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Quantitative analysis of poly(methyl methacrylate–butyl acrylate) copolymer composition by liquid chromatography–particle beam mass spectrometry

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Abstract

Current polymer formulations contain mixtures of copolymers to tailor the performance needs. Reversed-phase liquid chromatography is commonly used to separate polymers according to their chemical composition by adsorption, partition or precipitation mechanisms if retention is not influenced by molecular mass. Liquid chromatography–mass spectrometry (LC–MS) has mainly been used to identify low molecular mass polymers and additives. In this paper, we report on the use of LC–MS for the quantitative analysis of copolymer composition of several high-molecular-mass polymers by monitoring the low-mass fragments formed by thermal decomposition and electron impact ionization when using a particle beam interface. The fragment ions produced are proportional to the comonomers present and are quantitatively related to the copolymer composition. Area ratio calibration with copolymers of known composition is used to determine the composition of unknown copolymers of similar structure.

Keywords: Mass spectrometry; Electron impact fragmentation; Particle beam interface; Interfaces, LC–MS; Thermal degradation; Copolymer composition; Poly(methyl methacrylate–butyl acrylate)

1. Introduction

A current trend in polymer development is to blend copolymers to produce a new material with properties unique to each of the copolymers [1]. These polymer blends may be formulated with additives, as well as, plasticizers and stabilizers to tailor the desired performance characteristics. The identification and quantification of polymer blends is important for structure–property processing relationships [2], polymer deformulation [3], and quality control purposes.

The chromatographic separation of synthetic polymers has been the subject of on-going research for approximately 30 years [4]. Gel permeation chromatography (GPC) was developed for the analysis of organic solvent soluble polymers [4], and is the most widely used technique for the determination of molar mass distributions (MMD) of polymers after proper calibration [5]. The combination of GPC and spectroscopic techniques have been used to determine the MMD and composition of copolymers

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[2,6–8], however GPC does not have sufficient resolution to analyze the more complex polymer blends [2].

Both reversed-phase liquid chromatography (RPLC) and normal-phase liquid chromatography (NPLC) are capable of separating copolymers according to their chemical composition (comonomer ratio, sequence, structure, endgroup) [9,10]. The use of RPLC and NPLC is more amenable than GPC for the separation of polymer blends due to the fact that they are higher resolution techniques and are capable of separating materials based on composition.

Liquid chromatography–mass spectrometry (LC–MS) is a form of two-dimensional analysis where the first dimension fractionates mixtures using liquid chromatography and the second dimension separates by mass with subsequent detection. The combination of LC and MS is ideal for the separation of complex mixtures and identification of each component. Conventional on-line LC–MS has had limited applications for the analysis of polymers due to their limited volatility and the ease at which they thermally degrade [11].

Therefore, LC–MS utilizing various interfaces has been mainly used to analyze low-molecular-mass polymers such as polystyrene [11], surfactants [12], and polyesters [13]. Reversed-phase LC coupled to particle beam MS was used to separate and identify the low molecular mass oligomers of polystyrene and demonstrate the effect of ion source temperature on oligomer vaporization and chromatographic peak shape [11]. An ion source temperature of 315°C demonstrated enhanced volatilization as compared to 200°C for the particle beam LC–MS analysis of polystyrene oligomers, resulting in an improved separation and identification out to the 21st oligomer [11]. Electrospray (electrically nebulized and ionized) MS has been utilized with GPC for accurate GPC calibration of the low molecular mass ethylene oxide distribution analysis of octylphenol ethoxylates [12]. Atmospheric pressure chemical ionization (thermally nebulized and solvent mediated chemical ionization) was combined with RPLC for the identification of the lower-molecular-mass oligomers of poly(ethylene terephthalate) [13]. The analysis of higher-molecular-mass polymers has been accomplished by polymer hydrolysis and analysis of the low-molecular-mass by-products [14].

The use of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is a powerful tool for the analysis of polymer composition and molecular mass [15,16]. The resolution of current MALD-TOF-MS instruments allow oligomer characterization below a molecular mass of 36 000 [17]. Above a mass of 36 000 only molecular mass information is obtained since individual oligomers cannot be resolved and thus identified. The use of MALDI-TOF-MS in combination with HPLC has been mainly restricted to the low molecular mass ($<$1400) identification of collected fractions of alcohol ethoxylates [18], poly(decamethylene adipate) [18], poly(ethylene oxide–block–propylene oxide) copolymers [19], aliphatic polyesters [19], and poly(ethylene oxide) macromonomers [19]. The use of MALDI-TOF-MS for the analysis of low molecular mass polymer HPLC fractions has clearly demonstrated the utility of the technique [18]. However, no higher molecular mass synthetic polymer ($>$10 000 M_r) blends purified by HPLC have been analyzed by MALDI-TOF-MS to the authors' knowledge, and there is a need to analyze the composition of high mass ($>$100 000 M_r) polymer blends.

In this paper, we investigate the use of liquid chromatography/particle beam mass spectrometry (LC–PB-MS) for the quantitative compositional analysis of poly(methyl methacrylate–butyl acrylate) copolymers of approximately 200 000 molecular mass by HPLC separation, polymer decomposition and MS quantitation and identification of the resulting fragments. The chromatographic separation was studied in terms of the effect of polymer composition on retention time. The mass spectrometer intensity was evaluated as a function of ion source temperature, polymer composition, polymer molecular mass and concentration. The area ratio of a particular decomposition product relative to the total products (ion chromatogram/total ion chromatogram) was used to determine the composition of copolymers and a blend of similar composition and structure to the calibration polymers.

2. Experimental

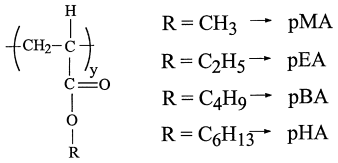
2.1. Chemicals

The homopolymers used throughout the study

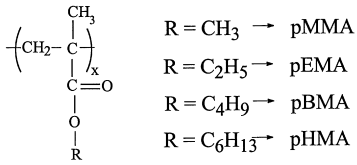
were purchased from either Polymer Labs (PL, Church Stretton, UK), Scientific Polymer Products (SPP, Ontario, NY), or Polymer Source (PS, Dorval, Quebec, Canada) and are listed in Table 1 and shown in Fig. 1a and b. The homopolymer mixtures were diluted in tetrahydrofuran to 1% (w/w) of each component.

