MALDI-TOF Mass Spectrometry in the Study of Statistical Copolymerizations and Its Application in Examining the Free Radical Copolymerization of Methyl Methacrylate and *n*-Butyl Methacrylate

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ABSTRACT: Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was used to obtain bivariate distributions of composition and chain length for a series of copolymers of methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) produced by free radical catalytic chain transfer polymerization. The relationship between the bivariate distributions of copolymers and the kinetics of the copolymerization reactions from which they were formed was derived using the terminal copolymerization model. This relationship was used with the mass spectra from the MMA/BMA copolymerizations studied to estimate kinetic parameters which describe the polymerizations. For this copolymerization the reactivity ratios, (catalytic) chain transfer coefficients, and initiator selectivity were determined to be $r_{\mathrm{MMA}} = 1.09$, $r_{\mathrm{BMA}} = 0.77$, $C_{S,\mathrm{MMA}} = 17\,900$, $C_{S,\mathrm{BMA}} = 6150$, and $S_{\mathrm{MMA}} = 0.535$, respectively. The reactivity ratios for these polymerizations were also determined from ^{1}H NMR to be $r_{\mathrm{MMA}} = 0.75$ and $r_{\mathrm{BMA}} = 0.98$, using an error-in-variables model (EVM) treatment. The parameters determined from the mass spectra were compared with both the NMR values and literature values, where available, and general agreement is shown.

Introduction and Theory

Statistical or random copolymerization is important from a scientific viewpoint for examining the reactivities of monomers and propagating centers, and from a technical perspective for the flexibility it offers in polymer synthesis. Reactivity ratios play a central role in the study of copolymerization and are obtained by establishing the relationship between the composition of the monomer feed and the composition of the copolymer produced from that feed. This can be achieved by measuring the concentrations of unreacted monomer (e.g., by GC) or by measuring the composition of the resultant copolymer (e.g., by NMR or IR). These techniques give average copolymer compositions or limited information about copolymer (short) sequence distributions and generally do not provide chain length information. In contrast, copolymer mass spectra are extremely rich in information, providing both chain length and composition data. This gives mass spectrometry the potential to become the ideal analytical technique for the study of copolymerizations since it is capable of providing not only the chain length distribution but also the *composition distribution at each chain length*. Currently, no other analytical technique offers this kind of potential.

Mass spectrometry requires gas phase ions. The low volatility of macromolecules has served to limit the application of these techniques in the study of polymers. However, recent advances in ionization, such as matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI), have made the analysis of intact synthetic polymers viable.[1−4] These ionization methods can be combined with any of the methods for ion discrimination and detection used in mass spectrometry. The resolution and mass range that can be studied is generally determined by the ion separation technique. Time-of-flight (TOF) and Fourier transform (FTICR) instruments are particularly important in the study of synthetic polymers. Mass spectrometry of low molecular weight polymers tends to be more straightforward than that of high molecular weight polymers, but mass spectra have been obtained for synthetic high polymers with masses on the order of 10^5 Da.[3,5−7] However, to be of use in the study of copolymerization, spectra must be obtained in the mass region where individual species can be resolved. Currently, in the mass range up to ∼10 000 Da, commercial MALDI-TOF instruments typically have a resolution of ∼4 Da, while FTICR instruments give isotopic resolution.

To obtain the bivariate distribution of composition and chain length from a mass spectrum, it is necessary to deconvolute the spectrum, assigning each peak to a unique molecular species. The feasibility of doing this is determined both by the chemistry of the copolymerization and by the resolution in the spectrum. If the mass spectrum is representative of the copolymer, it contains a record of all of the reactions that occurred during the formation of the copolymer. Thus, the mass spectrum is determined by the kinetics of the copolymerization. Two approaches for relating copolymer mass spectra to copolymerization kinetics are discussed. In the first, the composition and kinetics are related through the probabilities associated with each of the reactions which comprise the polymerization. In the second, the classical approach of relating the average polymer composition to the feed composition is used.

The Probability Approach. This approach relates the bivariate distributions of composition and chain length of copolymers to the kinetics of the copolymerization through conditional probabilities. The chain initiation, propagation, and chain termination reactions must all be considered. Termination kinetics are difficult to consider quantitatively, however, since termination is a complex diffusion-controlled process which is poorly understood. The termination kinetics can be simplified considerably if all the termination can be assumed to occur by chain transfer, as is the typical case in catalytic chain transfer polymerization.[8−12] Conse-

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quently, the relationship between the mass spectrum of a copolymer and its copolymerization kinetics will be described in terms of catalytic chain transfer. The relationship can be developed for any copolymerization model but for simplicity the terminal model, is used here.

Eight reactions must be considered to develop the probabilities for terminal model catalytic chain transfer copolymerization; two (re)initiation reactions, four propagation reactions, and two termination (transfer) reactions. In the case of catalytic chain transfer (or any polymerization that is dominated by chain transfer), initiation of the polymer chains is dominated by reinitiation from the chain transfer product.

