ELSEVIER

Journal of Chromatography A, 692 (1995) 221–232

JOURNAL OF CHROMATOGRAPHY A

Compositional distribution characterization of poly(methyl methacrylate)–graft-polydimethylsiloxane copolymers

Timothy C. Schunk[a,*], Timothy E. Long[b]

[a]*Analytical Technology Division, Research Laboratories, Eastman Kodak Company, Rochester, NY 14650-2136, USA*
[b]*Polymer Research, Eastman Chemical Company, Kingsport, TN 37662, USA*

Abstract

Graft copolymers prepared by radical polymerization of a low-molecular-mass monomer with a macromonomer display heterogeneity in both molecular mass and chemical composition. The characterization of these joint distributions by a single technique [e.g., size-exclusion chromatography (SEC)] is hindered by the effects of both variables on the separation mechanism. Separation emphasizing chemical composition heterogeneity can be efficiently performed by gradient elution high-performance liquid chromatography (HPLC) combining precipitation and adsorption retention. Comparison of Fourier transform IR and evaporative light-scattering detection indicated decreasing polydimethylsiloxane (PDMS) macromonomer incorporation corresponding to increasing retention time for a poly(methyl methacrylate) (PMMA)–graft-PDMS copolymer. More detailed information was obtained by multidetector SEC of composition fractions from gradient elution HPLC. SEC separation in an isorefractive solvent for PDMS (tetrahydrofuran) with low-angle laser-light scattering, differential viscometry, and differential refractive index detection allowed determination of the molecular mass of both the whole copolymer and that of the PMMA backbone for each HPLC fraction. Comparison with an independent SEC determination of the PDMS macromonomer molecular mass allowed estimation of the number of pendant PDMS chains per graft copolymer molecule across the HPLC chromatogram. Results indicated a relatively constant incorporation of the number of PDMS side chains with increasing PMMA backbone molecular mass, leading to a relative decrease in weight fraction PDMS incorporation with increasing molecular mass of the whole graft copolymer molecule.

1. Introduction

Graft copolymers are branched macromolecules with a backbone composed of one type of polymer and side chains (grafts) of another polymer. Several approaches have become common for the synthesis of graft copolymers with most falling into three categories: grafting-onto, grafting-from and the macromonomer technique. Grafting-onto reactions proceed by the reaction of a terminal group on the side-chain polymer with reactive functionalities distributed along the backbone polymer. Grafting-from reactions require the growth of polymer side chains from initiating sites on a backbone polymer by the polymerization of a low-molecular-mass monomer. Finally, the macromonomer technique employs the incorporation of a terminal polymerizable group on the eventual side-chain polymer into a growing backbone polymer during the polymerization of a low-molecular-mass monomer [1].

There are several advantages to the use of the macromonomer technique over the other two

* Corresponding author.

0021-9673/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0021-9673(94)01001-3

approaches which have attracted increasing interest in recent years [2,3]. A relatively large number of different macromonomers are available with convenient polymerizable terminal groups, allowing access to a wide range of copolymer compositions [4]. Living polymerization methods can be used to provide macromonomers of well-defined chain length, molecular mass distribution, and terminal functionality [5,6]. Macromonomers allow control of the number of grafts per copolymer macromolecule through choice of the polymerization reaction mixture ratio of macromonomer to low-molecular-mass monomer [4].

The chemical and physical properties of graft copolymers can be tailored to suit various applications by choice of the different chemical compositions of the copolymer backbone and side chain. In many cases the copolymer segments are immiscible in the solid phase leading to unique thermal, mechanical, and interfacial properties similar to diblock copolymers [7]. The tailoring of these chemical and physical properties has led to the application of graft copolymers as emulsifiers, surface modifiers, thermoplastic elastomers, and polymer blend compatibilizers [8].