The mixture of polymers used to calibrate the LC–PB–MS contained poly(methyl methacrylate), abbreviated as pMMA, and poly(butyl acrylate), abbreviated as pBA, homopolymers and four co-polymers containing pMMA and pBA at different compositions. The structures and composition of the six polymers (A–F) used in the calibration mixture are shown in Fig. 1c. The p(MMA/BA) copolymers were made in-house using emulsion polymerization and had a molecular mass of approximately 200 000, as determined by GPC with narrow polystyrene standard calibration. A small percentage (<1%) of methacrylic acid was present in the copolymers to aid in emulsion stability. The copolymers were supplied in water and dried on a petri dish at room temperature for several days before weighing. Each copolymer was initially diluted to 10% (w/w) in

a.) Poly(alkyl acrylate) homopolymers



b.) Poly(alkyl methacrylate) homopolymers



c.) Poly(methyl methacrylate/butyl acrylate) copolymers

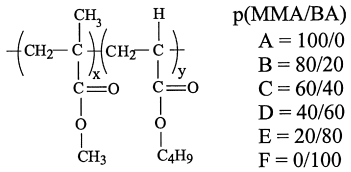


Fig. 1. Structure and composition of polymers used in this study.

Table 1
Homopolymers used in this study

Polymer	Acronym	Monomer molecular mass	Polymer molecular mass	Supplier
Poly(methyl acrylate)	pMA	86	35 000	SPP
Poly(ethyl acrylate)	pEA	100	100 000	SPP
Poly(butyl acrylate)	pBA	128	100 000	SPP
Poly(hexyl acrylate)	pHA	156	90 000	SPP
Poly(methyl methacrylate)	pMMA	100	185 000	PL
Poly(ethyl methacrylate)	pEMA	114	280 000	SPP
Poly(butyl methacrylate)	pBMA	142	85 000	SPP
Poly(hexyl methacrylate)	pHMA	170	400 000	SPP
Poly(methyl methacrylate)[a]	pMMA	100	1 232 700	PS
			132 000	
			70 900	
Poly(butyl acrylate)[a]	pBA	128	209 600	PS
			46 400	
			5 420	

[a] Polymers used in the molecular mass versus area ratio study.

tetrahydrofuran. The calibration mixture was composed of equal weight of the four copolymers and a 1% solution of each homopolymer (pMMA and pBA). The stock solution contained approximately 2% of each copolymer and 0.2% of each homopolymer. Serial dilution with tetrahydrofuran gave the different concentrations of the calibration mixture.

The polymers analyzed for composition (copolymer 1, copolymer 2, copolymer 3, copolymer 4, and polymer blend) were supplied in-house and were diluted in tetrahydrofuran to approximately 2% (w/w) for analysis. The copolymer blend is a mixture of copolymers, one of which contains MMA. The actual composition of each copolymer is the weight percent of monomer during emulsion polymerization. Similar to the copolymers used to calibrate the LC–PB-MS, a small percentage of methacrylic acid was present in the copolymers, and the quantity varies in the copolymers. The block copolymer was purchased from Polymer Source (catalog number P1091-nBAMMA). All solvents (uninhibited tetrahydrofuran and acetonitrile) were HPLC grade and purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Equipment

The LC–PB-MS was a Waters (Milford, MA) Integrity system and consisted of an Alliance quaternary HPLC pump with vacuum degassing, autosampler, model 996 diode array detector and thermabeam mass detector (TMD). The TMD utilizes a particle beam interface with an electron impact ion source operating in the positive mode with a quadrupole mass analyzer set to scan a mass spectrum every 2 s in the mass range of 75–800 amu. The operational temperatures of the nebulizer, expansion region, and ion source were 65°C, 75°C, and 300°C, respectively, unless stated otherwise. The diode array detector was set to acquire a UV spectrum every 2 s from 215–400 nm with a resolution of 4.8 nm. The HPLC pump was linearly programmed from 90/10 (acetonitrile/tetrahydrofuran) to 0/100 in 30 min. The injection volume was 2 μl. An injection volume larger than 2 μl caused peak splitting, due to the use of a strong injection solvent for these separations. The reversed-phase column was a Waters Symmetry C_{18}, 150×3.0 mm with 5-μm particles and 100 Å pores. The flow-rate was 0.5 ml/min. All the standards and samples were analyzed in triplicate and displayed in figures as an average and standard deviation.

3. Results

3.1. Degradation mechanisms

The various pathways whereby these polymers can degrade is important to understand so as to aid in the interpretation of the mass spectra. This is increasingly important as the polymer structure increases in complexity. Polymer degradation or pyrolysis occurs when sufficient thermal energy is applied to cause bond dissociation and free radical formation. If all the carbon–carbon bonds in a polymer backbone are of the same strength then chain scissioning produces polymer fragments with terminal free radicals (opposite of polymerization) [20]. Once initiated, several free radical degradation mechanisms may occur depending on the polymer backbone, side groups and the stability of the products.

Vinyl polymer radicals are known to degrade by a chain depolymerization mechanism, whereas, condensation polymers undergo a random depolymerization mechanism which is mainly due to random chain rupture [21]. Chain depolymerization results in the unzipping of monomer units from one end of the polymer by β-scission (bond dissociation at the β position) and produces mainly monomer units as displayed in Fig. 2a. β-Scission is propagated according to the stability of the free radical that is formed. Blockage of chain transfer (transfer of the radical to another molecule) occurs due to the presence of the α-methyl group in poly(alkyl methacrylate) polymers. In pMMA degradation, a monomer yield of 92–98% has been reported regardless of the temperature, as long as there is sufficient energy to break an initial carbon–carbon bond [21,22]. Poly(alkyl methacrylate)s with a longer alkyl side chain degrade in a similar manner to pMMA until the alkyl side chain gets too long then side-group scission takes place [22]. The production of monomer decreases as the alkyl side chain length increases [22].

