $M_{w,1}$ and $M_{w,2}$.

Use of Average Comonomer Composition Parameters. Benoit also provided a useful alternative representation of M_{ap} in terms of mass weighted moments of the copolymer composition distribution. Generalizing his method to N comonomers, $F_{j,i}$ is expressed as

$$F_{j,i} = y_j + \delta_{j,i} \qquad (12)$$

where $\delta_{j,i}$ is the deviation of the fractional composition of comonomer j in the element i from the average fraction y_j of comonomer j in the whole copolymer population. Using eq 12 in eq 7, then substituting into eq 5 (with $\Delta c_i/c$ in place of γ_i), and then simplifying and factoring, yields the alternative to eq 9

$$M_{ap} = M_w + 2\left(\frac{\nu_1 - \nu_2}{\nu}\right)P_1 + \left(\frac{\nu_1 - \nu_2}{\nu}\right)^2 Q_1 \qquad (13)$$

where P_1 is the mass-weighted first moment of the composition distribution for comonomer 1

$$P_1 = \frac{\sum c_i M_i \delta_{1,i}}{c} \tag{14}$$

and Q_1 is the mass weighted second moment of the composition distribution for comonomer 1.

$$Q_1 = \frac{\sum c_i M_i \delta_{1,i}{}^2}{c} \tag{15}$$

For the case where $N = 2$, $P_2 = -P_1$, and $Q_2 = Q_1$. Benoit and Bushuk have noted that P_1 and Q_1 vary between the limits

$$-y_1 M_w \le P_1 \le (1 - y_1) M_w \tag{16a}$$

$$0 \le Q_1 \le [1 - y_1(1 - y_1)] M_w \tag{16b}$$

If the mass distribution is monodisperse (i.e., M_i = constant) then $P_1 = 0$, although $Q_1 \neq 0$ in this case, unless there is also no compositional heterogeneity. In the case where the copolymer sample consists of a mixture of two homopolymers, then $P_1 = y_1(1 - y_1)[M_{w,1} - M_{w,2}]$, and $Q_1 = y_1(1 - y_1)[(1 - y_1)M_{w,1} + y_1 M_{w,2}]$.

Generalization to *N* Comonomers. Equation 13 was generalized to $N = 3$ previously.[14] Here, eq 9 is generalized to arbitrary N. Using eq 7, substituting into eq 5, expanding and using the various definitions and notation above, M_{ap} can be expressed, after a considerable number of manipulations, as

$$\nu^2 M_{ap} = \sum_{j=1}^{N} y_j \nu_j^2 M_{w,j} + 2 M_w \nu_1 \nu_2 + \frac{2}{c} \sum_i \Delta c_i M_i \{\Omega_i \nu_1 \nu_2 + \sum_{k=j+2}^{N} \sum_{j=1}^{k-1} F_{j,i} F_{k,i} \nu_j \nu_k\} \tag{17a}$$

where

$$\Omega_i = -F_{1,i} - F_{2,i} - 2\sum_{j=3}^{N} F_{j,i} + F_{2,i}\sum_{j=3}^{N} F_{j,i} + F_{1,i}\sum_{j=2}^{N} F_{j,i} + \sum_{j=3}^{N} F_{j,i}{}^2 + 2\sum_{k=j+1}^{N}\sum_{j=3}^{k-1} F_{j,i} F_{k,i} \tag{17b}$$

The minimum number of different solvents in which scattering measurements on the copolymers must be made is computed from N terms in ν_j^2 plus $N!/[2!(N - 2)!]$ cross terms in $\nu_j \nu_k$. The number of solvents needed increases at an alarming rate, viz.

$$\text{minimum no. of solvents} = \frac{N(N + 1)}{2} \tag{18a}$$

The number of $\partial n/\partial c$ values that must be known for the different comonomer species in polymer form in different solvents, plus $\partial n/\partial c$ of the copolymer is $N + 1$ times this:

$$\text{minimum no. of } \partial n/\partial c \text{ values} = \frac{N(N + 1)^2}{2} \tag{18b}$$

While the above treatment is exact, it is enormously unwieldy in practice. For the simplest case, that of $N = 2$, nine different differential refractive index values must be known. For a terpolymer, this becomes 24 values, and for $N = 5$, it becomes 90 values! Clearly an alternative method is needed.

ACOMP provides a direct means of determination of M_w for N comonomers in a single solvent.

Fortunately, ACOMP allows detailed characterization of all relevant copolymer parameters to be calculated, during synthesis, and in a single solvent. Only $N + 1$ values of $\partial n/\partial c$ are needed; e.g., only four values are needed for a terpolymer characterization vs 24 values for the multisolvent method.

ACOMP allows at each instant of time the measurement of multiangle light scattering and the concentration of each comonomer j, $c_{m,j}(t)$. Together with mass balance, the $c_{m,j}(t)$ allows computation of the corresponding concentration of comonomer j in copolymeric form $c_j(t)$. Hence, the total fractional conversion of all comonomers $f(t)$, is computed from the concentration of each copolymeric component at time t, $c_j(t)$, and the initial concentrations of comonomer $c_{m,j,0}$ according to

$$f(t) = \frac{\sum_j c_j(t)}{c_{m,0}} \tag{19}$$

where $c_{m,0}$ is the total initial concentration of comonomer; i.e. $c_{m,0} = \sum_j c_{m,j,0}$. The fractional conversion of each separate comonomer j, $f_j(t)$ is given by

$$f_j(t) = \frac{c_j(t)}{c_{m,j,0}} \tag{20}$$

Knowledge of $c_j(t)$ also yields the cumulative fraction of each component $y_j(t)$, introduced above, via

$$y_j(t) = \frac{c_j(t)}{\sum_j c_j(t)} \tag{21}$$

Furthermore, the average instantaneous composition of chains forming at instant t, $F_j(t)$ is given in differential form by[22]

$$F_j(t) = \frac{\partial c_j(t)}{\partial \sum_j c_j(t)} = \frac{\partial c_{m,j}(t)}{\partial \sum_j c_{m,j}(t)} \tag{22}$$

Equation 22 uses the fact that $dc_{m,j}(t) = -dc_j(t)$, since the concentration increment of comonomer j lost over time element dt appears as comonomer j in polymeric form. $F_j(t)$ is a direct measure of average composition drift of comonomer j.

Because ACOMP allows average instantaneous and cumulative compositions to be followed, as just outlined, and because multiangle light scattering is simultaneously obtained, so that $M_{ap}(t)$ is computed during copolymerization reactions, it is hence possible to manipulate and integrate the above equations and to determine M_w, $M_{w,1}$, $M_{w,2}$, ..., $M_{w,N}$ continuously during the reaction. Thus, ACOMP both avoids the use of multiple solvents and provides continuous values of composition and molar masses. This latter allows the possibility of controlling reactions to provide copolymers of desired composition and mass distributions, and also means the copolymer is “born characterized” , which can avoid tedious and costly “post-mortem” analyses of the endproduct.

