

Composition distribution separation of methyl methacrylate–methacrylic acid copolymers by normal-phase gradient elution high-performance liquid chromatography

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ABSTRACT

The characterization of copolymers requires the determination of chemical composition distribution in addition to molecular mass (M) distribution. Techniques commonly applied to copolymer analysis provide either average bulk composition or a convolution of M and composition distributions. The application of gradient elution adsorption chromatography, under appropriate conditions, allows the separation of copolymers based solely upon their chemical composition in a M -independent mode. Separation independent of M requires the elimination of size-exclusion effects with the porous adsorbent and the minimization of precipitation contributions. For separation over a wide copolymer composition range, the relative contributions of adsorption and precipitation retention mechanisms change with solvent composition. Under gradient elution conditions where adsorption retention dominates, composition fractionation can be combined with subsequent size-exclusion chromatography to provide a complete composition/ M map of the copolymer.

INTRODUCTION

Synthetic polymers present many unique separations challenges because, unlike small organic molecules, they consist of a distribution of structurally different molecules [1,2]. Each macromolecule can differ in chain length and end groups; stereochemical and structural isomers are possible along with unique branching architectures. Copolymers are further complicated by the combination of these potential variables with varying ratios and sequence distributions of their comonomer units. Liquid chromatography of synthetic polymers is limited by the solution properties of macromolecules to narrow selections of solvents for each polymer type. The application of liquid chromatography to the separation of synthetic polymers is characterized by the balance between solvation and adsorption interactions and is often complicated by polymer

solubility limitations in gradient elution separations [2].

Frequently synthetic polymers are described by single average values, such as average molecular mass, average chemical composition, average length between branch sites, etc. For many purposes these average values are sufficient. However, it is often the shape of a structural distribution not described by a single value which is most relevant to polymer properties. It is only after the joint structural distributions are deconvolved that this information is obtained. Separation by liquid chromatography thus becomes invaluable in elucidating these structural distributions [1,2].

The addition of selective detection systems to size-exclusion chromatography (SEC) can in some cases provide chemical composition information across the molecular size distribution [3,4]. However, SEC separates macromolecules

on the basis of solution hydrodynamic size rather than true molecular mass. The hydrodynamic size of copolymers in solution is a function of many variables including chemical composition and molecular chain length. At best, the chemical composition distribution information obtained from selective detection SEC is convolved with the molecular mass distribution of the copolymer sample [4]. Ideally it would be desirable to determine the chemical composition and molecular mass distributions independently.

HPLC compositional separation of copolymers has been documented by both precipitation and adsorption retention. Compositional separation of styrene–acrylonitrile (SAN) copolymers independent of column packing type has been demonstrated in tetrahydrofuran (THF)–isooctane gradients [5]. The comparison of the HPLC elution solvent concentration with turbidimetric titration solubility data indicated that the copolymers eluted immediately upon contacting mobile phase of sufficient strength to provide dissolution.

The compositional separation of styrene–methyl methacrylate (SMMA) copolymers in THF–methanol (90:10) in isooctane solvent gradient showed retention dependent upon the type of column packing. Non-polar bonded phase packings showed results similar to SAN precipitation separation. Separation on silica, however, provided retention in excess of the solubility limit [6]. These data indicated that retention occurred through a mixed mechanism of precipitation followed by adsorption interactions with the polar silica packing.

A primary difficulty lies in the selection of a gradient elution solvent pair capable of dissolving all copolymer compositions while possessing sufficient solvent strength range to allow both retention and displacement of the copolymer chains from the adsorbent. The compositional separation of ethyl methacrylate–butyl methacrylate (EMA–BMA) copolymers over the full composition range was obtained by Mori [7] with UV-absorbance detection at 233 nm. A shallow gradient of ethanol in 1,2-dichloroethane provided adsorption separation of increasing EMA content copolymers with increasing ethanol content. Although ethanol is a non-solvent for these

copolymers, increasing ethanol content acted as a displacer for the adsorbed polymers.

Mourey [8] demonstrated compositional separations of several acrylate and methacrylate ester homopolymers and copolymers [SMMA and poly(methyl methacrylate–methyl acrylate) in toluene–2-butanone eluents]. Both of these solvents are good solvents for these copolymers; however, both are also opaque to UV radiation below 285 nm. Mourey employed an evaporative light-scattering detector to provide chromatographic elution response of the nonvolatile copolymers. In agreement with the observations of Mori [7], polymer retention was shown to increase with decreasing ester chain length for a series of methacrylate and acrylate ester homopolymers. Since all copolymer compositions studied were soluble in both solvents, the separation was clearly based on adsorption interactions with the silica packing.

The current experimental studies examine the retention mechanism of poly(methyl methacrylate–methacrylic acid) (PMMA–MAA) copolymers on narrow-pore silica. Evaluation of the relative contributions of adsorption and precipitation retention interactions are made through solubility data and the effect of injected sample mass on peak shape. Orthogonal separation of HPLC followed by SEC for the determination of the complete composition/molecular mass distribution map of a copolymer sample is evaluated.