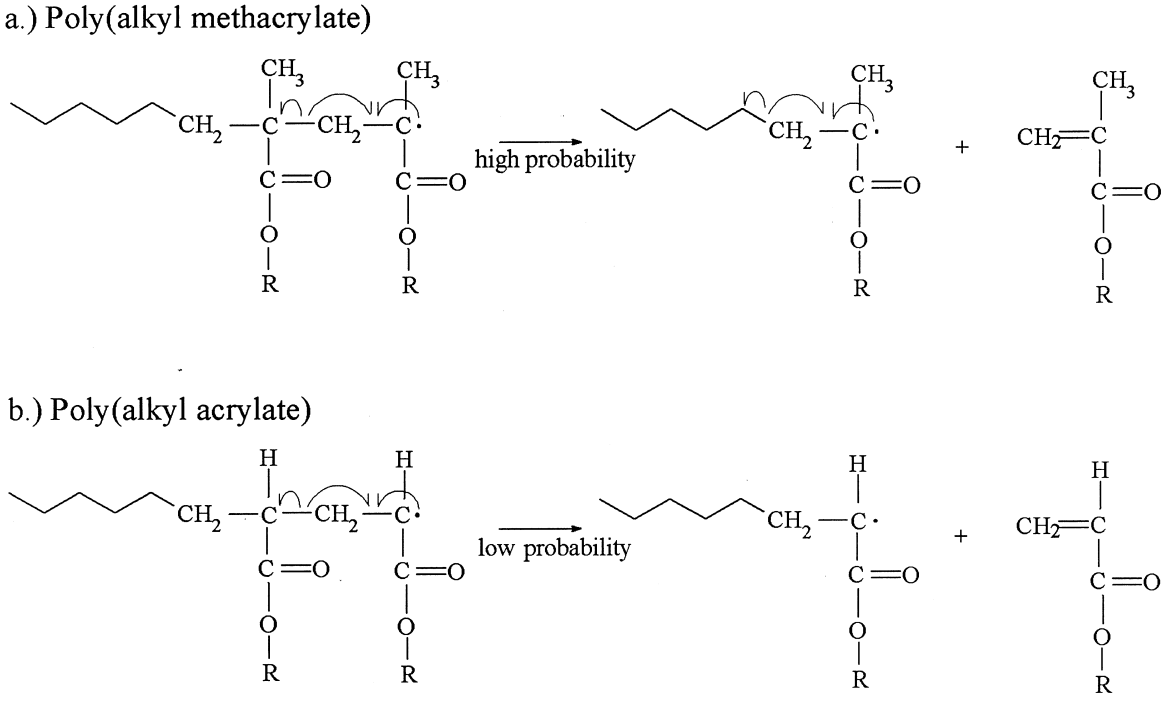


Fig. 2. Thermal degradation mechanism for (a) poly(alkyl methacrylate)s and (b) poly(alkyl acrylate)s.

In contrast to the degradation of poly(alkyl methacrylate) polymers described above, poly(alkyl acrylate) polymers (Fig. 2b) contain a hydrogen in the α position and do not form a stable radical upon β-scission, thus these polymers have a higher probability of inter- and intramolecular chain transfer and degrade by a random depolymerization mechanism [23,24]. A variety of products are produced in random depolymerization resulting in a lower monomer yield [21].

3.2. Effect of ion source temperature on homopolymer degradation

The analysis of a series of poly(alkyl acrylate) and poly(alkyl methacrylate) homopolymers is shown in Figs. 3 and 4, respectively, using two different ion source temperatures. The figures are displayed as spectrum index plots, which contain a total ion chromatogram (TIC) along the bottom and the corresponding mass spectra for each integrated peak along the top. The peak integrations shown are used for generating the mass spectra at the peak apex, not for area calculations. The HPLC retention times are listed in the top left-hand corner of each spectrum.

The mass spectra of four poly(alkyl acrylate) homopolymers with an ion source temperature of 200°C are shown in Fig. 3a. The electron impact mass spectra of pMA, pEA, and pBA are not consistent with the corresponding monomers [23] and thus appear to be degrading into many decomposition products which is common for polymers undergoing a random degradation mechanism [24,25]. The pHA degrades mainly into an 87 ion (protonated pMA), which could be due to side-group scission of the hexyl group. Of the poly(alkyl acrylate) polymers analyzed, only pBA produced a significant amount of deprotonated monomer molecular ion (m/z of 127).

As shown in Fig. 3b, there is an increase in signal intensity for the experiments conducted with an ion source temperature of 300°C, but the peak shape is approximately the same as at 200°C. The increase in signal intensity correlates with an increase in thermal volatilization of poly(alkyl acrylate) polymers in this temperature range as determined by thermal