To derive the appropriate forms for ACOMP analysis it is convenient to work in a continuous representation and express M_w and M_{ap} as a function of f, in integral form:

$$M_w(f) = \frac{1}{f}\int_0^f M_{w,inst}(f')\, df' \tag{23}$$

Equation 5 can then be cast as

$$M_{ap}(f) = \frac{1}{\nu^2 f}\int_0^f M_{w,inst}(f')\, df' \tag{24}$$

where $M_{w,inst}(f)$ is the instantaneous value of M_w at f, and it is recalled that $M_w(f)$ is the cumulative weight-average up to f. Furthermore,

$$\nu'(f) = \sum_j F_j(f)\nu_j \tag{25}$$

It is easily shown that any instantaneous quantity $q(f)$ is related to its cumulative value $Q(f)$ via

$$q(f) = \frac{d[fQ(f)]}{df} = Q(f) + f\frac{dQ}{df} \tag{26}$$

e.g.

$$M_{w,inst}(f) = M_w(f) + f\frac{dM_w(f)}{df} \tag{27}$$

and

$$F_j(f) = y_j(f) + f\frac{dy_j(f)}{df} \tag{28}$$

Hence,

$$M_{ap}(f) = \frac{1}{\nu^2 f}\int \nu'^2 \frac{d(f'M_w(f'))}{df'}\, df' = \frac{1}{\nu^2 f}\int \nu'^2\, d(f'M_w(f')) \tag{29}$$

from which it can readily be shown that

$$M_w(f) = \frac{1}{f}\int \frac{d[\nu(f')^2 f' M_{ap}(f')]}{\nu'(f')^2} \tag{30}$$

or

$$M_w(f) = \frac{1}{f}\int \frac{d\left[f' M_{ap}(f')\left(\sum_j y_j(f')\nu_j\right)^2\right]}{\left(\sum_j F_j(f')\nu_j\right)^2} \tag{31}$$

While this integral may seem formidable to integrate, especially in an experimental situation, it is actually very convenient and simple to perform numerically, as follows. The independent variable during an ACOMP experiment is time, against which *all* ACOMP values are *automatically* parametrized. Hence f, y_j, M_{ap}, and y_j, once computed from the relevant ACOMP detector signals, are automatically parametrized against t, and any combination of values can be parametrized against any other combination. Hence, the very peculiar differential $d[\nu(f')^2 f' M_{ap}(f')]$ in eq 30 can be formed, once F_j is also determined, and the denominator in the integrand, $\nu'(f')^2$, also formed, and the numerical integration of the latter against the former can be carried out immediately.

One important point concerns the difference between the cumulative values computed directly from the detector signals, such as $M_{ap}(t)$, $c_j(t)$, $\nu(t)$, $y_j(t)$, etc. and the instantaneous values, such as $F_j(t)$, that are computed from derivatives of the cumulative values. In the computation of $M_w(f)$ above, all the quantities appearing are cumulative, except F_j. Taking derivatives of data with inherent noise can lead to widely scattered values. Hence, it is generally necessary to apply a smoothing or fitting approach to computing the instantaneous quantities. In the case of eq 31, if the $c_j(t)$ are smoothed or fit, then all $F_j(t)$ can be computed from derivatives of the $c_j(t)$.

Once $M_w(f)$ is obtained, other characteristics of the copolymer can be computed during synthesis. In particular, setting $M_i = M_{w,inst}(f)$ in eqs 10, 11, 14, and 15 allows computation in each instant of $M_{w,1}$, $M_{w,2}$, ..., $M_{w,N}$, as well as P_1, Q_1, and any mass averaged or other moments of the composition distribution.

An expression similar to eq 31 was previously derived for $N = 2$ in the ACOMP context. Besides the restriction to $N = 2$, the expression required derivatives of $M_{ap}(f)$, in addition to derivatives of $y_j(f)$, making it much more difficult to apply in practice.[18]

Assessing the Magnitude of M_{ap}/M_w in Copolymerization ($N = 2$). It is not obvious by just regarding any of the several equations relating M_{ap} to M_w how much the ratio M_{ap}/M_w will differ from unity. One way to visualize this is by considering common forms for mass and composition drift in free radical copolymerization. The instantaneous mass as a function of conversion $M(f)$ is often found to be of the form

$$M(f) = M_0(1 - \beta f), \quad 0 \le \beta \le 1 \tag{32}$$

where M_0 is the initial instantaneous mass and β is a constant. In the quasi-steady-state approximation,[23,18] $\beta = 1$ when the initiator lifetime is long compared to the total time of the reaction, and no other processes such as transfer to solvent, monomer, polymer, or other agent occurs. In many instances $M(f)$ remains constant, or approximately constant, in which case $\beta = 0$.

Likewise, a simple expression for drift is

$$y_1(f) = y_{1,0} + \alpha f, \quad -\mathrm{y}_{1,0} \le \alpha \le 1 - \mathrm{y}_{1,0} \tag{33}$$

From eq 28 above,

$$F_1(f) = F_0 + 2\alpha f \tag{34}$$

So that

$$\delta_1(f) = \alpha(2f - 1) \tag{35}$$

and the Benoit composition parameters can be expressed in integral form

$$P_1 = \frac{1}{f}\int \delta_1(f')M(f')\, df' \tag{36}$$

and

$$Q_1 = \frac{1}{f}\int \delta_1(f')^2 M(f')\, df' \tag{37}$$

To yield, at $f = 1$

$$P_1 = \frac{M_0\alpha\beta}{6} \tag{38}$$

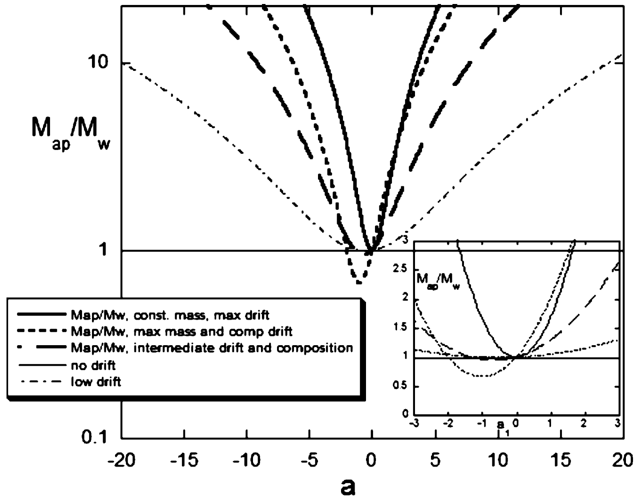

Figure 1. Theoretical predictions of M_w and for different scenarios. a_1 is defined in eq 40.