EXPERIMENTAL

Copolymer compositional separations were performed on a Perkin-Elmer (Norwalk, CT, USA) Series 4 quaternary HPLC with an Applied Chromatography Systems (Cheshire, UK) evaporative light-scattering (ELS) detector Model 750/14 [temperature setting 30, pressure setting 40 p.s.i.g nitrogen ($1 \text{ p.s.i.g} = 69 \cdot 10^2 \text{ Pa}$)]. All HPLC separations were performed on $250 \times 4.6 \text{ mm } 10\text{-}\mu\text{m}$ LiChrospher Si100 $100\text{-}\text{\AA}$ pore silica columns obtained from E.M. Science (Cherry Hill, NJ, USA). Linear gradient elution programs at 1.00 ml/min were produced with a strong solvent of either methanol (MeOH) or 5% glacial acetic acid (AcOH) in MeOH (v/v) in

the weak solvent toluene. Gradient conditions are specified in the discussion for individual experiments. Due to the potential for reaction between acetic acid and methanol, fresh solvent was prepared on a daily basis. Samples of each copolymer were dissolved in mobile phase solvent mixtures at least 10% higher than their solubility limit. Injection volume was 100 μ l throughout. The non-linear concentration response of the ELS detector [9] for PMMA-MAA copolymers was calibrated with third-order polynomial fit for gradient elution separations of copolymer A (Table II) samples in 2 to 40% [AcOH-MeOH (5:95)] in toluene over 75 min. Third-order polynomial regression was applied to ELS detector peak height response for a series of standard concentrations to provide a calibration equation relating ELS detector response to instantaneous concentration across a chromatogram. No ELS detector response variation was observed as a function of polymer composition or molecular mass.

All solvents were used as received. HPLC-grade toluene and MeOH were obtained from J.T. Baker (Phillipsburg, NJ, USA). ACS reagent-grade glacial acetic acid was obtained from Eastman Kodak (Rochester, NY, USA).

The system gradient lag volume for calculation of elution solvent concentration was measured from the midpoint of a 2 to 100% [AcOH-MeOH (5:95)] in toluene, 5-min gradient. Solvent concentration was detected immediately prior to the column inlet by a Kratos Model 783

(Ramsey, NJ, USA) UV absorbance detector at 280 nm. An average of four determinations was used for calculation of the gradient lag and subsequent elution solvent concentration. Error propagation of measured values was used for the determination of data precision. Column void volume was measured as 2.6 min by isocratic elution of PMMA in 50% [AcOH-MeOH (5:95)] in toluene.

Copolymer compositional standards of PMMA-MAA were synthesized by solution polymerization in MeOH at 20% solids with AIBN (azobisisobutyronitrile, Eastman Kodak) initiator to approximately 10% conversion at 65°C. Monomers were obtained from Eastman Kodak and were vacuum distilled prior to use. Copolymers were isolated by precipitation into diethyl ether (J.T. Baker) followed by filtration and vacuum drying at 60°C.

Mole percent methacrylic acid incorporation was determined by potentiometric titration in MeOH-THF (3.8:96.2) with hexadecyltrimethylammonium hydroxide (Eastman Kodak) in MeOH-toluene (10:90). The combination glass electrode (Brinkmann Instruments, Westbury, NY, USA) containing tetramethylammonium chloride in MeOH was standardized with a benzoic acid primary standard (Fisher Scientific, Fairlawn, NJ, USA). Table I lists the composition of the copolymer standards determined by titration, as well as the polystyrene (PS) equivalent weight average molecular masses and polydispersities as determined by SEC.

TABLE I
LOW-CONVERSION PMMA-MAA COPOLYMERS

Mole% MAA incorporation by titration	% (w/w) conversion	Monomer feed composition mole% MAA	Weight average M (PS equiv.)	Polydispersity (M_w/M_n)
PMMA-4.0% MAA	12.9	5.0	156 000	1.67
PMMA-8.5% MAA	10.7	10	140 000	1.54
PMMA-17.5% MAA	8.2	20	153 000	1.54
PMMA-35.6% MAA	7.7	40	185 000	1.60
PMMA-61.2% MAA	7.7	70	179 000	1.82
PMMA-78.6% MAA	4.0	90	163 000	1.98
PMMA-85.5% MAA	13.4	90	234 000	1.97
PMAA	15.8	100	215 000	1.87

Molecular masses were determined by SEC in THF (HPLC grade without BHT, J.T. Baker) with a Waters Assoc., Div. of Millipore (Milford, MA, USA) Model R401 differential refractive index (DRI) detector. The methacrylic acid containing copolymers were methylated by reaction with diazomethane in THF solution prior to SEC to minimize adsorption interactions. Methylated samples were reduced to dryness under a N₂ stream and redissolved at 2.0 mg/ml and 200- μ l aliquots injected for SEC. The samples were chromatographed on three Polymer Laboratories (Amherst, MA, USA) PLgel 10 μ m 300 \times 7.5 mm mixed bed columns. Third-order polynomial regression calibration of the columns was performed with narrow PS standards obtained from American Polymer Standards (Mentor, OH, USA).

Semipreparative gradient HPLC separation of copolymer A was performed with a 100- μ l injection of a 100 mg/ml solution on a 2 to 40% [AcOH–MeOH (5:95)] in toluene gradient over 75 min. Two-minute fractions were collected with an ISCO (Lincoln, NE, USA) Model FOXY fraction collector and reduced to dryness under a N₂ stream. Fractions were then methylated as above, dried, and redissolved in either 0.80 or 5.0 ml of THF. SEC of the methylated fractions was performed with 200- μ l injections on the PLgel columns described above in THF calibrated with narrow PMMA standards. PMMA narrow standards were obtained from American Polymer Standards Corp. ELS

detection was used with a temperature setting of 50 and N₂ gas pressure of 20 p.s.i.g. ELS concentration response calibration was performed with a 198 000 dalton PMMA (Eastman Kodak) and third-order polynomial fit. Copolymer composition was calibrated with the elution times of a mixture of the first four samples in Table I plus the 198 000 dalton PMMA. The calibration equation was determined by third-order polynomial regression of the peak elution times from four repeat separations of the standards mixture.