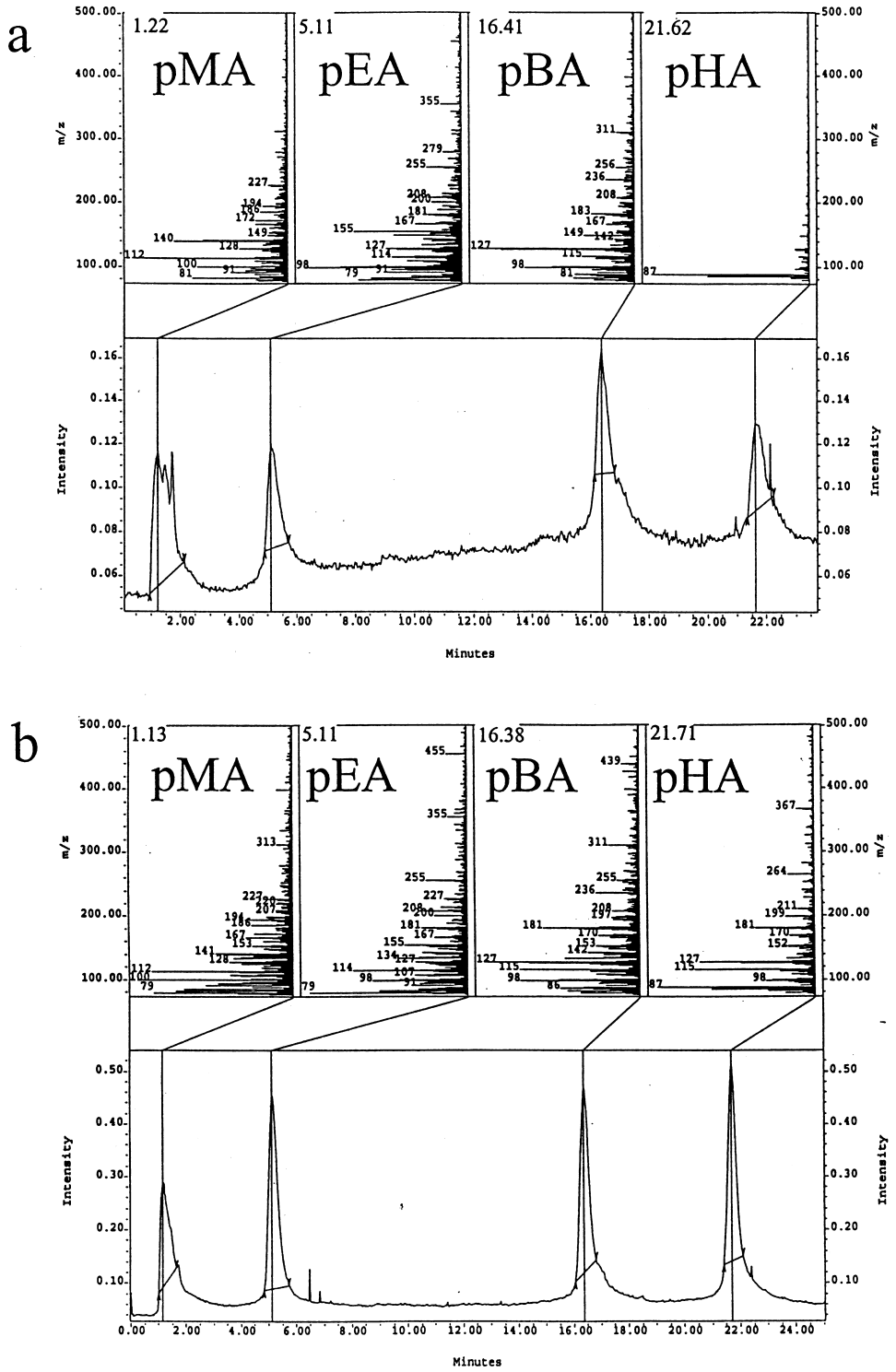


Fig. 3. LC–PB-MS index plot of a mixture of poly(alkyl acrylate) homopolymers with an ion source temperature of 200°C (a) and 300°C (b). Retention times are in the upper left hand corner of the mass spectra.

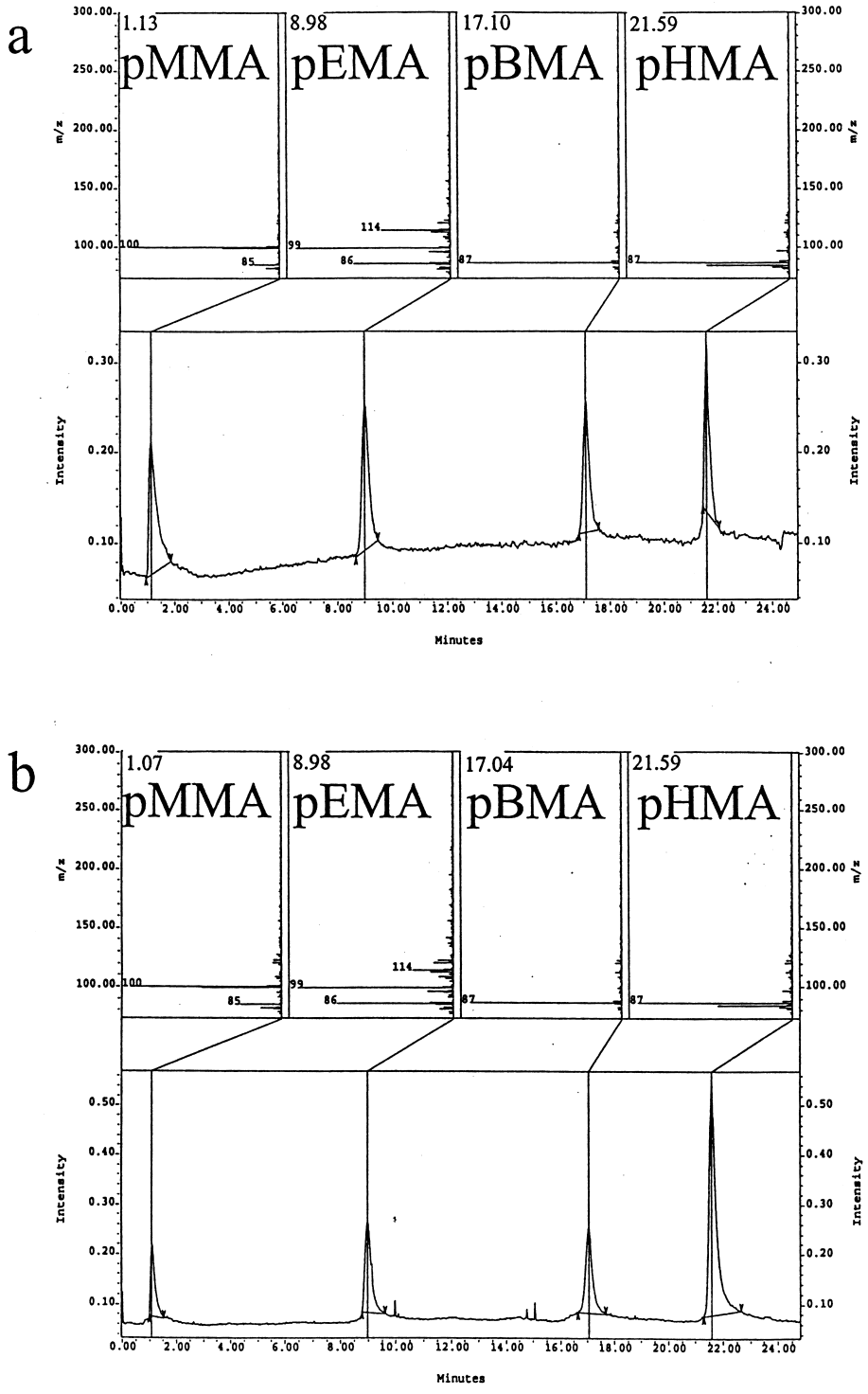


Fig. 4. LC–PB-MS index plot of a mixture of poly(alkyl methacrylate) homopolymers with an ion source temperature of 200°C (a) and 300°C (b). Retention times are in the upper left hand corner of the mass spectra.

gravimetric analysis [26]. The pHA is more fragmented at 300°C and may have reached the onset temperature of random depolymerization. An increase in MS fragmentation is also observed for pMA, pEA, and pBA at 300°C as compared to 200°C. The increase in fragmentation of the poly(alkyl acrylate) homopolymers at the higher ion source temperature is probably due to an increased production of thermal degradation products from random degradation of the homopolymers, or an enhanced volatilization of the degradation products.