(re)initiation

$$\mathrm{I} + \mathrm{M}_1 \xrightarrow{k_{\mathrm{I}1}} \mathrm{M}_1^{\bullet} \tag{1}$$

$$\mathrm{I} + \mathrm{M}_2 \xrightarrow{k_{\mathrm{I}2}} \mathrm{M}_2^{\bullet} \tag{2}$$

propagation

$$\mathrm{M}_1^{\bullet} + \mathrm{M}_1 \xrightarrow{k_{11}} \mathrm{M}_1^{\bullet} \tag{3}$$

$$\mathrm{M}_1^{\bullet} + \mathrm{M}_2 \xrightarrow{k_{12}} \mathrm{M}_2^{\bullet} \tag{4}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{M}_1 \xrightarrow{k_{21}} \mathrm{M}_1^{\bullet} \tag{5}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{M}_2 \xrightarrow{k_{22}} \mathrm{M}_2^{\bullet} \tag{6}$$

termination (chain transfer)

$$\mathrm{M}_1^{\bullet} + \mathrm{CCTA} \xrightarrow{k_{\mathrm{tr}1}} \text{dead polymer} + \mathrm{I} \tag{7}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{CCTA} \xrightarrow{k_{\mathrm{tr}2}} \text{dead polymer} + \mathrm{I} \tag{8}$$

CCTA represents the catalytic chain transfer agent, and the other symbols have their standard meanings in copolymerization.

The selectivity of the initiation toward monomer 1 can be expressed as $S_1 = k_{\mathrm{I}1}/k_{\mathrm{I}2}$. Two reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and two chain transfer constants, $C_{S_1} = k_{\mathrm{tr}1}/k_{11}$ and $C_{S_2} = k_{\mathrm{tr}2}/k_{22}$, can also be defined in terms of the rate constants of these equations.

The probability of a chain being initiated through monomer 1, $p_{\mathrm{I}1}$, is equal to the fraction of chains initiated through monomer one, ϕ, and can be expressed in terms of the selectivity of the initiator and the relative concentrations of the two monomers.

$$\phi = p_{\mathrm{I}1} = \frac{R_{\mathrm{I}1}}{R_{\mathrm{I}1} + R_{\mathrm{I}2}} = \frac{1}{1 + \frac{1\,[\mathrm{M}_2]}{S_1[\mathrm{M}_1]}} \tag{9}$$

Equation 9 determines the relative numbers of monomer 1- and 2-ended radicals of chain length 1, where R denotes rate of each appropriate reaction. The fates of these radicals can then be expressed in terms of six conditional probabilities which follow from the relative rates of the propagation and termination reactions. These conditional probabilities can be expressed in terms of the reactivity ratios, the chain transfer constants, and the relative concentrations of the reagents in the reaction mixture. The probability of a monomer 1-ended radical adding a monomer 1 unit to produce a monomer 1-ended radical is

$$p_{11} = \frac{R_{11}}{R_{11} + R_{12} + R_{\mathrm{tr}1}} = \frac{1}{1 + \frac{1\,[\mathrm{M}_2]}{r_1[\mathrm{M}_1]} + C_{S_1}\frac{[\mathrm{CCTA}]}{[\mathrm{M}_1]}} \tag{10}$$

Similarly, the probability of a monomer 1 radical adding a monomer 2 unit is

$$p_{12} = \frac{1}{r_1\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} + 1 + C_{S_1} r_1 \frac{[\mathrm{CCTA}]}{[\mathrm{M}_2]}} \tag{11}$$

and the probability of a monomer 1 radical terminating is given by eq 12.

$$p_{\mathrm{t}1} = \frac{1}{\frac{1\,[\mathrm{M}_1]}{C_{S_1}[\mathrm{CCTA}]} + \frac{1\,[\mathrm{M}_2]}{C_{S_1} r_1[\mathrm{CCTA}]} + 1} \tag{12}$$

A similar set of probabilities can be obtained for monomer 2-ended radicals.

In the case of a terminal model copolymerization, all of the species of interest in the copolymerization can be represented in three arrays representing the monomer 1-ended radicals, the monomer 2-ended radicals, and the dead polymer. The rows and columns in these arrays correspond to the degree of polymerization (chain length) and composition (e.g., number of monomer 2 units), respectively. The first terms in the arrays for monomer 1- and 2-ended radicals (those corresponding to radicals of a chain length of 1) can be determined from eq 9. All other terms in the arrays are related to these through the conditional probability equations.

The relationship between the terms in the three arrays is illustrated schematically in Figure 1. The array representing dead polymer can be calculated if the reaction conditions (i.e., the relative quantities of the two monomers and CCTA) and values for the selectivity of initiation, the reactivity ratios, and the chain transfer constants are known. The terms calculated in the dead polymer array can be specified as $C_{\mathrm{feed,DP,\#M2}}$, where the subscript "feed" specifies the feed composition.

Conversely, given the experimental distribution of the dead polymer and the feed composition, estimates for the reactivity ratios, chain transfer constants, and selectivity of initiation can be obtained by nonlinear optimization.