Solubility limits of the PMMA–MAA copolymer samples of Table I were obtained in the same solvents as employed in the HPLC separations by a method similar to that used by Shalliker *et al.* [10]. Solutions of 1.0 mg/ml of each copolymer standard were prepared in a series of solvent concentrations. After standing overnight, a 100- μ l aliquot of each solution was injected on a 5 to 100% [AcOH–MeOH (5:95)] in toluene, 30-min gradient. The ELS response peak areas were plotted *versus* solvent concentration and the midpoint determined by third-order polynomial fit. Solvent composition solubility midpoint precision was taken as one half of the range between 40 and 60% solubility points.

High-conversion PMMA–MAA copolymer samples were also prepared by three different polymerization methods (Table II). Sample A was prepared by solution polymerization at 20% solids in 60% acetone (J.T. Baker)–40% ethanol

TABLE II
HIGH-CONVERSION PMMA–MAA COPOLYMERS

Sample ID	Mole% MAA incorporation by titration	Weight average M (PS equiv.)	Polydispersity (M_w/M_n)
Copolymer A from solution polymerization	14.1	155 000	2.09
Copolymer B from batch suspension polymerization	14.1	38 900	1.91
Copolymer C from semi-continuous addition suspension polymerization	14.0	368 000	7.06

(Quantum Chemical, Tuscola, IL, USA) with benzoyl peroxide (Aldrich, Milwaukee, WI, USA) initiator. Sample B was prepared by batch suspension polymerization at 25% solids in water with lauroyl peroxide (Aldrich) initiator and 2% polyvinyl alcohol (PVA, Eastman Kodak) dispersant. Sample C was prepared by semicontinuous addition suspension polymerization under the same conditions as sample B with 1% PVA and monomer addition over two hours. Mole percent MAA incorporation and PS equivalent molecular mass of all three samples are shown in Table II. The ELS detector concentration response was calibrated with copolymer A sample (Fig. 7) by third order polynomial regression. The ELS detector response was also determined to be independent of M for PMMA narrow standards over the range from 2000 to 1 450 000 dalton.

RESULTS AND DISCUSSION

PMMA-MAA copolymers can be eluted in order of increasing mole percent MAA on 100-Å pore silica adsorbent with a MeOH–toluene gradient as shown in Fig. 1. Excessive peak broadening is observed with increasing MAA

content of the copolymer samples. In fact, copolymers containing greater than 36% MAA could not be eluted. The addition of glacial acetic acid to the MeOH provided a strong displacer effect in reducing the elution volume of copolymers and narrowing the peak widths of the low-conversion samples to a more consistent value (Fig. 2). It was found that 5% AcOH was needed to provide consistent peak shape over the entire composition range from PMMA to PMAA (Fig. 3). This elution behavior change upon addition of acetic acid is indicative of the contribution of the strong adsorption interactions of the carboxylic acid functionality of MAA with the silica surface. This is consistent with the observations of Mori [11] on the improvement of elution profiles of methacrylate ester containing copolymers on the addition of a strongly hydrogen-bonding solvent to the eluent.

The influence of polymer molecular mass (M) on retention is demonstrated for two PMMA standards in Fig. 4. A 43 500 dalton PMMA with polydispersity $M_w/M_n = 2.00$ shows a highly asymmetrical elution profile under shallow gradient elution conditions. The low M components of this sample are resolved over a 9-min range, but the higher M components elute within 1 min.

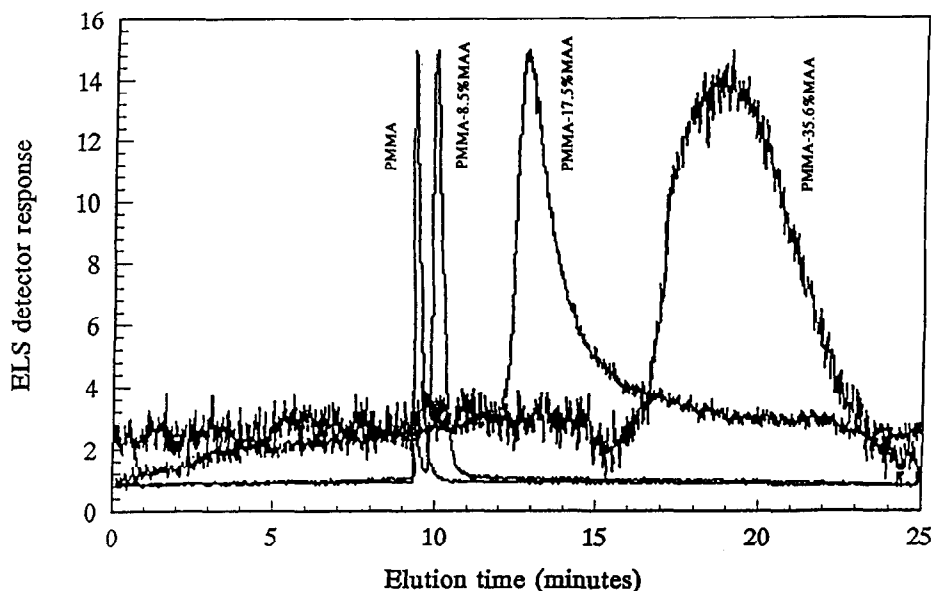


Fig. 1. Gradient elution separation of a mixture of low conversion PMMA-MAA copolymers on 100-Å pore silica. Linear gradient from 2 to 100% MeOH in toluene over 25 min. Injected sample 5 mg/ml each PMMA 198 000 dalton, PMMA-8.5% MAA, PMMA-17.5% MAA, and PMMA-35.6% MAA in MeOH-toluene (30:70).