The analysis of a series of poly(alkyl methacrylate) homopolymers with an ion source temperature of 200°C is shown in Fig. 4a. Poly(alkyl methacrylate) polymers are more likely to chain depolymerize and the result is less decomposition products which is evident when comparing Figs. 3 and 4. The monomer molecular ions appear for both pMMA (m/z 100) and pEMA (m/z 114), but significant amounts of monomer molecular ions were not detected for the higher alkyl poly(alkyl methacrylate)s. These mass spectra are consistent with the electron impact mass spectra of the corresponding monomers [23], thus gas phase neutrals are most likely produced during thermal decomposition and then fragmented by electron impact ionization.

The same mixture of poly(alkyl methacrylate)s was analyzed at 300°C (Fig. 4b), resulting in similar fragmentation results to that at 200°C. The pHMA has greater sensitivity at 300°C which was also seen in the poly(alkyl acrylate) sample. It appears that the mechanism for production of detectable ions for the hexyl functional homopolymers may be some combination of desorption, volatilization and degradation, and these temperature studies suggest that polymers with hexyl functionality need higher ion source temperatures for maximum signal intensity.

The particle beam interface is capable of thermally degrading poly(alkyl acrylate) and poly(alkyl methacrylate) homopolymers under different thermal degradation mechanisms. The poly(alkyl methacrylate)s produce mainly monomer, whereas, the poly(alkyl acrylate)s produce a variety of degradation products, as evident by the number of MS fragment ions produced. A higher ion source temperature produced a larger quantity of degradation products. The maximum ion source temperature on the instrument is 300°C, thus 300°C was used for the remainder of the experiments.

3.3. Effect of random copolymer composition on mass spectrometer ion intensity

A mixture of random poly(methyl methacrylate–butyl acrylate) copolymers was analyzed to determine the effect of MS fragmentation patterns on polymers containing the same monomers, but in different proportions. Fig. 5 is a spectrum index plot of a mixture of polymers described in Fig. 1c. The copolymers (B,C, D, and E) elute between the two homopolymers (A and F), and an increasing number of fragment ions are produced with increasing BA content. The ion produced from the MMA monomer (m/z 100) decreases with increasing BA content (decreasing MMA content), and the ion produced from the BA monomer (m/z 127) increases with increasing BA content. If a copolymer has a high content of BA then the m/z 127 is a major ion in the mass spectrum. Conversely, if a copolymer has a high content of MMA then the m/z 100 ion is predominant. These results shown in Fig. 5 indicate that the thermal degradation fragmentation appears to be quantitative with respect to composition for these particular monomers. This relation between ion intensity and polymer content is shown in Fig. 6 by plotting the reconstructed ion chromatograms (RIC) at m/z 100 and m/z 127, along with the TIC. The small peak eluting after the pMMA peak at 1.5 min is an artifact due to the injection process. The p(MMA/BA) copolymer with a composition of 80/20 eluting at approximately 6 min is slightly higher in concentration than the other copolymers, thus yielding a proportionally larger signal. The RIC at m/z 100 shown in Fig. 6b demonstrates that the polymers containing a higher content of MMA are more intense and have a larger peak area. Conversely, the RIC at m/z 127 shown in Fig. 6c demonstrates that intensity and area are proportional to the BA content.

The quantitative analysis of copolymer composition using pyrolysis degradation products involves ratioing the peak area of a particular product to the sum of the areas of all products [27,28]. In LC–MS the integrated area of the RIC is representative of a particular ion and the TIC is representative of the sum of all ions. A plot of the area percent of the major ion produced in pMMA (m/z 100) and pBA (m/z 127) relative to the TIC versus composition of the six polymers is shown in Fig. 7. A fairly good fit