The Classical Approach. This approach uses experimentally determined average copolymer composition data and relates these to the composition of the feed through the well-known differential form of the terminal (Mayo–Lewis) model copolymer composition equation[13,14] given by eq 13. The terms F_1 and f_1 represent

$$F_1 = \frac{r_1 f_1^{\,2} + f_1(1 - f_1)}{r_1 f_1^{\,2} + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \tag{13}$$

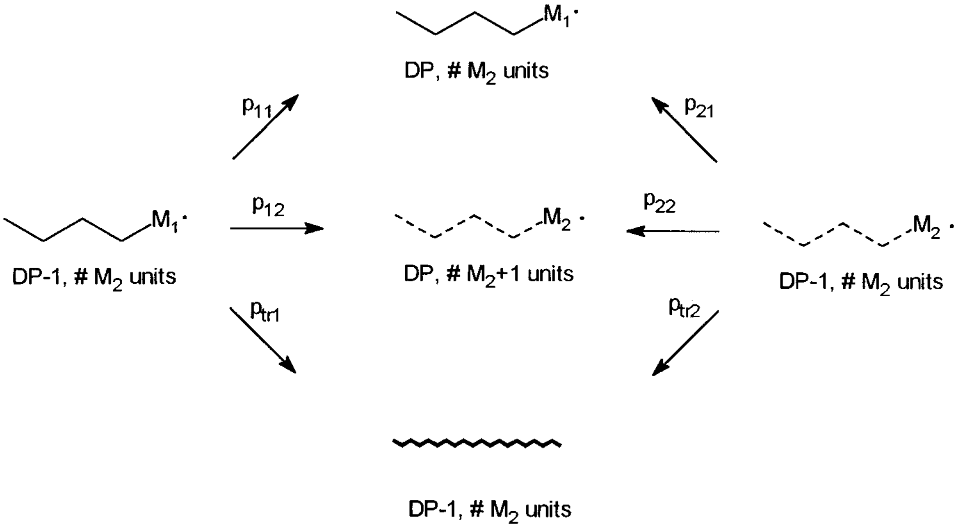


Figure 1. Schematic representation of the relationship between the conditional probabilities and the monomer 1-ended radicals, the monomer 2-ended radicals, and the dead polymer chains.

the mole fractions of monomer 1 in the polymer and monomer feed, respectively. Because eq 13 is the differential form of the copolymerization equation, its use is limited to low-conversion copolymerizations (typically < 5%). However, an integrated form does exist. The use of the copolymer equation is the most commonly used approach for copolymer analysis since the analytical techniques common to study copolymerizations give the average composition of the whole polymer. Mass spectrometry is also compatible with eq 13, since the average compositions of the whole copolymer can be ascertained from copolymer mass spectra. It has the further advantage that the samples contain internal replicates, since the average composition at each degree of polymerization can be determined.

A number of assumptions are used in the derivation of eq 13.[13] One of these is the long-chain assumption, which states that the monomer incorporated into the chain by initiation, transfer, and termination reactions is negligible compared to the monomer incorporated by propagation. Clearly, this assumption is violated in copolymerizations where short chains are produced, such as those described in this work. A second assumption is the equal reactivity assumption, which assumes that the relative rates of all the propagation reactions are independent of chain length and depend on the composition of the macroradical only through the terminal unit. Significant violation of these assumptions should show up as trends in the copolymer composition with chain length. This should be examined when reactivity ratios are being determined from relatively short polymer chains.

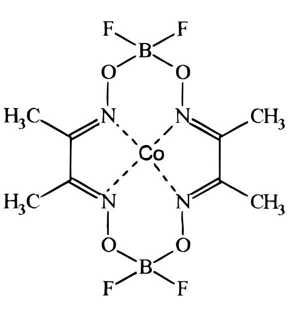
A number of procedures have been developed for the estimation of r_1 and r_1 based on the Mayo–Lewis model. Most of these procedures have involved the linearization of eq 13 and have been statistically unsound.[15] The popularity of these methods has contributed to the large variation in reactivity ratios reported in the literature. It has also resulted in poor estimates of reactivity ratios with misleading confidence intervals. Better estimates are obtained by the use of the error-in-variables model (EVM) approach. This work used an implementation of the EVM approach for estimating reactivity ratios from the differential form of the Mayo–Lewis equation.[15] The EVM approach is a more satisfactory method of analyzing copolymerization data since it is statistically sound and allows for the major sources of experimental error to be properly accounted for.

The MMA/BMA System. The copolymerization studied in this work was that of methyl methacrylate and *n*-butyl methacrylate. This system has a number of advantages, making it well suited for this work. Catalytic chain transfer occurs with both monomers and COBF. Not only does this allow low molecular weight copolymer to be made (facilitating mass spectrometry), but it also results in simplification of the termination kinetics. Furthermore, MALDI spectra of polymers of both monomers can be readily obtained and have similar behavior in MALDI mass spectrometry (i.e., they can be run using the same matrices and cations).