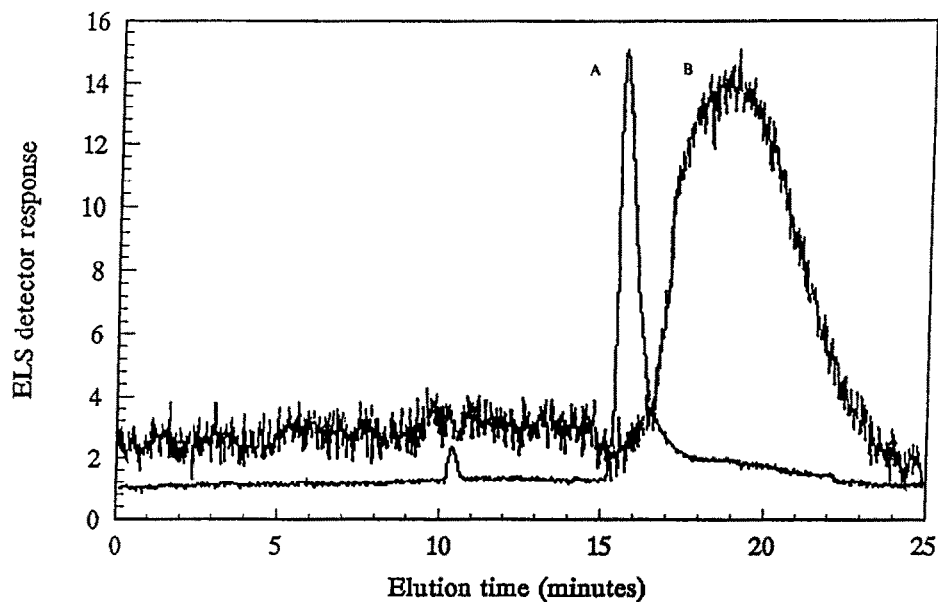


Fig. 2. Comparison of the elution profiles of 5 mg/ml injections of PMMA–35.6% MAA copolymer in MeOH–toluene (30:70) for gradients with (chromatogram A) and without (chromatogram B) 5% acetic acid in the MeOH strong solvent. Separations were performed with the same gradient slope and initial mobile phase concentration as Fig. 1.

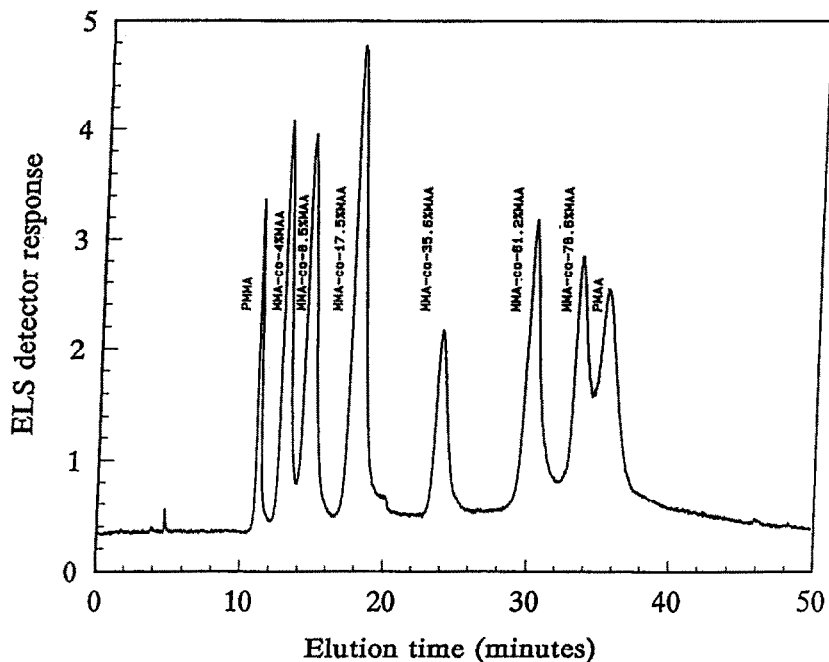


Fig. 3. Chromatogram of a mixture of PMMA–MAA copolymers plus PMMA and PMAA homopolymers. Injected sample 2 mg/ml of each polymer in 70% [AcOH–MeOH (5:95)] in toluene. Gradient conditions 2% to 100% in 55 min with [AcOH–MeOH (5:95)] strong solvent.

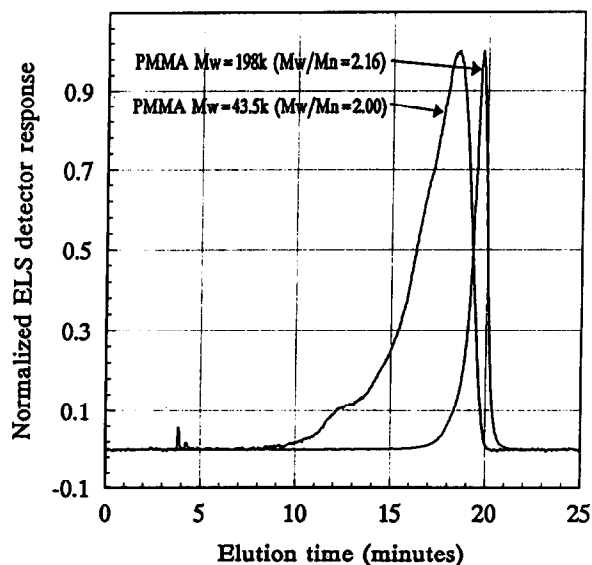


Fig. 4. Comparison of the profile of two different molecular mass PMMA samples. Gradient conditions 2 to 40% [AcOH–MeOH (5:95)] in toluene over 75 min. Each injected sample was 10 mg/ml in toluene.