The performance of these tailored graft copolymers is in part dependent upon the choice of the constituent polymers and their molecular mass, but also on the distributions in molecular mass and chemical composition present in the final graft copolymer. It is common for a graft copolymer sample to contain both ungrafted backbone and side-chain homopolymers, as well as a range of copolymer compositions [9]. As with any copolymer, the molecular mass and chemical composition of graft copolymers share a joint distribution in heterogeneity. Techniques such as size-exclusion chromatography (SEC) with selective detection cannot provide complete copolymer characterization due to the dependence of polymer hydrodynamic size on chemical composition. In addition, techniques such as solvent precipitation fractionation or fractional dissolution can be unreliable with graft copolymers due to their surface-active properties that can inhibit clean phase separation behavior [9–11]. An alternative technique has been suggested recently by Stejskal et al. [12] for the separation of a graft copolymer into fractions for subsequent analysis. This approach involves fractionation in demixing solvents, which although effective can be quite time consuming and difficult to predict the separation dependence on molecular mass and chemical composition (see Table 3 of Ref. [12]).

The focus of the current experimental investigation was to provide a chemical composition separation of a graft copolymer into fractions suitable for SEC with molecular-mass-sensitive detection. The free-radical-polymerized graft (g) copolymer poly(methyl methacrylate)–g-polydimethylsiloxane (PMMA–g-PDMS) was separated by gradient elution HPLC into a series of chemical composition fractions. Chemical composition across the HPLC and SEC separations was evaluated by use of a solvent-evaporation Fourier transform infrared (FT-IR) interface. SEC of a series of HPLC fractions in a solvent isorefractive with the PDMS side chains allowed low-angle laser-light scattering (LALLS) determination of the molecular mass of the PMMA backbone polymer. Universal calibration with differential viscometry detection allowed determination of the overall molecular mass of each narrow composition graft copolymer fraction. With these data along with the molecular mass of the narrow-dispersity PDMS macromonomer, the number of side chains grafted on the PMMA backbone polymer was determined for each HPLC fraction.

2. Experimental

2.1. Synthesis

The PDMS macromonomer was prepared by anionic polymerization of hexamethylcyclotrisiloxane (Petrarch Systems, Bristol, PA, USA) in freshly distilled cyclohexane (Eastman Kodak, Rochester, NY, USA) with sec-butyllithium initiator (Lithco, Division of FMC, Philadelphia, PA, USA) and distilled tetrahydrofuran (THF) promoter (Fisher Scientific, Pittsburgh, PA,

USA). The polymerizable terminal functional group was formed by termination with [3-(methacryloxy)propyl]dimethylchlorosilane (Petrarch Systems) after 48 h polymerization. The PDMS macromonomer was then precipitated in methanol (Eastman Kodak) and dried under vacuum at 60°C.

PMMA–g-PDMS copolymer was prepared by free radical polymerization at 20% solids using the above macromonomer and methyl methacrylate [freshly distilled from calcium hydride (both Eastman Kodak Company)] in chlorobenzene (Aldrich, Milwaukee, WI, USA, distilled from phosphorus pentoxide (Eastman Kodak) under nitrogen) at 60°C with 2,2′-azobisisobutyronitrile initiator (Eastman Kodak). The polymerization feed ratio was 40% weight PDMS macromonomer. The isolated copolymer was extracted with *n*-hexane (Eastman Kodak) to remove excess PDMS macromonomer and dried under vacuum at 60°C. NMR analysis of the raw copolymer yielded an average value of 40% weight PDMS which was reduced to 32% weight after *n*-hexane extraction. NMR spectra were obtained with a General Electric QE300 300 MHz spectrometer (Fremont, CA, USA).