Experimental Section

General. All reactions were carried out using standard Schlenk line techniques under nitrogen atmosphere. Methyl methacrylate and *n*-butyl methacrylate were obtained from ICI Acrylics, stabilized with 5 ppm Topanol. Monomers were weighed and mixed prior to being stored under nitrogen over a mixture of 4 Å and 13× molecular sieves and activated basic alumina so as to remove inhibitor, water, and other protic impurities. Three monomer mixtures were prepared with the following [MMA]/[BMA] ratios: 75/25 (563.05 g of MMA, 265.57 g of BMA), 50/50 (374.90 g of MMA, 533.89 g of BMA), and 25/75 (188.72 g of MMA, 799.28 g of BMA).

[Bis[*μ*-[(2,3-butanedione dioximato)(2−)-*O*,*O*′]] tetrafluorodiborato(2−)-*N*,*N*′,*N*″,*N*‴]cobalt (COBF, see structure **1**) was used as the catalytic chain transfer agent.



1 COBF

COBF was prepared according to the procedure of

Table 1. Composition of the Reaction Mixtures for the Copolymerization Reactions

polymerization	monomer (mL)	[MMA]/ [BMA]	AIBN (g)	COBF solution (mL)
A	20	3.011	0.0303	1.5
B	20	0.9973	0.0302	3
C	20	0.3353	0.0308	4
D	20	0.3353	0.0306	4

Table 2. Conversion and Molecular Weight Data for the Copolymerizations

polymerization	% conversion	M_n	PDI
A	5.29	2021	2.137
B	4.43	1606	2.139
C	4.11	2367	1.874
D	4.17	2266	1.843

Espenson et al.[16] and was assumed to be the bis-methanol adduct. COBF was added from a stock solution prepared by dissolving COBF (0.0104 g, 2.32×10^{-5} mol) in toluene (50 mL).

Polymerizations. The initiator used was AIBN (2,2′-azobis(isobutyronitrile), BDH GPR grade used as received). The reagents were mixed in a Schlenk tube and placed in a 60 °C water bath for 45 min prior to being quenched by rapidly cooling to 0 °C. The sample was allowed to evaporate overnight and then placed in a vacuum oven at 60 °C until it achieved constant weight (~3 days). Table 1 contains the details of the composition of the reaction mixtures used in this work. Conversion (based on total mass monomer) was determined by gravimetry, and SEC was used to estimate molecular weight. These data are found in Table 2.

Analysis Methods. SEC was carried out using a Polymer Laboratories (PL) guard column (50 mm 7.5 mm) and one PL Mixed-E column (300 mm × 7.5 mm). THF was used as the eluent at a flow rate of 1 mL/min, and data were collected at 1 point/s from a DRI detector. The system was calibrated with log molecular weight expressed as a third-order polynomial of elution volume based on sixPolymer Laboratories PMMA standards (peak masses between 1000 and 62 600) and pure samples of MMA dimer and trimer.[17] No account was taken of the samples being copolymers, and the SEC data are presented as "PMMA equivalent" molecular weights.

Copolymer compositions were ascertained using ^{1}H NMR in CDCl$_3$ at 250 MHz by integration of the alkoxy regions of the polymer, which had resonances centered at ~4.0 (BMA) and 3.6 ppm (MMA), see Figure 2. Note that the resonances at ~5.45 and 6.2 ppm are not a result of residual monomer but correspond to the vinyl protons on the chains possessing a terminal double bond, as produced from catalytic chain transfer. The resonances from alkoxy groups associated with this terminal unsaturation appear slightly downfield (~0.15 ppm) from the main alkoxy signals.

MALDI-TOF mass spectrometry was carried out on a Kratos Kompact III spectrometer in reflectron mode. This instrument uses a 337 nm nitrogen laser with a 3 ns pulse duration for ionization and an electron multiplier detector. 2,5-Dihydroxybenzoic acid doped with sodium acetate was used as the matrix. It was deposited from acetone solution onto the MALDI substrate, and the solvent was allowed to evaporate. The polymer was then deposited as a dilute (~1 mg/mL) solution in THF. This resulted in each polymeric species being observed as its Na$^+$ adduct with molecular mass M + 23. The spectrometer was calibrated using bovine insulin (5734) and sodium (22.9898).

Results and Discussion

A MALDI-TOF spectrum of the product from polymerization B (50/50 MMA/BMA copolymerization) is shown in Figure 3. This is typical of the spectra obtained for these copolymers. Each showed a large number of peaks (between 104 and 190, with an average of 169), which can be unambiguously assigned to peaks with masses corresponding to copolymer species (mass $= x[100.12] + y[142.20] + 22.99$, where x and y correspond to the numbers of MMA and BMA units, respectively). The large number of peaks is indicative of the amount of information contained in copolymer mass spectra. The copolymer mass spectrum can be deconvoluted into a bivariate distribution of composition and chain length. The distribution obtained from deconvolution of Figure 3 is shown in Figure 4. Here, composition is expressed as the number of BMA units. The other two axes are the degree of polymerization and the relative areas under the peaks. The data are discrete points, but data corresponding to polymers of the same degree of polymerization have been joined together by ribbons for clarity.