Elution of a PMMA standard of over four times higher molecular mass (198 000) and slightly higher polydispersity ($M_w/M_n = 2.16$) shows only minor peak asymmetry and elution over a narrow range at the same location as the high M tail of the 43 500 dalton PMMA. In a more quantitative format, the variation of PMMA peak elution volume in terms of eluent composition as a function of $\log M$ is shown in Fig. 5 for a series of narrow M standards. Note that for the 100-Å pore silica employed in these separations, the eluent composition required to elute PMMA becomes very nearly independent of M in excess of 54 400 dalton.

Based merely upon adsorption interactions, the increase in retention with increasing M is expected to be a monotonic function of M . Deviation from low M linearity has been documented as a function of the increasing contribution of polymer coil structure [12]. However, the behavior seen in Figs. 4 and 5 indicates a sudden deviation to elution nearly independent of M . This is attributable to the exclusion of the polymer molecules from the porous packing with a resultant dramatic decrease in available surface area [13]. This effect was clearly demonstrated

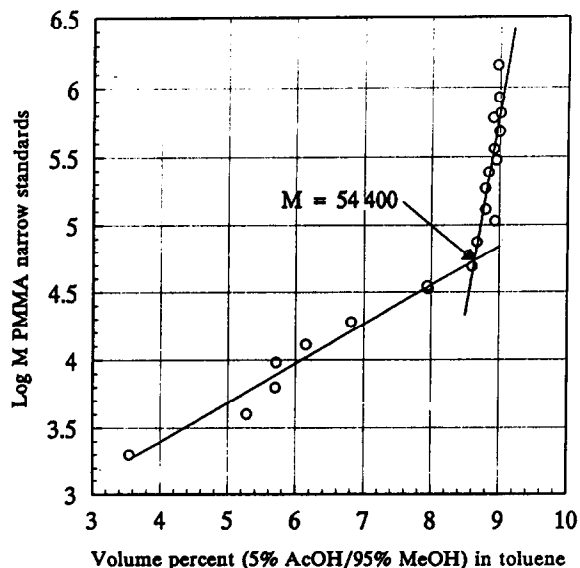


Fig. 5. Variation of the PMMA elution solvent concentration with molecular mass on 100-Å pore silica.

by Shalliker *et al.* [10] for PS retention on C_{18} -bonded phase packings in dichloromethane–MeOH eluent. Under weak adsorption interactions, retention in excess of the solubility limit was observed at high M only for wide pore packings which did not provide exclusion of the polymer molecules.

PMMA is soluble in all proportions of the elution solvents, but is not eluted from silica by pure toluene. Therefore, it is concluded that PMMA is retained through adsorption interactions with the silica packing. Although the same molecular mass experimental data was not available for the copolymer samples studied, it is considered a reasonable assumption, based upon the results of other workers [11,14], that this molecular mass independent elution behavior applies to the PMMA–MAA copolymers eluted under adsorption conditions.

Retention mechanism

Since it is observed that the copolymer samples of PMMA–MAA having greater than approximately 8 mole% MAA are insoluble in the initial gradient solvent conditions, the separation mechanism falls into question. Mourey [8] has

shown that polyalkyl acrylates can be compositionally separated by adsorption chromatography on silica using 2-butanone–toluene gradients. Under these conditions all of the eluting sample components are soluble in all solvent ratios of the gradient solvents. This insures adsorption interactions are responsible for the compositional resolution between copolymers. Extensive work has also been published by Glöckner et al. (ref. 15 and refs. cited therein) employing gradient systems which are intentionally chosen to produce precipitation of the copolymer components in the solvent gradient. As the solvent strength of the elution solvent is gradually increased, the copolymer components redissolve and may then be eluted from the column under either of two possible mechanisms. Pure precipitation HPLC separation provides elution of the copolymer components immediately upon reaching the gradient conditions required for solubility [5,6,13]. On more strongly interacting adsorbents, such as bare silica, further adsorptive interactions may retard the elution of copolymer components after the solubility condition has been exceeded. Elution is observed only when the solvent reaches sufficient strength to displace the adsorptive interactions of the retained copolymer. Glöckner has verified that this behavior is effective in SMMA separation on silica by comparing the eluent concentration on copolymer elution to the solubility limit solvent concentration as determined by turbidimetric titration [6].

The comparison of turbidimetric titration results with HPLC elution solvent data must be done with care in the interpretation of retention mechanisms. Turbidimetric titration requires that the polymer behavior is compatible with the optical turbidity probe and data must be corrected for polymer dilution during the titration. Although time-consuming, the method used in the current study for the determination of copolymer solubility limits allows direct comparison in the HPLC solvent mixtures and does not require correction for polymer concentration effects.