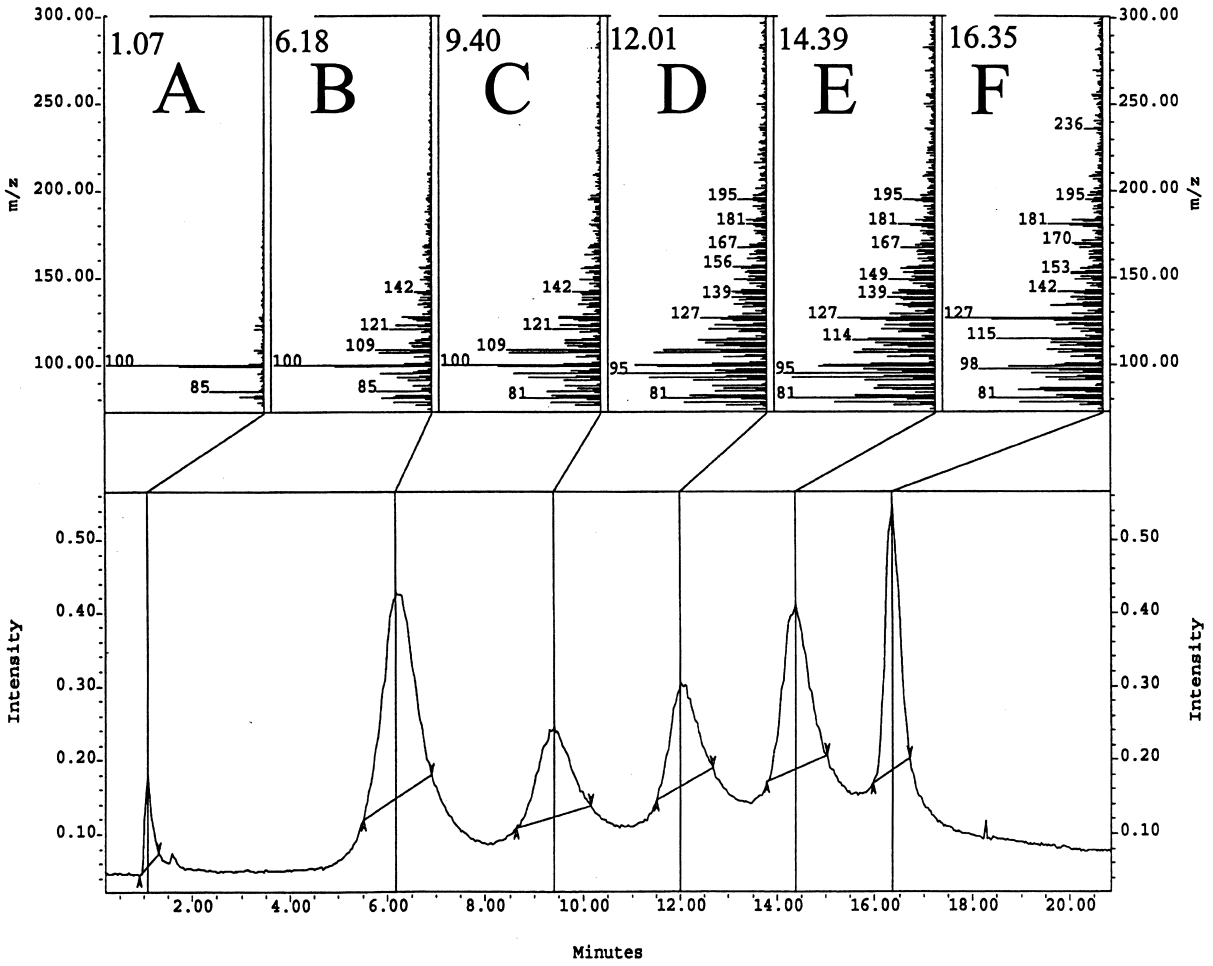


Fig. 5. LC–PB-MS index plots of the calibration mixture of poly(methyl methacrylate–butyl acrylate) copolymers and homopolymer with an ion source temperature of 300°C. The peaks are labelled according to the polymers in Fig. 1c. Retention times are in the upper left hand corner of the mass spectra.

(R>0.95) is obtained on the semi-log plot for both the MMA and BA fragment ions. The slope and area ratio of the MMA results are of larger magnitude than the BA due to the chain depolymerization mechanism of pMMA which produces mainly monomer. The m/z 127 ion is produced by a random degradation of pBA which also produces many other products, and thus its area is a smaller percentage of total area.

3.4. Effect of polymer concentration on area ratio

The relationship between area % RIC/TIC for determination of copolymer composition would be most beneficial if the relationship was not concentration or molecular mass dependent. Fig. 8 shows a plot of the m/z 100 and m/z 127 area ratio versus composition analyzed at three different concentrations of the six polymers. The results at different concentrations are very similar and are within one standard deviation of each other. These plots show that the area ratio is independent of polymer concentration over the range examined, and allows this method of compositional analysis to be easily implemented since the absolute copolymer concentration does not need to be determined.

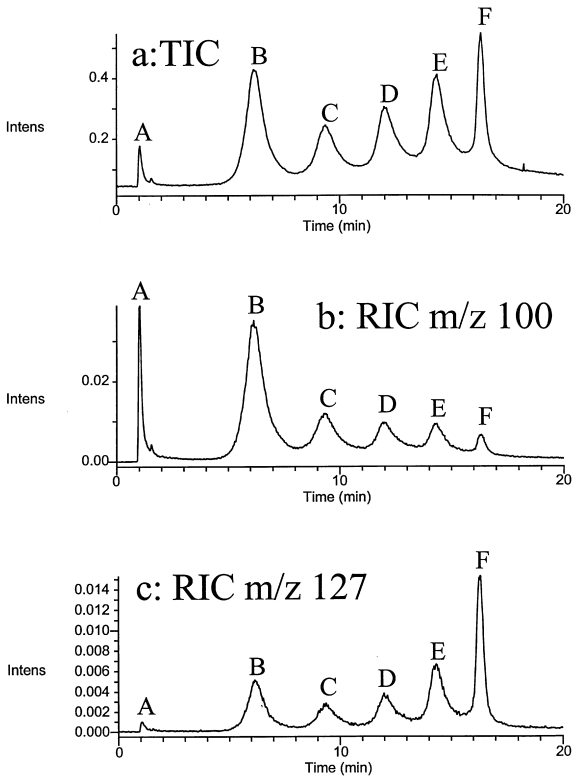


Fig. 6. HPLC separations of the mixture of poly(methyl methacrylate–butyl acrylate) copolymers and homopolymer assigned in Fig. 5. Displayed are the TIC (a), RIC at m/z 100 corresponding to MMA content (b), and RIC at m/z 127 corresponding to BA content (c).

3.5. Effect of homopolymer molecular mass on area ratio

The relationship between the homopolymer molecular mass and the area ratio is shown in Fig. 9. The pBA (m/z 127) homopolymer area ratio response is fairly constant from a molecular mass of 5000 to 210 000 at the same concentration. The pMMA (m/z 100) homopolymer area ratio is relatively constant from 71 000 to 1.2 million molecular mass for the same mass injected on-column. Similar to Fig. 7, the pMMA (m/z 100) produces a higher percentage of the total area as compared to pBA (m/z 127) due to the different degradation mechanisms. Figs. 8 and 9 show that area ratio is mainly dependent on polymer composition and independent of concentration and molecular mass.

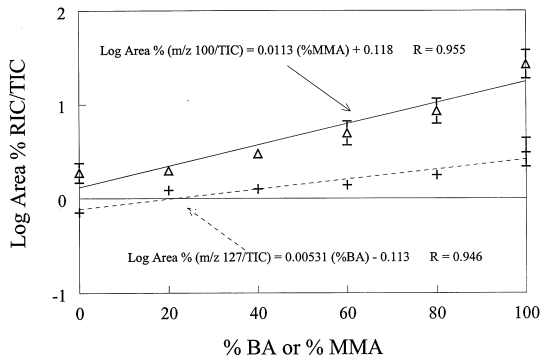


Fig. 7. Polymer composition effect on area percentage ratio (RIC/TIC) for the p(MMA–BA) mixture in Fig. 5 at a polymer concentration of 1%. The pMMA is represented with the m/z 100 ion and pBA is represented with the m/z 127 ion. The results are an average (symbol) and standard deviation (error bars) of three replicate injections. Error bars are displayed when the standard deviation is larger than the size of the symbol.