and

$$Q_1 = M_0\alpha^2\left[\frac{1}{3} - \frac{\beta}{6}\right] \tag{39}$$

P_1 and Q_1 are then substituted into eq 13 to compute M_{ap}/M_w. Figure 1 shows some predictions for M_{ap}/M_w vs a_1 for five cases; (i) the trivial case of no composition drift, $\alpha = 0$, with β taking any value from 0 to 1, and $M_{ap}/M_w = 1$ for all a_1 in this case; (ii) the case of no mass drift ($\beta = 0$) and maximum composition drift ($\alpha = 1$); (iii) the case of maximum mass and composition drift ($\alpha = 1$, $\beta = 1$); (iv) the case of intermediate composition and mass drift ($\alpha = 0.5$, $\beta = 0.5$); (v) low composition and mass drift ($\alpha = \beta = 0.2$). As is well-known $M_{ap}/M_w = 1$ for $a_1 = 0$ (i.e., $n_1 = n_2$). It is seen that the error can become very large as a_1 grows, in all cases shown, except those of low or no composition drift. In the graph

$$a_1 = \frac{\nu_1 - \nu_2}{\nu} \tag{40}$$

The inset to Figure 1 shows that M_{ap}/M_w is not generally symmetric about the origin with respect to $+a_1$ and $-a_1$. If a_1 is replaced by a_2 then M_{ap}/M_w vs a_2 is the mirror image of M_{ap}/M_w vs a_1 about the ordinate axis, since $a_2 = -a_1$.

Some Important Limiting Cases for $N = 2$. As pointed out, $M_{ap} = M_w$, if there is no composition drift or if $\nu_1 = \nu_2$. An important case concerns water-soluble polymers. The vast majority of water-soluble polymers in aqueous solutions (without extremely high ionic strength) typically range from 0.1 to 0.2 cm^3/g; e.g., most proteins have $\partial n/\partial c \sim 0.15$. Most aqueous copolymers will hence have $0 \leq |a_1| \leq 1$, which should lead to values of M_{ap}/M_w not far from unity for cases of small to moderate drift.

Another case involves acrylic monomers, where in general $\partial n/\partial c$ are quite similar in a given solvent. Hence, except in the cases where $\partial n/\partial c$ is close to zero, or the values straddle zero, $M_{ap} \sim M_w$. Table 1 summarizes some limiting cases.

Interpolymer Interactions. Angular Dependent Scattering. In the case where the polymer size is not constrained to be much smaller than λ, and $\partial n/\partial c$ of one or more comonomers is close to zero, the angular dependence of the Zimm plot (Kc/I_R vs q^2) becomes distorted, and the $\langle S^2\rangle_z$ obtained is now an apparent value. Designating $R_{ap}{}^2$ as the apparent value of $\langle S^2\rangle_z$ obtained in the homopolymeric analysis of the copolymer scattering, it can be expressed as[24,25]

$$R_{ap}{}^2 = \beta_1{}^2R_1{}^2 + \beta_2{}^2R_2{}^2 + 2\beta_1\beta_2R_{12}{}^2 \tag{41}$$

where

$$\beta_1 = y_1\nu_1/\nu \text{ and } \beta_2 = y_2\nu_2/\nu \tag{42}$$

$R_1{}^2$ and $R_2{}^2$ are the mean-square radii of gyration about the centers of gravity of the copolymeric portions of the copolymer constituted by comonomer 1 and 2, respectively, and $R_{12}{}^2$ is given by the relation

$$R_{12}{}^2 = (1/2)[R_1{}^2 + R_2{}^2 + (G_1G_2)^2] \tag{43}$$

in which $(G_1G_2)^2$ is the mean-square distance between the centers of gravity of 1 and 2.

For comonomers with similar refractive indices in either Θ or good solvents, the equation for $R_{ap}{}^2$ above gives the desired results for the radius of gyration. If ν_2 is very low compared to ν_1, then $R_{ap}{}^2 \approx R_1{}^2$.

The relationship between scattering and intermolecular excluded volume is likewise more complex than in the homopolymer case, so that the A_2 measured by eq 1 is also only an apparent value. The excluded volume that determines A_2 is a function of the size of the whole copolymer chain, whereas the different comonomers in the copolymer chain scatter light differently, depending on their respective values of $\partial n/\partial c$.

In the experimental cases presented below the copolymers were Rayleigh scatterers, obviating the use of the $R_{ap}{}^2$ analysis, and the concentration in the detector train was low enough to avoid any significant effect of interactions on scattering intensity.

Experimental Section

Two reactions were chosen to test and illustrate the above results; (i) copolymerization of butyl acrylate (BA) and styrene (sty) in butyl acetate (BuAce) in the starting mass ratio of 50/50, (ii) the same copolymerization reaction carried out in DMF (dimethylformamide), where $\partial n/\partial c$ of the comonomers is less than in BuAce. The reaction conditions are given in Table 2.

ACOMP measurements for experiment no. 1 were carried out on the first commercial ACOMP prototype unit delivered to Tulane University from Polymer Laboratories (Church Stretton, U.K., now a division of Varian Inc.) in August 2006. This unit is based on the authors' previous ACOMP designs and uses dual dilution stages with high and low pressure mixing and advanced National Instruments based software for data acquisition and instrument control. The detector train included a PL differential refractive index detector (RI), a Brookhaven Instruments Corp. BI-M_wA multiangle light scattering photometer (LS), a Shimadzu VP-10 dual wavelength UV spectrophotometer (UV), and a custom built single capillary viscometer. Some ACOMP experiments were also carried out on a

Table 1. Some Limiting Cases for $N = 2$

type of system	conditions on ν_1, ν_2	restrictions on composition drift	restrictions on M_{ap} drift	result
any	$\nu_1 = \nu_2$	none	none	homopolymer analysis is valid
any	ν_1, ν_2 arbitrary	very low drift	none	homopolymer analysis approximately valid
e.g., acrylics	$\nu_1 \cong \nu_2$	none	none	homopolymer analysis approximately valid
aqueous	$0.1 \leq \nu_1, \nu_2 \leq 0.2$	low to moderate	low to moderate	homopolymer analysis approximately valid

Table 2. Summary of Reaction Conditions[a]

experiment	1	2
solvent	BuAc	DMF
solvent density(g/cm^3)	0.881	0.949
n_{solvent}	1.394	1.431
T (°C)	65 then stepped to 75	75
% initiator by tot. mass	1.2	2.4
$\partial n/\partial c$sty	0.1595	0.1095
$\partial n/\partial c\|_{\mathrm{BA}}$	0.0338	−0.0103
$\partial n/\partial c\|_{\mathrm{PS}}$	0.2040	0.1506
$\partial n/\partial c\|_{\mathrm{pBA}}$	0.0840	0.0410
c_{sty} in det. (g/mL)	0.001 64	0.001 51
c_{BA} in det. (g/mL)	0.001 64	0.001 50
dilution ratio	1:110	1:90
$f_{\mathrm{final,sty}}$	0.70	0.9
$f_{\mathrm{final,BA}}$	0.85	0.92
reaction rate:[b] STY	NA	2.50E-4
reaction rate:[b] BA	NA	1.35E-4
$[\eta]_{\mathrm{w}}$[c]	9.9	4.3

[a] NA, not applicable. Starting mass of BA and styrene was 50%/50% in each case. [b] Defined as α if conversion if fit according to $f(t) = 1 - \exp(-\alpha t)$. [c] Final ACOMP value

custom built instrument, previously described. Data analysis followed procedures previously established by the authors, using customized software.