The retention mechanism effective for the PMMA–MAA separation can be verified by solubility evaluation. Fig. 6 shows the eluent

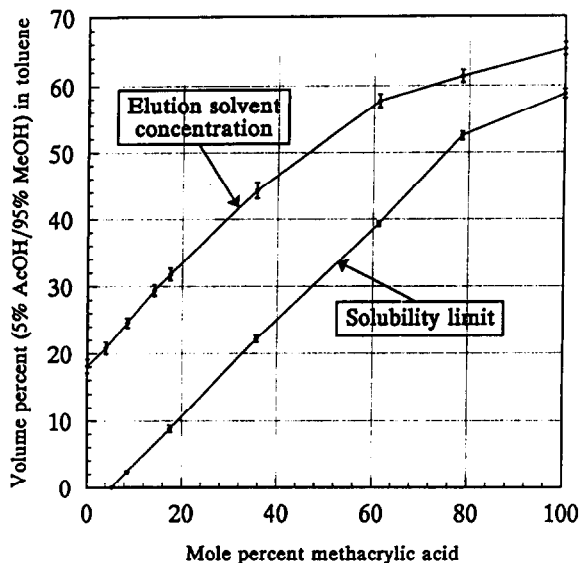


Fig. 6. Comparison of the elution solvent concentration and solubility limit for PMMA–MAA copolymers.

solvent composition corresponding to copolymer elution for the entire range of PMMA–MAA samples studied. Determination of the solubility limits of the same PMMA–MAA copolymer samples in the same solvents employed for gradient elution provided the values shown by the lower curve of Fig. 6. It is observed that for all PMMA–MAA compositions, the solvent concentration required for copolymer elution from the silica adsorbent is in excess of that required for solubilization.

Copolymer solubility in terms of the volume fraction of non-solvent (Φ_{NS}) at incipient precipitation has been described by Glöckner [15] as a function of polymer solution concentration (c_{polym}^*)

$$\Phi_{NS} = A + B \log c_{\text{polym}}^*$$

where A and B are empirical constants. For the copolymer A sample with 14.1% MAA, the non-solvent (toluene) concentration necessary to precipitate the copolymer decreased from 95.8% to 87.2% on going from 1.0 to 58 mg/ml concentration ($\Phi_{NS} = 0.9567 - 0.04812 \log [c_{\text{polym}}^* (\text{mg/ml})]$). When compared to the solubility limit in Fig. 6, this indicates that a range of strong solvent concentration is still required to elute

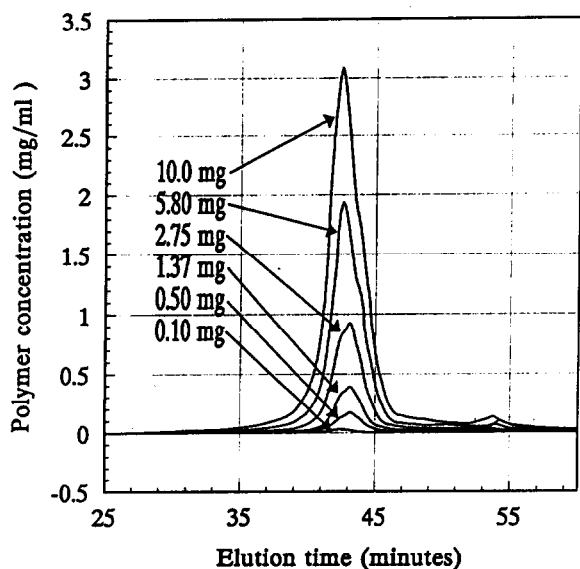


Fig. 7. Variation of the peak profile of PMMA–14.1% MAA (copolymer A) with injected sample mass. Gradient conditions 2 to 40% [AcOH–MeOH (5:95)] in toluene over 75 min.

copolymer A even at such extreme concentration as 100 mg/ml injected as shown in Fig. 7.

Arguments regarding the dominant polymer retention mechanism have also been made by evaluating the change in peak shape as a function of injected polymer mass. These effects were demonstrated by Schultz and Engelhardt [16] for PS under both precipitation and adsorption retention conditions. In THF–water eluent, precipitation dominates and polymer elution shifts to higher retention with increasingly fronting distortion for increasing injected sample mass. This is in opposition to the observed decrease in retention with increasing tailing distortion observed for overloaded adsorption retention. Fig. 7 shows the effect of a two-orders-of-magnitude increase in injected sample mass for copolymer A. Only a slight shift to earlier elution with no peak distortion indicates a wide linear adsorption isotherm range for this separation. No peak distortion characteristic of polymer precipitation was observed despite the noted decrease in solubility with increasing polymer concentration and the fact that this sample is insoluble in the initial gradient conditions for all injected concentrations.

Orthogonal separation

Previous studies have used a combination of SEC fractionation and subsequent HPLC compositional separation to determine the joint composition/molecular mass map of copolymer samples [17–19]. As stated previously, SEC separates based upon molecular size which can be a function of chemical composition. It would be preferable to separate the copolymer sample into a series of fractions based on a single physical property and subsequently determine the other. Gradient HPLC has a much broader linear sample mass range (Fig. 7) than SEC, so that a single HPLC fractionation can provide sufficient material for several SEC separations.

In the present study a high-conversion solution-polymerized PMMA–MAA copolymer (copolymer A, Table II) was separated into ten fractions by gradient elution HPLC. The gradient HPLC separation was calibrated by the elution times of a series of low-conversion copolymer standards (Table I). Subsequently, each fraction was characterized by SEC for polymer molecular mass distribution. The PMMA–MAA copolymers provide the capability of conversion to PMMA homopolymer by methylation with diazomethane. Absolute molecular mass distribution is then readily obtained by SEC separation and PMMA narrow standard calibration with total suppression of any remaining composition effects on molecular size.