3.6. Effect of polymer composition on retention time

The relationship between retention time and composition of the p(MMA–BA) copolymer calibration mixture is shown in Fig. 10. The poly(methyl methacrylate) homopolymer was omitted from this plot since it did not have significant retention ($k=$ 0.2). There is a linear relationship between BA content and elution time which is typical for the separation of copolymers by RPLC [10,29].

3.7. Calculation of polymer composition from area ratio and retention time

Several commercial polymers of known composition made by different polymerization processes were examined to determine the accuracy and precision of the determination of the MMA and BA content by the MS area ratio and retention time methods. The results of calculating % BA and % MMA in five p(MMA–BA) copolymers and a polymer blend using the MS area ratio and retention time calibrations are listed in Table 2.

The calculated BA content in Table 2 of four random copolymers using retention time demonstrates that the actual polymer composition is estimated with good precision (<1% R.S.D.) and ac-

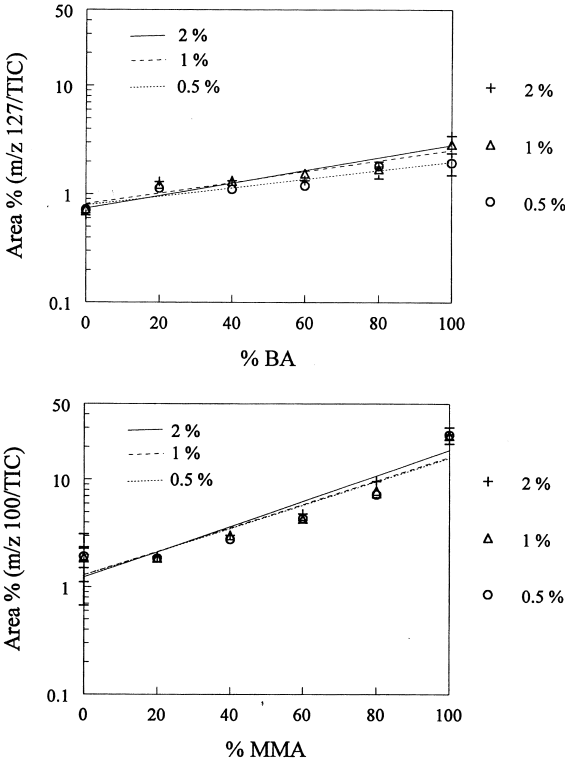


Fig. 8. Polymer concentration effect on area % ratio (RIC/TIC) for the p(MMA–BA) mixture. The pBA is represented with the m/z 127 ion (top) and pMMA is represented with the m/z 100 ion (bottom). The results are an average (symbol) and standard deviation (error bars) of three replicate injections. Error bars are displayed when the standard deviation is larger than the size of the symbol.

curacy, except for random copolymer 2. The calculated % BA using retention time for random copolymer 2 was slightly lower than the actual value. The block copolymer was more retained than the random copolymers used in the calibration which resulted in an approximate 20% difference from the actual composition. Block copolymers are known to be more retained than random copolymers due to the additive effect of similar neighbors enhancing the interaction with the stationary phase [29]. This interaction is not present in random copolymers. The polymer blend did not contain BA, thus the retention time result is meaningless, and will be further discussed below.

The calculated BA content in Table 2 of the random copolymers determined by the MS area ratio

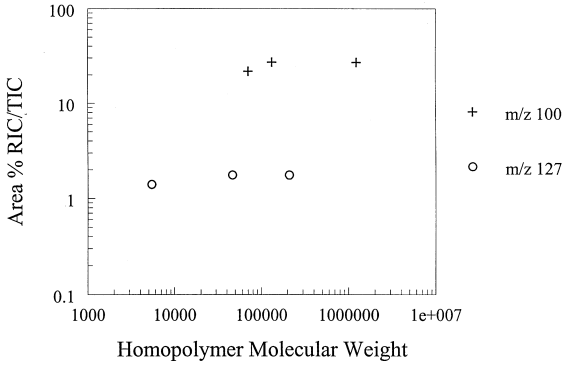


Fig. 9. Homopolymer molecular mass effect on area % ratio (RIC/TIC) for pMMA and pBA at the 1% concentration level of each. The pMMA is represented with the m/z 100 ion and pBA is represented with the m/z 127 ion. The results are an average (symbol) and standard deviation (error bars) of three replicate injections. Error bars are displayed when the standard deviation is larger than the size of the symbol.

method results in similar averages to the retention time data, but with a decreased precision (approximately 10% R.S.D.). This decrease in precision may be due to thermal degradation processes or difficulty in peak area integration reproducibility. The % BA of the block copolymer by the MS area ratio is lower than the actual composition, but is within experimental error. Block copolymers are known to thermally degrade through different pathways as compared to random copolymers [27], and this may be part of the

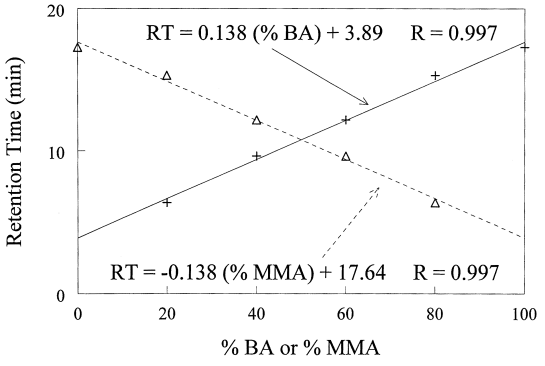


Fig. 10. Polymer composition effect on retention time for p(MMA–BA) mixture. The pMMA calibration is represented with the dashed line and pBA calibration is represented with the solid line. The results are an average (symbol) and standard deviation (error bars) of three replicate injections. Error bars are displayed when the standard deviation is larger than the size of the symbol.