The custom-built five pump ACOMP system reported by Mignard et al.[26] was used for experiment no. 2 (carried out shortly after Hurricane Katrina, when the PL system had not yet been delivered to New Orleans). Then, 0.2 mL/min of solution (reactor solution diluted with solvent) from the low pressure mixing chamber was withdrawn using a Shimadzu pump and mixed in a high pressure mixing chamber with solvent flowing at 1.8 mL/min with the help of another Shimadzu HPLC pump, to give a total detector flow rate of 2.0 mL/min. As usual, before beginning the reaction, pure DMF was pumped at 2.0 mL/min through the entire detector train to obtain the baseline for each instrument.

In all of the experiments, the diluted solution always reached the detector train at about room temperature (25 °C).

In the polymerization reaction, the comonomers, styrene and BA, the initiator, azobisizobutyronitrile (AIBN), and the carrier solvent, butyl acetate (BuAce), were used as received from Aldrich. The reactions were carried out at 30% by mass. The reactor containing the solvent (BuAce) was heated to the desired temperature. Before beginning the reaction pure BuAce was pumped at 2.0 mL/min through the entire detector train to obtain the baseline for each instrument. After stabilization of the detector baselines by pure solvent and after the reactor solution reached the desired temperature, BA was added (at 2700 s) into the reactor, and its baseline was established by withdrawing from the reactor at 0.2 mL/min, and mixing with solvent at 1.8 mL/min. These flow rates were maintained throughout the entire experiment, and the diluted solution always reached the detector train at about room temperature (25 °C). At 5000 s, styrene was added and a baseline for styrene and BA was collected. 1.2% by mass of AIBN was added to initiate the reaction at 8000 s and polymerization started. Detector data were simultaneously collected every 2 s throughout the reaction. The UV wavelengths were set at 245 and 260 nm, and the viscometer used a capillary of length 20 cm and internal diameter of 0.02 in.

During the ACOMP experiment, small amounts of aliquots were collected at the end of the line after about every 30 min. These aliquots were injected into a Multidetector gel permeation chromatography[27] (GPC) system using Polymer Laboratories PL gel 5μ, 50 Å columns, a Shimadzu LC-10AT vp pump, a Brookhaven Instruments BI-M_{w}A multiangle LS detector, and Shimadzu RID-10A RI and SPD-10AV UV detectors. The columns were calibrated using a series of Polymer Laboratories polystyrene standards. The areas under the UV monomer peaks were integrated and were used as cross-checks to the concentration calculated from the ACOMP data.

The three solvent traditional method of copolymer characterization was carried out on the Polymer Labs ACOMP unit, bypassing the reactor withdrawal and first dilution stages, and using just the dual-pump high pressure mixing stage to automatically create concentration steps, according to the automatic continuous mixing (ACM) methods.[28]

ACOMP Data Acquisition and Analysis Procedure. Data from all detectors are collected at regular intervals, every 2 s in this work. The baselines for each detector are determined when pure solvent (BuAce here) flows. Comonomers are introduced sequentially, and the baselines for all detectors for each comonomer are measured. The reaction begins when the initiator is injected into the reactor. The delay time between the reactor and the detector train is accounted for in computations. In this work the delay time was about 300 s.

Once the solvent and comonomer baselines for each detector have been determined and the reaction initiated, the combined UV and RI data stream allows computation of each comonomer concentration $c_{\mathrm{m},j}(t)$, and hence the polymer based quantities $c_j(t)$, $c(t)$, $f(t)$, $f_j(t)$, $y_j(t)$, and $\nu(f)$, according to the equations given above. Since $F_j(t)$ is required to compute $\nu'(t)$, $y_j(t)$ must be smoothed and/or fit in order to take the necessary derivative without being overwhelmed with noise. As described below, a pure smoothing approach via averaging over moving windows was used in analyzing experiment no. 1, and a functional form fitting approach was used for experiment no. 2.

$I_{\mathrm{R}}(t)$ is computed from the raw light scattering detector at each of seven angles using the method of Florenzano et al.,[17] allowing extrapolation to $q = 0$ if needed. Combining $I_{\mathrm{R}}(t)$ with $c(t)$ allows computation of $M_{\mathrm{ap}}(t)$ at each sampling instant. From these quantities eq 31 can then be used to compute $M_{\mathrm{w}}(f)$, as well as $M_{\mathrm{w},j}(f)$, and $P_1(f)$ and $Q_1(f)$.

The viscometer signal is combined with $c(t)$ to compute the weight-average reduced viscosity $\eta_{\mathrm{r,w}}(t)$ according to

$$\eta_{r,\mathrm{w}}(t) = \frac{V(t) - V_{\mathrm{b}}}{c(t)V_{\mathrm{b}}} \tag{44}$$

where $V(t)$ is the raw viscosity signal (volts) at sampling instant t, and V_{b} is the viscometer's solvent baseline voltage. As determined by complementary ACM measurements on endproducts from this work, $\eta_{\mathrm{r,w}}(t)$ is essentially equal to the weight-average intrinsic viscosity $[\eta]_{\mathrm{w}}$, at the low concentrations used in the ACOMP detection train.

Results

The methods for determination of M_{w} and associated quantities from ACOMP detailed above are applied to experiments nos. 1 and 2. Experiment no. 1 is worked in detail, and the M_{w} and M_{ap} results for experiment no. 2 are simply summarized.

In this work polystyrene (PS) is assigned $j = 1$ and polybutyl acrylate pBA is assigned $j = 2$.

Figure 2 shows raw data for some of the signals from this reaction. The temperature of the reactor was increased from 65 to 75 °C at 21000 s, which is reflected especially in the UV signal. The reactor temperature is shown in the overlay to Figure 2.

Figure 3 shows the comonomer concentrations vs time, where 7400 s have been subtracted from the time scale of Figure 2 so that $t = 0$ in Figure 3 coincides with the beginning of the reaction. The effect of the temperature change on comonomer conversion rates is clearly seen. This has no effect on the analysis, however, as no assumptions concerning conversion are made. The combined UV and RI data provide two signals, allowing the concentrations of each comonomer to be determined at each instant.