Use of the Entire Mass Spectra with the Probability Approach. An implementation of the probability approach was examined. A total of six mass spectra representing three feed compositions were deconvoluted. The six spectra were two spectra each of the products of polymerizations A and B, and one spectrum each of the products from polymerizations C and D (which were replicates). Each spectrum had a corresponding array with the rows and columns representing the degree of polymerization and copolymer composition, respectively. The relative areas of each of the peaks in the spectra were assigned to the terms of the array representing the dead polymer in that sample.

The actual experimental peaks were specified as $A_{\text{spectrum,DP,\#M2}}$. These data were then compared to the relative areas expected for the dead polymer, given a set of the parameters S_1, r_1, r_2, C_{S_1}, and C_{S_2}. These parameters were estimated by varying them to give the optimal fit between the experimental and calculated dead polymer distributions. In this work, nonlinear optimization was used to estimate these parameters by minimizing expression 14, which was used as the objective function for the Solver add-in of Microsoft Excel 5.0c. No constraints were placed on the parameters.

$$\sum_{\text{spectrum}} \sum_{\text{DP}} \sum_{\#\text{M2}} (A_{\text{spectrum,DP,\#M2}} - C_{\text{feed,DP,\#M2}})^2 \quad (14)$$

The summation occurs over all spectra used (the subscript feed refers to the feed conditions corresponding to the spectrum), over the degrees of polymerization specified in Table 3, and over every possible number of M2 units within this range. A value of 0 was used for $A_{\text{spectrum,DP,\#M2}}$ if no corresponding peak was present in the spectrum. Peaks associated with species with low degrees of polymerization (less than 6) were excluded from all the calculations in this work since volatile oligomers are not generally observed under the MALDI-TOF conditions used. Furthermore, under the conditions used, MALDI-TOF has been observed to exhibit mass discrimination at low degrees of polymerization, so that low molecular weight material is under-

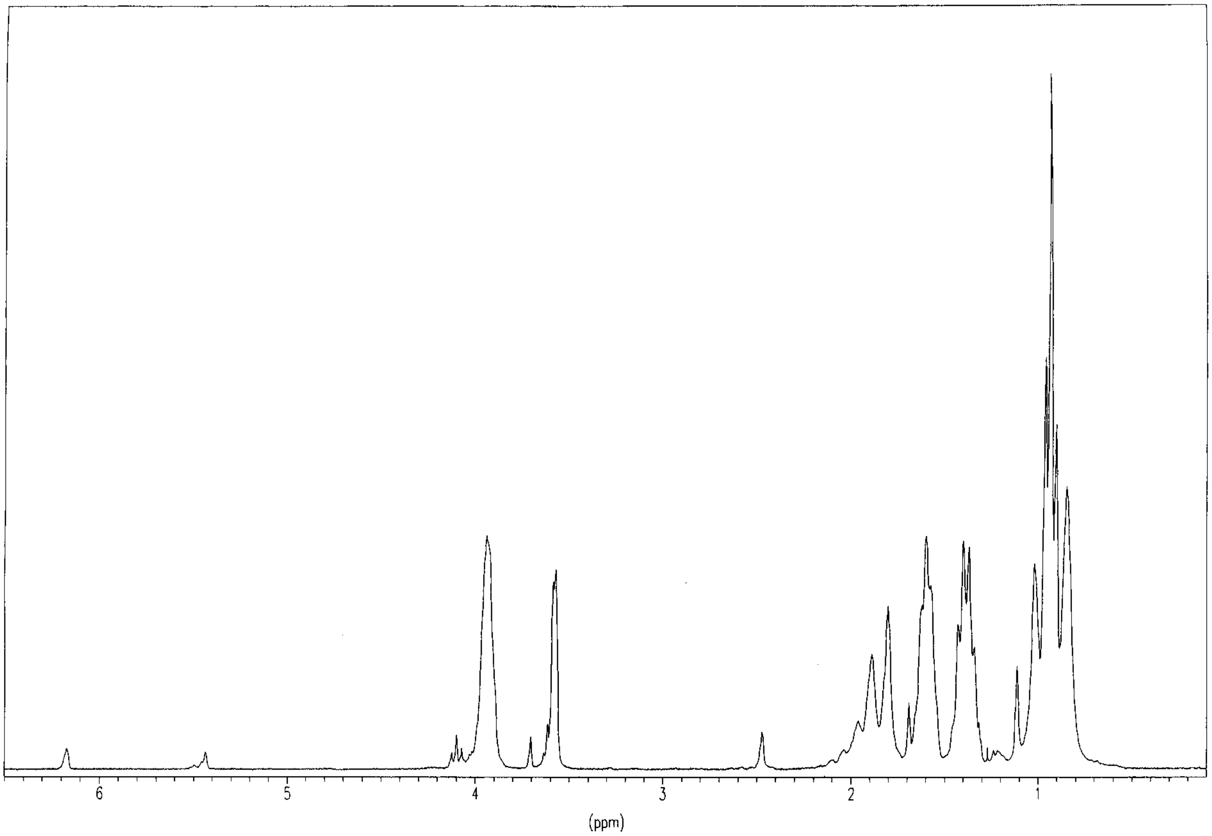


Figure 2. ^{1}H NMR spectrum of MMA/BMA copolymer from polymerization C.