Table 2
Comparison of butyl acrylate and methyl methacrylate composition determined by retention time and area ratio

Polymer	Determined % BA from retention time[a]	Determined % BA from area ratio[a]	Determined % MMA from retention time[a]	Determined % MMA from area ratio[a]	Actual % BA/MMA[b]
Random copolymer 1	90.7±0.1	93.0±6.7	9.0±0.1	1.9±1.6	91/7
Random copolymer 2	60.4±0.2	63.0±3.8	39.3±0.5	40.2±5.3	65/35
Random copolymer 3	51.2±0.1	51.1±3.6	48.5±0.1	51.4±2.8	51/46
Random copolymer 4	52.0±0.2	52.1±2.2	47.7±0.2	51.8±1.1	52/45
Block copolymer	65.8±0.5	37.1±13.6	33.8±0.5	110.0±5.0	47/53
Polymer blend	38.8±0.3	18.0±9.8	60.8±0.3	100.0±2.0	0/58

[a] Average±standard deviation of three replicate injections.
[b] Actual composition determination is discussed in the Section 2. The difference in total MMA and BA content and 100% is the amount of methacrylic acid.

reason for the difference in the accuracy of the block copolymer determination as compared to the random copolymer determination.

Similar to the BA results, the determined MMA content in Table 2 of all the polymers is very precise using the retention time data (<1% R.S.D.), but the actual % MMA is overestimated in all of the random copolymers. In the case of the block copolymer the retention time calibration yielded a 20% lower value than the actual. The lower MMA content calculation by retention time shows that the BA chain is more dominant in the retention mechanism of block copolymers using this HPLC method.

The calculation of the MMA content in Table 2 from the MS area ratio has similar results to the retention time and actual values for the random copolymers, except for copolymer 1 which has a low value of MMA relative to the other copolymers. The poor accuracy for random copolymer 1 may be due to the dominance of BA in the thermal degradation process of this copolymer, and the MMA may degrade randomly, thus producing less monomer. The copolymers with higher levels of MMA result in slightly higher than the actual value. The reason for the higher values in the random copolymers 2, 3, and 4 may be due to a slightly different arrangement (sequence) of the MMA monomer as compared to the copolymers used in the calibration. The block copolymer is an extreme case of this arrangement, whereas the calculated MMA is similar to the homopolymer and twice the actual amount. In this case, the MMA block may be degrading much more quickly than the BA block which results in a higher MMA intensity and lower BA intensity relative to the calibration copolymers.

The thermal degradation yield relative to the actual monomer content is called the normalized yield [30], and has been found to vary depending on the copolymer structure (random, alternating, block, or a blend). Certain comonomers enhance thermal degradation and the normalized yield of other monomers, whereas some comonomers may hinder thermal degradation and the normalized yield [30]. The ratio of peak areas for random versus block copolymers has been used to evaluate the sequence length distribution [27]. In the p(MMA/BA) block copolymers and pMMA homopolymer, the MMA block structure can unzip uninterrupted. In random copolymers of different MMA sequence lengths, the MMA unzipping is frequently interrupted. Thus, the normalized yield will vary on MMA sequence length, and this may be the reason for some of the variation seen in the analyzed copolymers using the MS area technique. Thus, random and block copolymers of the same composition need to be calibrated separately for accurate determination of composition. Polymer adsorption, rate of comonomer degradation, and detector non-linearity may also effect the determination of polymer composition by thermal degradation of copolymers.

The analysis of polymer blends containing only one of the calibrated monomers was examined for method generality. This method was used to separate a polymer blend into individual copolymers, one of which is known to contain MMA, but not BA. The MMA content of one of the copolymers in the

polymer blend is accurately determined by the retention time calibration, but is higher than expected for the area ratio calibration. Similar to the other random copolymers, the arrangement of MMA in the polymer blend may cause it to degrade differently than the polymers used in the calibration.

From all these results it appears that using the MS area ratio and retention time are only applicable for calculation of a copolymer's composition if the same monomers are used in the calibration and the polymers have the same sequence length.

4. Discussion

In this paper we have introduced the technique of quantitative copolymer analysis using LC–PB-MS. The effect of polymer composition, concentration, molecular mass, and monomer unit sequence on HPLC retention and MS ion intensity were studied. Liquid chromatography with particle beam mass spectrometric detection is capable of thermally degrading high-molecular-mass polymers, with different fragmentation patterns for poly(alkyl acrylate)s and poly(alkyl methacrylate)s. The poly(alkyl methacrylate)s fragment mainly into monomer ions and appear to decompose by chain depolymerization, whereas, poly(alkyl acrylate)s fragment into many decomposition products probably by random degradation processes. The area percent ratio of MS ions associated with MMA and BA were correlated with composition, independent of the polymer concentration and molecular mass.

The prediction of copolymer composition by the MS area ratio method proved to be reasonably accurate for polymers made by the same process as the calibration copolymers. Block copolymers containing the same comonomers did not decompose in the same manner as the random copolymers, and thus did not give accurate results with a random copolymer calibration. The differences between block and random copolymers seen in this study may be an area for future work. If the area ratio is calibrated for block copolymers of known sequence length, then the retention time and area ratio relationship could be used to determine the composition and sequence length. The analysis of a polymer blend containing only one of the comonomers did not provide meaningful results.

Pyrolysis–gas chromatography has been used to calculate the molecular mass of homopolymers by ratioing the monomer to endgroup area [31]. In a similar manner LC–PB-MS could be used to separate polymer blends and measure the molecular mass using the area ratio of the monomer to endgroup. The extension of this concept for the LC–PB-MS analysis of copolymers will be the subject of future work.

Liquid chromatography–particle beam-mass spectrometry was shown to be useful for the determination of MMA and BA containing copolymers of similar structure after calibration, and should be able to perform similarly for other copolymers if distinct fragment ions are produced and no interfering ions are present. This technique is very similar to off-line HPLC pyrolysis GC, but will not perform well for all polymers due to this particular instrument design. Poly(alkyl acrylate) and poly(alkyl methacrylate) polymers were analyzed in this study, but higher ion source temperatures are needed for polymers that decompose at higher temperatures (e.g. polystyrene). The limitations of this particular instrument as compared to off-line techniques (e.g. pyrolysis–GC) are the ion source temperature and ionization conditions. The use of LC–PB-MS has the advantage of separating polymer mixtures and determination of the composition of each component, and is mass and concentration independent. The ability to utilize higher temperatures, chemical ionization, or MS–MS would allow a wider range of polymers to be analyzed, and increase the specificity and selectivity of the technique. Overall, the results are encouraging and further work is needed to show more application of this technique for copolymer analysis.

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