The discrete points in Figure 3 correspond to GPC determinations on manually withdrawn aliquots. The agreement is generally good, although there is more noise in the GPC data. The effect of the temperature change from 65 to 75 °C at about

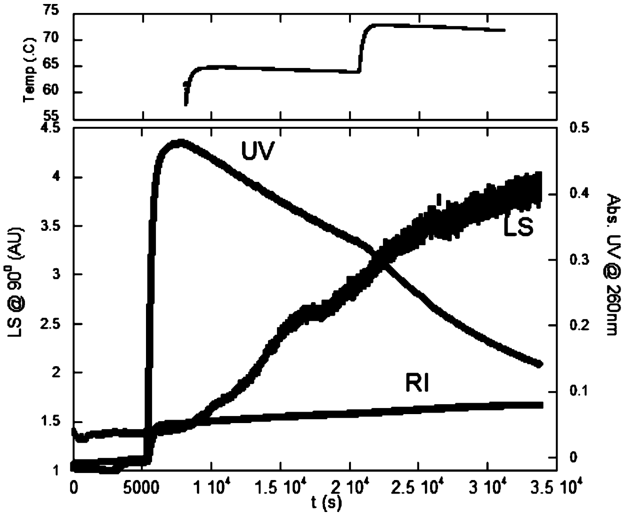

Figure 2. Some of the raw data signals for experiment no. 1. The overlay shows the reactor temperature.

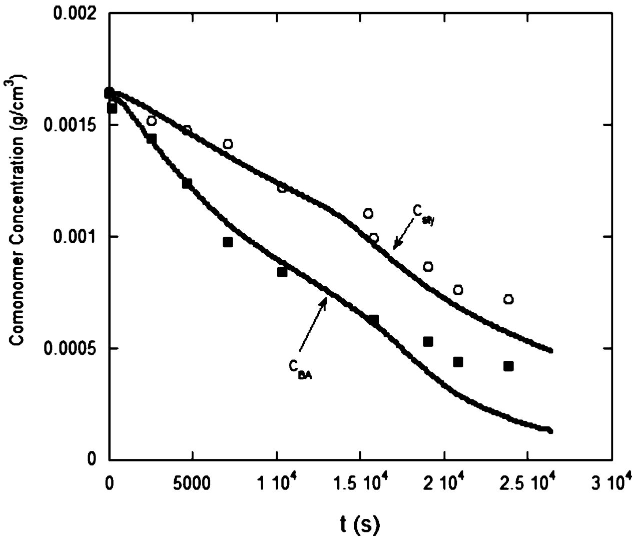

Figure 3. Comonomer concentrations from ACOMP data for experiment no. 1. Continuous curves are from ACOMP, and discrete points are from GPC measurements on aliquots. The inflections in the continuous data coincide with the temperature jump in Figure 2 (with the 7400 s subtracted so that $t = 0$ coincides with the beginning of the reaction).

14 000 s is clearly seen as an increase in polymerization rate. The temperature change illustrates the fact that the ACOMP method and analysis procedures make no assumptions about the reaction conditions and how they may change the polymerization characteristics; ACOMP simply reports and analyzes the resulting effects. The GPC data imply that conversion has basically stopped prematurely by the end of the reaction, whereas the ACOMP values show a continued, smooth decline in comonomer concentrations. We surmise that the ACOMP values are more accurate, since the initiator half-life is not reached by the reaction's end, and there is no deterioration in the quality of the ACOMP signals toward the end of the reaction, whereas the GPC data gets noisier as the signals approach the baseline levels.

Figure 4 shows the composition drift in terms of PS. The lower line shows y_1, the cumulative fraction of PS at each instant. Computation of F_1 is more problematic because it involves the derivative of data with noise. The upper line gives F_1, as computed by eq 28. The F_1 shown was computed by taking the derivative on data smoothed by windowing, to which a second-order polynomial fit was then made to represent F_1. The inset shows the average composition distribution of the final product from this latter fit. The average composition distribution is expressed in terms of $\mathrm{d}f/\mathrm{d}F_1$ vs F_1.

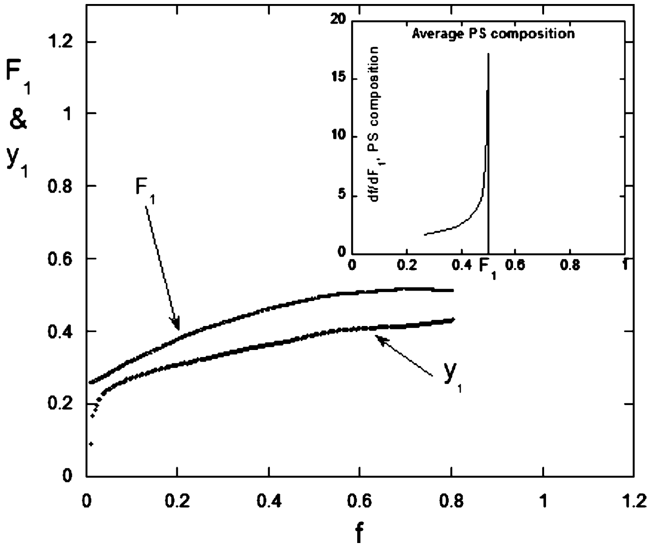

Figure 4. Cumulative fraction of PS at each instant, y_1. Average composition drift in terms of instantaneous fraction of PS, F_1. The inset shows the average composition distribution of the final product from this latter fit.

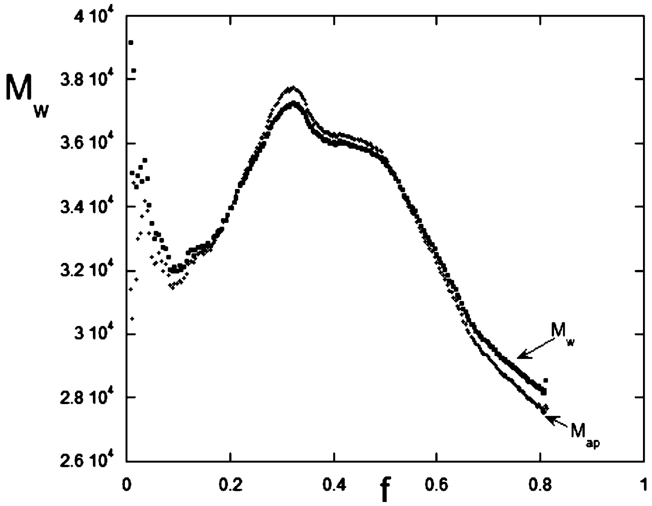

Figure 5. M_{ap} and M_w for the experiment, where the direct numerical integration of eq 35 is used to compute M_w from M_{ap}.