The composition/molecular mass map can be represented by either a three-dimensional plot as in Fig. 8 or by a projection contour plot as in Fig. 9. Note that the large majority of the sample is in excess of the molecular mass independent limit as determined in Fig. 5. This provides good confidence that the HPLC gradient elution separation was based purely upon composition. In addition, the lack of peak profile distortion shown in Fig. 7 provides support that the composition/molecular mass map is not distorted by HPLC overload conditions. Note that the composition drift in the high-conversion copolymer map for the solution-polymerized sample is similar in distribution to that determined by Mori [17] for a high-conversion SMMA copolymer by HPLC of SEC fractions. The composition drift of copolymer A is shown in Fig. 10 by plotting

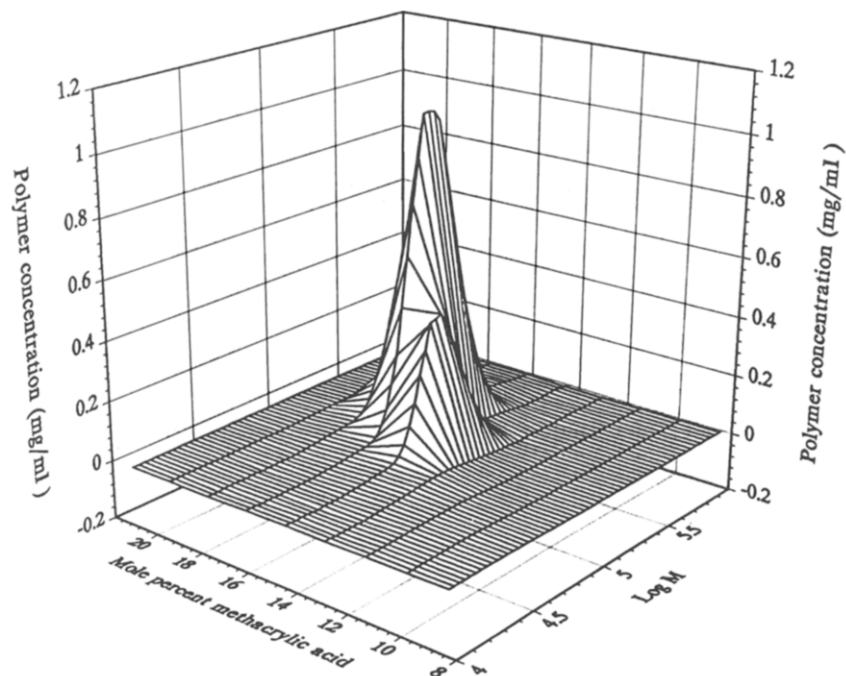


Fig. 8. Joint chemical composition and molecular mass distribution of a 10-mg sample of copolymer A separated into fractions by HPLC under the same conditions as Fig. 7. Molecular mass distributions of the methylated HPLC fractions were determined by SEC in THF.

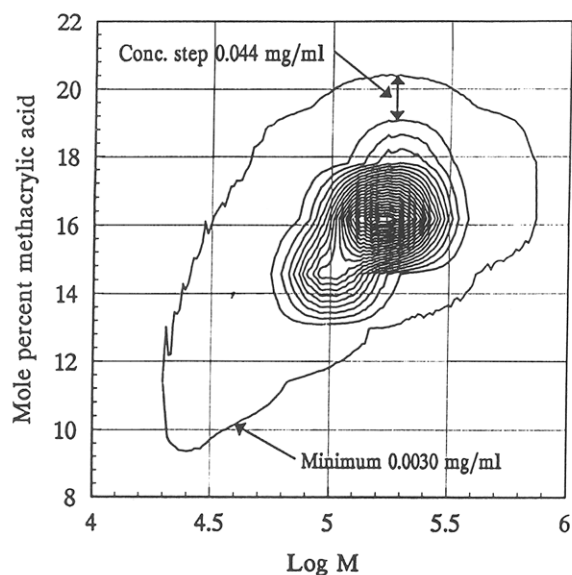


Fig. 9. Contour plot of the joint composition and molecular mass distribution of copolymer A corresponding to the data of Fig. 8.

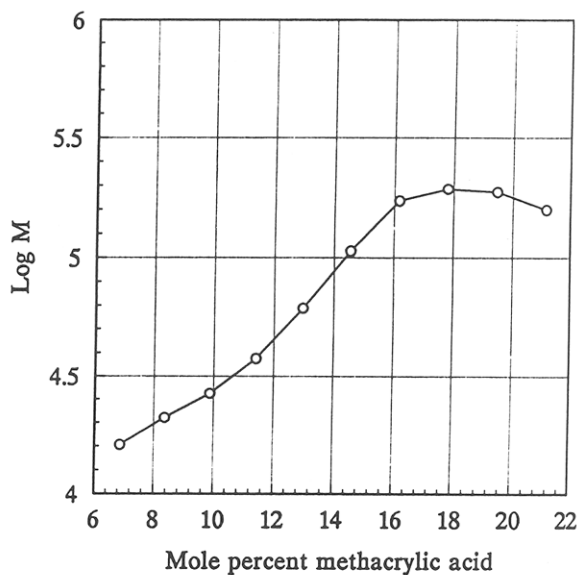


Fig. 10. Variation of the peak molecular mass as a function of chemical composition for the copolymer A HPLC fractions of Figs. 8 and 9.

the composition at the SEC peak maxima. The molecular mass gradually increases to a plateau with increasing MAA incorporation.

General applicability of composition distribution separation

The chemical composition distributions of three high-conversion PMMA–MAA copolymer samples prepared by three different polymerization techniques were compared. Figs. 11–13 show the composition profiles of the three copolymers described in Table II. Titration of the MAA content showed all three to have nearly equivalent average MAA incorporation at 14.1 mole%. SEC of the methylated samples provided evidence of widely differing molecular mass distributions (Table II). However, only HPLC composition separation demonstrates that all three samples also have significantly different composition distributions.