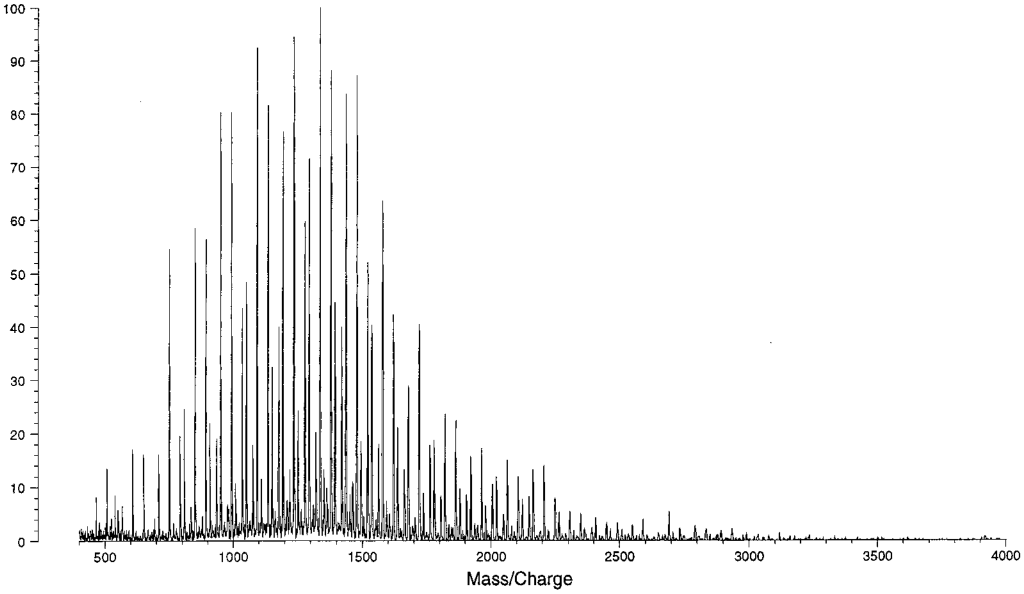


Figure 3. MALDI-TOF spectrum obtained from polymerization B which had a 50/50 MMA/BMA feed.

represented in these spectra.[18] The upper limit to the degree of polymerization used in the optimization was determined by the last peak identified in the spectrum. Since peaks in the mass spectra were not present for all possible species, the normalization conditions given by eq 15 were used for each mass spectrum.

$$\sum_{\mathrm{DP}}\sum_{\#\mathrm{M2}} A_{\mathrm{DP},\#\mathrm{M2}} = \sum_{\mathrm{DP}}\sum_{\#\mathrm{M2}} C_{\mathrm{DP},\#\mathrm{M2}} \qquad (15)$$

Table 4 contains the optimal parameter estimates obtained from applying this analysis method to the data. The reactivity ratio estimates are compared with others in Figure 5. Two observations can be made on the basis of the reactivity ratio data in this table and figure. The first is that literature values for the free radical reactivity ratios for MMA/BMA copolymerizations are scarce, and there is a discrepancy in these values.[19−21] Furthermore, one set of literature data is compiled incorrectly (ref 22 reports the incorrect values of $r_{\mathrm{MMA}} = 0.52$, $r_{\mathrm{BMA}} = 2.11$ for the data in ref 19). The scarcity and variability in the literature data make it difficult to assess the present estimated values exclusively in terms of values previously reported. The second observation is that the reactivity ratios estimated from the bivariate