To determine $M_w(f)$ from M_{ap} the case of $N = 2$ of eq 31 is used. Figure 5 shows M_{ap} and M_w for the experiment, where the direct numerical integration of eq 31 is used to compute M_w from M_{ap}. Because the polymer is small, extrapolation of the multiangle data to $q = 0$ yielded a line of essentially zero slope. Likewise, the polymers were small enough and polymer concentration dilute enough in the detectors that intermolecular effects on light scattering were minimal.

The differences between M_w and M_{ap} are noticeable but small. M_w is slightly lower than M_{ap} until about $f = 0.5$, at which point it crosses over to become higher. This small difference in M_{ap} and M_w is due to the fact that composition drift was only moderate, and, while ν_1 and ν_2 are significantly different (0.204 and 0.084, respectively), they are not starkly different; e.g. neither is zero or negative. Considered in the light of eq 44 and Figure 1, the value of a_1 starts at about 1.2 at the beginning of the reaction and ends at 0.88. For cases of low to moderate

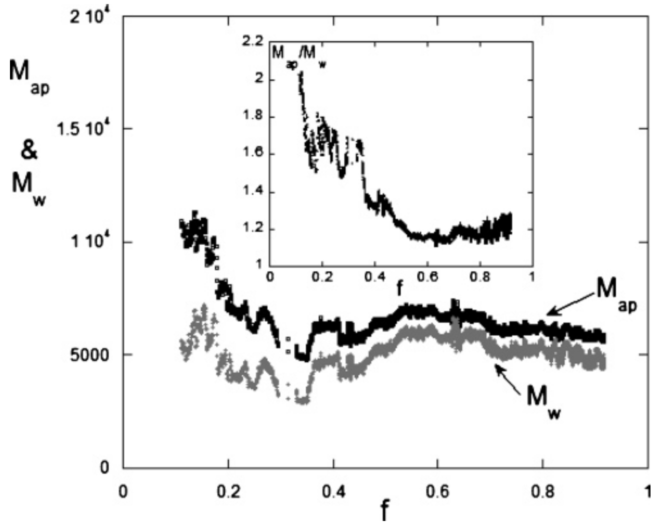

Figure 6. M_{ap} and M_w for experiment no. 2 (in DMF). The inset shows M_{ap}/M_w.

drift, it is seen in Figure 1 that M_{ap} will not be far different from M_w.

The results of M_{ap} and M_w are shown for experiment no. 2 in Figure 6. The results are much noisier than for experiment no. 1, reflecting two facts: (i) the copolymer ν is much smaller in DMF at all compositions than in BuAce, yielding lower scattering intensity for any value of M_w and (ii) M_w is much smaller than for experiment no. 1, due, at least in part, to the higher initiator/monomer ratio in experiment no. 2. The ratio M_{ap}/M_w is significantly larger than in experiment no. 1. This is due chiefly to the fact that a_1 is larger at every point in experiment no. 2 than in no. 1. a_1 starts at about 1.02 and increases to 1.18 by the end of the reaction. In experiment no. 2 the $c_j(t)$ were well fit by exponential decays, which were then used to compute F_j.

Another feature distinguishing experiments nos. 1 and 2 is that M_w is fairly constant in no. 2, whereas it drops considerably in no. 1. This latter effect if due to the increase in temperature during the reaction, whose consequence in free radical reactions is to produce smaller chains.

In neither experiment no. 1 nor experiment no. 2 is M_{ap}/M_w much different from unity. Nonetheless, the formalism and experimental procedure and analysis sequence established in this work are completely general. The difference in M_{ap} and M_w can become very large for some cases (e.g., see Figure 1), and the ACOMP methodology will be fully applicable.

Comparison of Traditional Multisolvent Approach and ACOMP (Experiment No. 1). A traditional three solvent analysis was made on the endproduct from this reaction, and the Benoit−Stockmayer approach was carried out. The solvents were BuAce, toluene, and styrene. For these measurements, the reactor endproduct liquid was rotary evaporated at 39 °C (the advisable temperature for BuAce solvent), precipitated with methanol, and dried in a vacuum oven at room temperature. In each solvent, ten copolymer concentration steps were automatically run using the automatic continuous mixing approach (ACM). In BuAce and toluene c_{max} was 0.010 g/cm^3, whereas in styrene it was necessary to go to $c_{max} = 0.070$ g/cm^3 because the scattering was so weak. GPC measurements on the redissolved material were performed to ensure that only polymer was present, and no residual monomer or methanol. RI measurements were made during the stepped ACM determinations, so that ν was measured directly. ν_1 was determined directly in each solvent from separate steps using pure PS. It was not possible for the authors to render pure pBA into a suitably dry form for subsequent determination of ν_2 in each solvent, so ν_2 was computed in each solvent from the measured values of ν, ν_1, and the ACOMP end value for y_1 ($y_2 = 1 - y_1$). Table 3 shows the parameters for the three solvent determination. Also shown are the values of the comonomers, ν_{sty} and ν_{BA}, (ν_1 and ν_2, respectively) used in the ACOMP computation of comonomer concentrations using combined RI and UV signals.

Results for the three solvent on the endproduct, and ACOMP at the final conversion point are given in Table 4. The M_w values are within 1.3% agreement with each other , but the weight-average molar masses of each component, $M_{w,1}$ and $M_{w,2}$ are significantly different between the two approaches. Whereas the three solvent approach yields nearly equal values for $M_{w,1}$ and $M_{w,2}$, the ACOMP approach reveals that $M_{w,2}$ is 40% larger than $M_{w,1}$. This reflects the fact that more BA was incorporated into the final polymer, and there was neither strong drift in composition nor M_w.

Also of interest are the values of weight-average intrinsic viscosity $[\eta]_w$ in the same table. Its value for the copolymer is essentially the same in BuAce and toluene (10 cm^3/g), and only 20% larger in styrene (12 cm^3/g), which is a better solvent. This highlights the fact that the dramatic difference in M_{ap} of 29060 in BuAce going to 7360 in styrene, is purely an optical effect, which is the starting point for the entire analysis in eqs 1−31.

ACOMP of course allows M_w and any conceivable composition average to be computed at each instant of the reaction, including the P_1 and Q_1 composition moments. P_1 and Q_1 are also quite different between the multisolvent and ACOMP methods. The ACOMP values should be far better since composition is closely and accurately followed during the reaction. P_1 is quite small, −230, reflecting very little drift in M_w, and its negative value reflects the left-skewed average PS composition distribution seen in the inset to Figure 4, while $Q_1 = +270$ indicates the distribution is not very wide, consistent with the fairly low composition drift.

The Q_1 for the three solvent experiment is negative, which is physically impossible, by its definition (eq 17). This unphysical value arises from the mathematical necessity of fitting three data points (the values of M_{ap} in the three solvents) with three parameters. There are nine separate values of differential index of refraction used in this experiment, leading to large sources of error, in addition to errors in M_{ap}. Suffice it to say that the three solvent method requires very accurate values for the nine parameters, good measurements of M_{ap}, and also a large amount of time to carry out the separate determinations. Benoit and Bushuk also pointed out the large potential errors in their measurements arising from so many necessary auxiliary parameters. When going to terpolymers, six solvents are needed, requiring 24 refractive index increment values in addition to laborious measurements. Needless to say, such results may contain very large errors.