Copolymer A (Fig. 11) was produced by solution polymerization and has been thoroughly characterized in Figs. 8 and 9. Note that there is a consistent bias in the peak composition relative to that determined by titration in Figs. 11–13. This has also been observed in a wide variety of other PMMA–MAA copolymers characterized by this method. This has been attributed to the

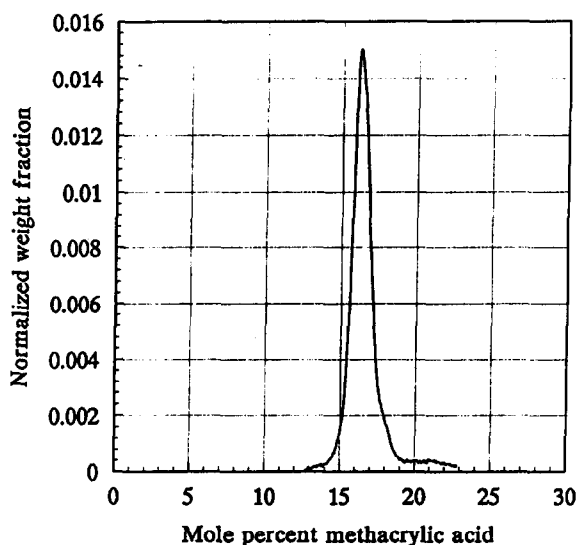


Fig. 11. The chemical composition distribution of a 5.0 mg/ml sample of copolymer A separated under the gradient conditions of Fig. 7.

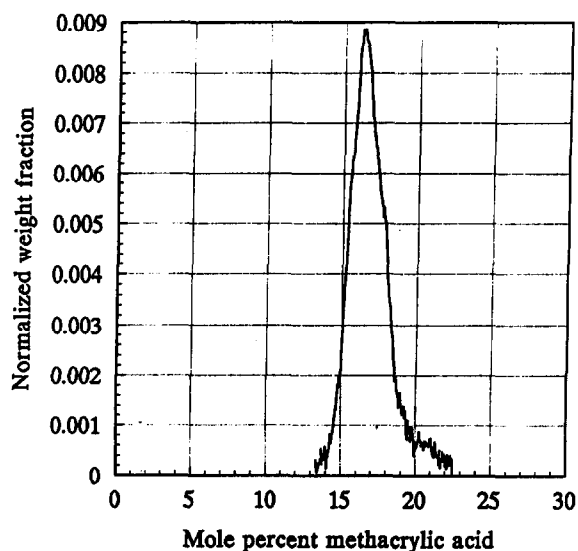


Fig. 12. The chemical composition distribution of a 5.0 mg/ml sample of copolymer B separated under the gradient conditions of Fig. 7.

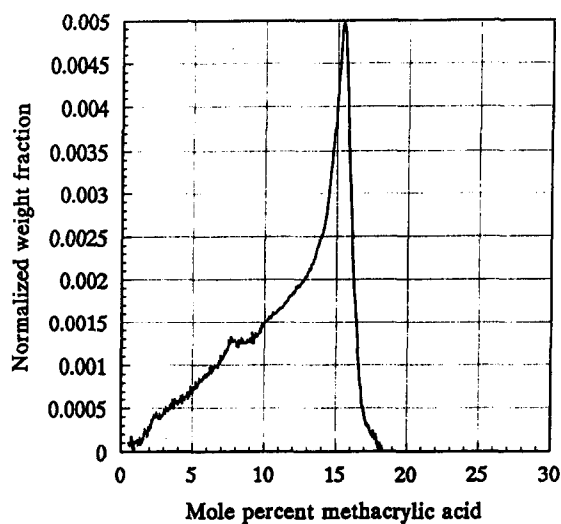


Fig. 13. The chemical composition distribution of a 5.0 mg/ml sample of copolymer C separated under the gradient conditions of Fig. 7.

manner in which the titration method provides an average value of MAA incorporation.

The composition distribution of the batch suspension-polymerized copolymer B sample is much broader than the solution-polymerized sample and tails to higher MAA incorporation (Fig. 12). The composition profile of this sample must be interpreted with additional caution,

however, because of its relatively low molecular mass. Despite the fact that the M_w of this sample is only 38 900 dalton, the peak composition agrees well with that of the other two samples. In addition, retention effects due to molecular mass would be expected to shift polymer elution to earlier time (Fig. 5). However, the broadening observed in Fig. 12 is predominantly toward higher retention, *i.e.*, higher percent MAA incorporation.

The copolymer C sample prepared by semi-continuous addition suspension polymerization is much higher in molecular mass and shows the most dramatic difference in composition distribution (Fig. 13). Composition tailing all the way to PMMA is observed. This sample was also observed to contain a small amount of insoluble gel which may be attributable to either very high M copolymer or some degree of crosslinking.

CONCLUSIONS

(1) The chemical composition separation of PMMA–MAA copolymers on silica has been shown to be predominantly through adsorption interactions. (2) Despite initial precipitation of higher mole% MAA copolymers, no elution is observed until well past the solubility limit. (3) A very wide linear adsorption range was observed for a 14.1 mole% MAA copolymer demonstrating that adsorption interactions dominate the polymer retention process after redissolution in the solvent gradient. (4) Molecular mass independent elution of PMMA was observed on 100-Å pore silica in excess of 54 400 dalton and inferred to occur for PMMA–MAA copolymers. (5) Orthogonal separation by HPLC followed by SEC provided a full composition/molecular mass map of a solution polymerized copolymer sample. Methylation of HPLC fractions prior to SEC provided for complete elimi-

nation of composition effects on M determination. (6) The general applicability of this composition separation was demonstrated in the composition distribution determination of PMMA–MAA copolymers prepared under different polymerization conditions.

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