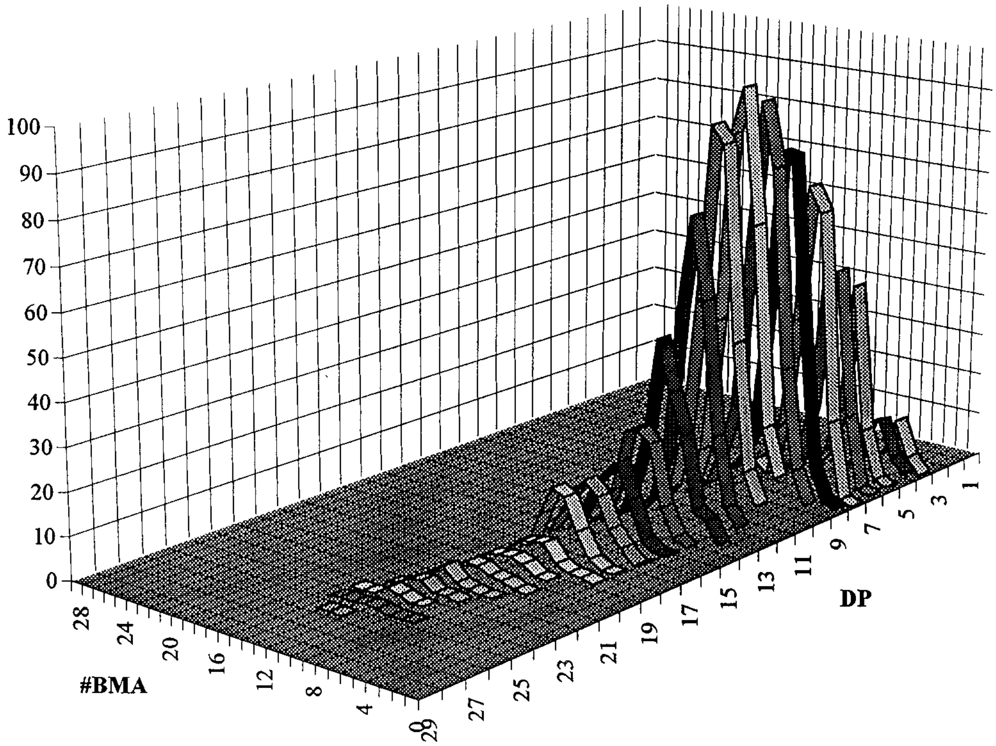


Figure 4. Bivariate distribution in composition and chain length obtained from deconvolution of the spectrum shown in Figure 2.

Table 3. Ranges of Degree of Polymerization Used

spectrum	lower limit of DP	upper limit of DP
A1	6	34
A2	6	34
B1	6	28
B2	6	26
C	6	26
D	6	19

Table 4. Copolymerization Parameters from the Literature and This Work

method	r_1	r_2	C_{S_1}	C_{S_2}	S_1
MALDI bivariate dist	1.09	0.77	17 900	6150	0.535
MALDI composition (average)	1.00	0.94			
MALDI composition (points)	1.18	0.93			
NMR composition	0.75	0.98			
ref 19	0.79	1.27			
ref 20	1.27	1.20			
ref 21	0.91	1.09			
ref 23				(24 100)[a]	
ref 18			24 300 (36 140)[a]		

[a] Values for bulk polymerization.

distribution differ from those determined from NMR composition data using the same samples.

Table 4 also shows the chain transfer coefficient estimated for COBF with MMA and BMA in toluene and the selectivity of initiation estimated from these data. The value obtained for COBF in toluene with MMA is lower than expected from the traditional Mayo equation[18] (17 900 as opposed to 24 300). It should be noted that COBF is found to exhibit solvent effects in toluene with MMA[18] (see Table 4). The value determined for COBF in toluene with BMA is lower than that found for BMA by applying the Mayo equation to data obtained in the bulk (6150 as opposed to 24 100).[23] The chain transfer coefficient for the bulk polymerizations is only approximate, since the molecular weight information was obtained from SEC using a PMMA calibration curve. SEC calibration standards are not available for most polymers, introducing errors into the molecular weight data obtained for these polymers by conventional SEC. The approximation of using a PMMA calibration curve to determine the bulk C_S value and the known effect of toluene on the chain transfer activty of COBF preclude direct comparison between the bulk value and that estimated in this work for BMA in toluene. The selectivity of initiation was estimated to be 0.535 from this data. No literature data are available for the relative rates of initiation of MMA and BMA COBF hydride, but the value is reasonable since it falls close to 1, as would be expected given the similarity between the two monomers.

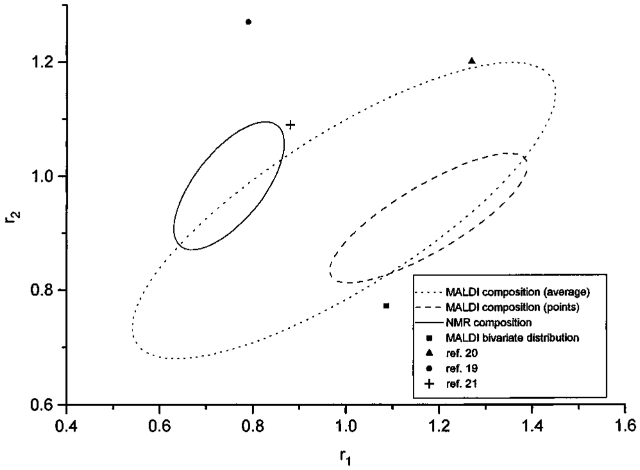


Figure 5. Plot of the reactivity ratio data from this work and literature values.

Although the parameter estimates determined from the bivariate distribution are not in complete accord with those obtained from other methods, they are reasonable. Furthermore, the reactivity ratios deter-

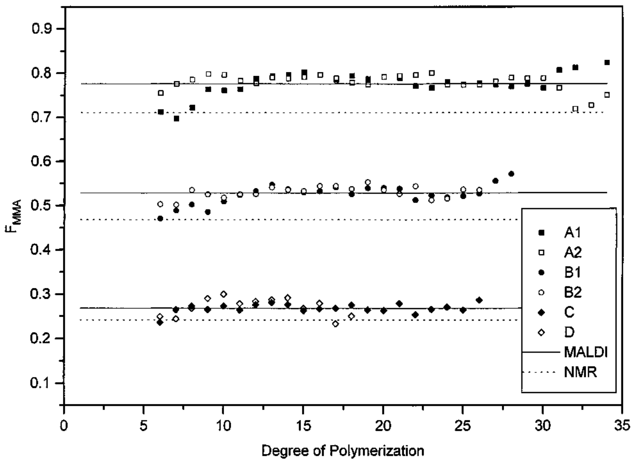


Figure 6. Average copolymer composition as a function of chain length obtained from the mass spectra. The solid and dotted lines were calculated from the feed compositions and reactivity ratios determined from MALDI (using compositions at different chain lengths within a spectrum as replicates) and NMR, respectively.

mined from the bivariate distribution show fair agreement with those obtained from MALDI using composition data alone. This suggests that the shortcomings of utilizing the bivariate distribution are not catastrophic and may be a reflection of current limitations of the relatively new mass spectrometry techniques or of the conditions used in this work.