ACOMP circumvents the need to know so many auxiliary parameters, totally avoids the tedious measurements in separate solvents, and furnishes much more detailed and accurate information on the average mass and composition distributions, as well as their evolution during synthesis.

Failure of GPC Using Calibration by Standards (Experiments Nos. 1 and 2). PS standards (Polymer Laboratories Ltd.) were used to calibrate the GPC columns. Table 4 gives the results for GPC-apparent M_w (18 630) and GPC-apparent M_w/M_n (2.31) for experiment no. 1. Also computed was M_{ap} from the light scattering detector in the GPC line. In this, it was

Table 3. Parameters Used and Results of a Three-Solvent Stepped ACM Experiment for Reaction No. 1[a]

solvent	n_{solvent}	ν^a	$\nu_1{}^a$	$\nu_2{}^b$	M_{ap}	$\nu_{\text{sty}}{}^c$	$\nu_{\text{BA}}{}^c$	$[\eta]_w$	$A_{2,\text{ap}} \times 10^{4\ d}$
BuAce	1.394	0.1287	0.2040	0.0720	29 060	0.1597	0.0335	9.9	3.75
toluene	1.493	0.0429	0.1046	−0.0036	31 260	NA	NA	10.1	4.69
styrene	1.544	−0.0168	0.0819	−0.0913	7360	NA	NA	12.0	4.44

[a] Measured using RI during ACM step experiment. [b] Computed from measured ν and ν_1. [c] Used to compute comonomer concentrations in ACOMP experiments, obtained from ACOMP monomer baseline values. [d] $A_{2,\text{ap}}$ are apparent A_2 values obtained from eq 1 in the ACM step experiment. [e] NA, not applicable.

Table 4. Comparison of Copolymer Endproduct Characteristics from 3 Solvent Method, from the Final ACOMP Data Points, and GPC for Reaction No. 1

	M_{ap} in Bu Ace	M_w	$M_{w,1}$ (PS)	$M_{w,2}$ (pBA)	P_1	Q_1
three solvent traditional method	29 060	27 460	13 300	13 980	796	−35
ACOMP end point values	27 700	28 200	11 950	16 840	−230	270
GPC	30 100[b]	18 630[c]	NA	NA	NA	NA

[a] NA = not applicable [b] Value using LS in GPC. [c] Apparent M_w using PS standards and UV signal. Apparent $M_w/M_n = 2.31$.

Table 5. ACOMP and GPC Results for Reaction No. 2[a]

	M_{ap} in BuAce	M_w	$M_{w,1}$	$M_{w,2}$	P_1	Q_1
ACOMP end point values	5800	4500	2200	2400	−40	50
GPC	NA	1740[b]	NA	NA	NA	NA

[a] NA = not applicable. [b] Apparent M_w using PS standards and UV signal. Apparent $M_w/M_n = 1.04$, which is spurious and shows breakdown of the column calibration method.

necessary to know y_1 in order to compute ν. The final ACOMP value for y_1 (=0.43) was used; i.e. in order to obtain M_{ap} (30 100) by GPC coupled to LS and a concentration detector, it is necessary to either measure ν directly, or compute it from knowledge of y_1.

Table 5 gives similar results for experiment no. 2. The GPC value of $M_w = 1740$ from column calibration by standards is quite far off from $M_w = 4500$ from ACOMP. The value of $M_w/M_n = 1.04$ is spurious, and reflects a failure in resolution of the columns at these low masses. P_1 and Q_1 were computed from the ACOMP data. P_1 is close to zero, −40, reflecting the fact that there is very little change in M_w during conversion. $Q_1 \sim 50$, so that $Q_1/M_w = 0.011$, which is about the value of $Q_1/M_w = 0.011$ for experiment no. 1; i.e., the drift in both cases is similar.

From the various computations of M_w it is clear that use of traditional GPC with column calibration using polymer standards gives the least reliable value. It is possible that corrections to the GPC data using "universal calibration" [29] might yield better results, but this topic is not pursued here, as it has been demonstrated that the ACOMP approach involves the minimum number of auxiliary values, independent steps, and assumptions.

Reactivity Ratios as Model Dependent Parameters. Up to this point the quantities computed from ACOMP are independent of any specific kinetic models.[30,31] Reactivity ratios and sequence length distributions embody specific models. The reactivity ratios can be useful for predicting composition drift and distributions (which are nonetheless measured directly by ACOMP, free of model dependent assumptions) and sequence length distributions. It has previously been shown how the reactivity ratios themselves can be determined from ACOMP, and the subject is not pursued further here.

Summary

The many advantages of ACOMP for characterization of copolymers for $N = 2$ have been illustrated, and expressions have been developed for arbitrary N. A compact and useful expression linking M_w and M_{ap}, valid for all N, is given in eq 31. The traditional multisolvent method is unwieldy and prone to many sources of error, even for the case of $N = 2$, because so many separate values of $\partial n/\partial c$ are required.

GPC measurements, whether by column calibration or light scattering, must be treated with great caution. If homopolymer standards are used to calibrate the column(s) the results can be highly erroneous (Tables 4 and 5) due to the usually inaccurate assumption that the homopolymer and copolymer dimensions and elution behavior are identical for any given mass. Light scattering coupled to GPC will give the same M_{ap} as ACOMP (Table 4), but GPC does not usually furnish the composition distribution needed to extract M_w from M_{ap}.

Nonetheless, it is frequently not possible to have ACOMP available during copolymer synthesis. In such as case it is very useful to assess how large M_{ap}/M_w is likely to be. A reasonable approximation of M_w can be obtained from M_{ap} in a single solvent by making a_1 as close to zero as possible. This can be approximated by using a single solvent which gives large values of ν_1 and ν_2 of the same sign.

The approach presented here is readily applicable to $N \geq 2$, and current work involves assessing the robustness of the ACOMP approach to terpolymers. While it seems likely that a wide range of terpolymers will be measurable, it is probable that additional detectors, e.g., FTIR, will be needed in the detector train to resolve the concentrations of increasing numbers of comonomers.

This approach will also be valuable in semibatch operation, where comonomers and/or initiator can be flowed at various rates to achieve an azeotropic composition, or to taper the composition and molar mass distributions as desired.

Acknowledgment. The authors acknowledge support from NSF CBET 0623531, the Louisiana Board of Regents ITRS RD-B-5, the Tulane Institute for Macromolecular Engineering and Science, NASA Grant NCC3-946, and the Tulane Center for Polymer Reaction Monitoring and Characterization (PolyRMC).