Use of Composition Data from Mass Spectra. In the probability approach, the reactivity ratios are coupled to the other parameters used to model the copolymerization, since the entire bivariate distribution was used. Reactivity ratios were determined that were decoupled from the other parameters by using the average composition data from the mass spectra and the differential form of the terminal model copolymer equation, eq 13. Having the dependence of the average composition on chain length is extremely useful for short-chain copolymers since it allows the significance of the violation of the long-chain and equal reactivity assumptions on which eq 13 is based to be gauged. Figure 6 shows the average composition as a function of chain length for spectra used in this work. No strong trends are seen in these data, implying that the effects of violating these assumptions are minor.

The EVM program[15] was used to estimate reactivity ratios from the average composition of the whole polymer as determined in the six MALDI spectra. The EVM program requires an estimate of the uncertainty in the data used to calculate the reactivity ratios. In this work, an error of 1% was assumed for the feed composition, and 10% was assumed for the copolymer composition, as determined by MALDI. The point estimates for the reactivity ratios are contained in Table 4, and the 95% posterior probability ellipse is shown in Figure 5.

Since the average composition of the copolymer can be determined at each chain length, each mass spectrum can be considered to contain internal replicates. Thus, the data at each chain length can be used in the estimation of the reactivity ratios. The limitations of the EVM program employed did not allow the use of the data for all of the degrees of polymerization for all six of the spectra. Data from all six spectra were used, and the composition at every third degree of polymerization was used to reduce the number of data to a size which the program could handle. The reactivity ratios determined from these points are contained in Table 4, and the 95% confidence contour is shown in Figure 5. These point estimates of the reactivity ratios are different from the values obtained from the averages of the whole samples since there is a difference in the weighting of data in the two different methods. When the averages were used, the compositions were weighted by peak area, and thus the average was more strongly influenced by the short chains. When the composition at each degree of polymerization was used, all chain lengths were given the same weighting. The results from the two treatments of the data are in reasonable agreement since the confidence contour obtained from the data at different chain lengths is almost completely encompassed in the contour from the average composition data. The smaller posterior probability contour results from the compositions at different chain lengths since there is increased precision in the parameter estimates, resulting from the large number of internal replicates.

Comparisons with NMR. It was necessary to evaluate the accuracy of the values obtained from the mass spectrometry work. The paucity of and variation in the literature values for the reactivity ratios for the MMA/BMA system made it necessary to do this experimentally. The more traditional technique of ^{1}H NMR was used. An NMR spectrum was obtained for each of the four copolymer samples, and the average copolymer composition was determined from the areas in the alkoxy region, Figure 2. These data were used in the EVM program, assuming a 1% uncertainty in the feed composition and a 5% uncertainty in the copolymer composition. The resultant point estimates for the reactivity ratios and 95% confidence contour are shown in Table 4 and Figure 5, respectively. The NMR data give reactivity ratios that differ from those obtained from the MALDI data. Figure 6 shows that there was a bias in the MALDI spectra toward chains rich in PMMA under the conditions used. This may indicate that, under these conditions, ionization is favored by MMA units over the more hydrophobic BMA units. This is currently under investigation in our laboratory. The NMR data are consistent with the literature data set from ref 21, which lies just outside the 95% confidence contour. It is likely there that there will be significant overlap of the two joint confidence intervals.

Conclusions

It has been demonstrated that MALDI-TOF spectra of copolymers are extremely rich in information and that both the composition and chain length distribution of MMA/BMA copolymers can be obtained simultaneously by deconvolution of mass spectra. When used with an appropriate description of the copolymerization, kinetics estimates can be obtained for the underlying kinetic parameters. Two reactivity ratios, two chain transfer constants, and a measure of the selectivity of the reinitiation reaction were determined simultaneously for the catalytic chain transfer copolymerization of MMA and BMA using just three reaction conditions employing the methodology described. Comparison of the reactivity ratios and chain transfer constants resulting from this treatment of the mass spectrometry data with those in the literature or determined from NMR showed that reasonable values were obtained, but a bias in the MALDI-TOF data was suggested. This work illustrates the power of mass spectrometry as a tool for the characterization of synthetic polymers that are relatively complex, such as statistical copolymers. Furthermore, it shows the great promise that these emerging techniques offer in areas such as the study of copolymerization kinetics. It is noted that the use of CCTP to produce low molecular weight products suited to a MS study restricts the current approach to poly(methacrylic) polymers and copolymers containing at least some methacrylate comonomer.

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Supporting Information Available: State arrays used to determine objective function (8 pages). Ordering information is given on any current masthead page.

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