Glossary of Notation Used

j, comonomer (copolymer) number; e.g. in this work $j = 1$ for PS, $j = 2$ for pBA
i, numbering index for sequential conversion intervals during the synthesis reaction
a_1, see eq 40
A_2, second virial coefficient (cm^3 mol/g^2)
c, total copolymer concentration
c_i, concentration of copolymer at the end of conversion interval i
$c_{m,j,0}$, initial concentration of comonomer j
Δc_i, concentration of copolymer produced during conversion interval i

$\Delta c_{j,i}$, concentration of copolymer j produced during conversion interval i
$f(t)$, fraction of all comonomers converted by time t (eq 19)
$f_j(t)$, fraction of comonomer j converted by time t (eq 20)
$F_{j,i}$, average fraction of comonomer j in the copolymer produced over interval i (eq 8)
$F_j(t)$, average instantaneous fraction of comonomer j in copolymer formed at instant t (eq 22)
$I_R(q,c)$, absolute Rayleigh scattering ratio (cm^{-1})
K', light scattering optical constant (eq 3)
M_{ap}, apparent weight-average molar mass (eq 4)
M_i, average molar mass of concentration element i; for ACOMP approach this is average copolymer weight-average mass over conversion interval i
M_w, weight-average molar mass of the copolymer (eq 11)
$M_{w,inst}(f)$, weight-average instantaneous molar mass at conversion instant f (eq 27)
$M_{w,j}$, weight-average mass of comonomer j in the copolymer (eq 10)
n, index of refraction of solvent
N, total number of comonomers
$P_{j,}$ mass-weighted first moment of composition distribution for comonomer j (eq 14)
$Q_{j,}$ mass-weighted second moment of composition distribution for comonomer j (eq 15)
q = magnitude of scattering vector (eq 2)

$\langle S^2 \rangle_z$, z average mean square radius of gyration
y_j, total fraction of copolymer concentration composed of copolymer j
γ_i, Benoit et al.'s notation for mass fraction of concentration element i; replaced by $\Delta c_i/c$
$\partial n/\partial c$, differential refractive index increment
$\delta_{j,i}$, the deviation from the average of the instantaneous composition of comonomer j in the copolymer for concentration element I (eq 12)
ν_j, value of $\partial n/\partial c$ for a homopolymer of comonomer j
ν, cumulative value of copolymer $\partial n/\partial c$ (eq 6)
$\nu'(f)$, instantaneous value of copolymer $\partial n/\partial c$ at conversion instant f (eq 7)
θ, scattering angle in the scattering plane for vertically polarized incident light

References and Notes

(1) Dammert, R.; Jussila, M.; Vastamaki, P.; Riekkola, M.-L.; Sundholm, F. *Polymer* **1997**, *38*, 6273−6280.
(2) Feng, Y.; Hay, J. N. *Polymer* **1998**, *39*, 6723−6731.
(3) Xu, J.; Feng, L. *Eur. Polym. J.* **2000**, *36*, 867−878.
(4) Wignall, G. D.; Alamo, R. G.; Ritchson, E. J.; Mandelkern, L.; Schwahn, D. *Macromolecules* **2001**, *34*, 8160−8165.
(5) Faldi, A.; Soares, J. B. P. *Polymer* **2001**, *42*, 3057−3066.
(6) Cools, P. J. C.; Maesen, F.; Klumperman, B.; van Herk, A. M.; German, A. L. *J. Chromatogr. A* **1996**, *736*, 125−130.
(7) Verhelst, V.; Vandereecken, P. *J. Chromatogr. A* **2000**, *87*, 269−277.
(8) Schunk, T. C.; Long, T. E. *J. Chromatogr. A* **1995**, *692*, 221−232.
(9) Kikuchi, A.; Nose, T. *Polymer* **1995**, *36*, 2781−2786.
(10) Yau, W. W.; Gillespie, D. *Polymer* **2001**, *42*, 8947−8958.
(11) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093−1099.
(12) Stockmayer, W. H.; Moore, L. D.; Fixman, M.; Epstein, B. N. *J. Polym. Sci.* **1955**, *16*, 517.
(13) Bushuk, W.; Benoit, H. *Can. J. Chem.* **1958**, *36*, 1616.
(14) Kambe, H.; Kambe, Y.; Honda, C. *Polymer* **1973**, *14*, 460.
(15) Berry, G. C. in *Soft Matter: Scattering, Manipulation and Imaging*; Pecora, R., Borsali, R., Eds.; Springer: Berlin, 2007.
(16) *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: New York, 1972.
(17) Florenzano, F. H.; Strelitzki, R.; Reed, W. F. *Macromolecules* **1998**, *31*, 7226.
(18) Catalgil-Giz, H.; Giz, A.; Alb, A. M.; Oncul, A. K.; Reed, W. F. *Macromolecules* **2002**, *35*, 6557.
(19) $F_{j,i}$ takes the place of $z_i = c_{pA,i}/(c_{pA,i} + c_{pB,i})$ in our previous work, and is what we have also usually denoted $F_{inst,A.}$
(20) Alb, A. M.; Enohnyaket, P.; Drenski, M. F.; Head, A.; Reed, A. W.; Reed, W. F. *Macromolecules* **2006**, *39*, 5705.
(21) Alb, A. M.; Enohnyaket, P.; Shunmugam, R.; Tew, G. N.; Reed, W. F. *Macromolecules* **2006**, *39*, 8283.
(22) For free radical polymerization $F_j(t)$ is the average fractional composition in component j of chains that are initiated, propagate, and terminate around a short interval of time around t. This leads to an average composition distribution of dead chains in the final product. In contrast, where "living" copolymerization is involved $F_j(t)$ is the average local composition on the slowly growing living chains, so that $F_i(t)$ monitors the "gradient" along the copolymer chain.
(23) Dotson, N. A.; Galvan, R.; Laurence, R. L.; Tirrel, M. *Polymerization Process Modelling*; VCH Pub.: New York, 1996.
(24) Prud'homme, J.; Bywater, S. *Macromolecules* **1971**, *4*, 543.
(25) Benoit, H.; Wippler, J. *Chim. Phys. Physiochem. Biol.* **1960**, *57*, 524.
(26) Mignard, E.; Leblanc, T.; Bertin, D.; Guerret, O.; Reed, W. F. *Macromolecules* **2004**, *37*, 966.
(27) Reed, W. F. Chapter 2 In *SEC and related methods*; ACS Symposium Series 893, Multiple Detection Size-Exclusion Chromatography; Striegel, A. M., Ed.; American Chemical Society: Washington, DC, 2004.
(28) Strelitzki, R.; Reed, W. F. *J. Appl. Polym. Sci.* **1999**, *73*, 2359.
(29) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D. *J. Chim. Phys.* **1966**, *63*, 1506.
(30) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(31) Alfrey, T.; Goldfinger, G. *J. Chem. Phys.* **1944**, *12*, 205.

MA0717338