2.2. Gradient HPLC

Semipreparative-scale high-performance liquid chromatography (HPLC) separations were performed on a Varian Analytical Instruments (San Fernando, CA, USA) Model 5060 ternary gradient chromatograph with a LiChrospher Si100 10 μm silica 250 × 4.6 mm column (EM Separations, Gibbstown, NJ, USA). Gradient elution separations were performed at 1.0 ml/min on 100-μl sample injections from 40 to 100% (v/v) solvent B in cyclohexane linear over 50 min followed by a 10-min hold. Solvent B was 10% (v/v) ethanol in toluene. No attempt was made optimize the gradient shape beyond linear. Column void volume was determined as 2.45 ml and gradient pumping system lag volume 3.27 ml to the column inlet. Solvents were obtained from J.T. Baker (Phillipsburg, NJ, USA) (toluene and cyclohexane, HPLC grade) and Quantum Chemical (Tuscola, IL, USA) (absolute ethanol). The eluent flow was split 20:1 to an ISCO (Lincoln, NE, USA) Model FOXY fraction collector and an Applied Chromatography Systems (Cheshire, UK) Model 750/14 evaporative light-scattering (ELS) detector with an evaporator temperature setting of 80 and nitrogen gas flow pressure of 25 p.s.i.g. (1 p.s.i. = 6894.76 Pa).

The solubility of a PMMA narrow standard (molecular mass M_{peak} = 185 000) was evaluated in the HPLC solvent system (cyclohexane–toluene–ethanol) by a method similar to that of Ref. [13]. A stock solution of 10 mg/ml PMMA was prepared in ethanol–toluene (10:90) and subsequently used to prepare a series of 1.0 mg/ml solutions varying in cyclohexane content from 40% to 90% by volume. After standing overnight, 100-μl aliquots of these solutions were injected on the LiChrospher Si100 column with a 15 min linear gradient from 40 to 100% solvent B in cyclohexane. The peak area by ELS detection was plotted as a function of sample solvent concentration and the midpoint of 40.3% (v/v) cyclohexane determined as the solubility limit of PMMA in this solvent system.

Gradient elution HPLC separation with a solvent-evaporation FT-IR interface was performed on a Perkin-Elmer (Norwalk, CT, USA) Series 4 quaternary gradient chromatograph with the same column and solvent conditions as above. The solvent-evaporation FT-IR interface was of our own design, but similar to those of Dekmezian et al. [14] and Cheung and co-workers [15,16]. Copolymer fractions of 75 s duration starting at 20 min elution time were spray deposited onto 115°C 13 × 2 mm polished germanium disks (Spectral Systems, Hopewell Junction, NY, USA) at 50 Torr (1 Torr = 133.322 Pa) in a 75°C chamber.

2.3. Size-exclusion chromatography

Graft copolymer SEC was performed on either of two systems. For copolymer analysis with the solvent-evaporation FT-IR interface, SEC separations were performed with a Perkin-Elmer Series 4 chromatograph on a three-column set of PLgel 10 μm 300 × 7.5 mm mixed bed columns

(Polymer Labs., Amherst, MA, USA) at 1.0 ml/min freshly distilled THF (J.T. Baker) with 200-μl injections of 3.0 mg/ml. Differential refractive index (DRI) detection was done using a Waters–Millipore (Milford, MA, USA) Model R401. The SEC column set was calibrated with narrow polystyrene (PS) standards and the log M–retention volume data fitted with a third-order polynomial. Copolymer fractions were deposited with the solvent-evaporation FT-IR interface on 100°C disks at 50 Torr in a 65°C chamber in 30-s increments starting at 17 min elution time. SEC with molecular-mass-sensitive detection was performed on a system described previously [17] using DRI, LALLS and differential viscometry detection with three PLgel 5 μm 300 × 7.5 mm mixed bed columns. Universal calibration was done with narrow PS standards ranging from 0.01 to 2.5 mg/ml decreasing with increasing molecular mass at minimum detectable concentrations.

SEC of the PDMS macromonomer in toluene (J.T. Baker) was at 1.0 ml/min on a three-column set of 10 μm 300 × 7.5 mm PLgel mixed bed columns. Detection was with a model R401 DRI detector from 200-μl injections of 2.0 mg/ml samples and narrow PS standard calibration. PS equivalent weight average $\bar{M}_w = 12\,300$ and number average $\bar{M}_n = 10\,600$. Conversion to PDMS equivalent values with Mark–Houwink coefficients yielded $\bar{M}_w = 13\,100$ and $\bar{M}_n = 11\,400$. Mark–Houwink coefficients in toluene were PS: $K = 1.12 \cdot 10^{-4}$ dl/g, $\alpha = 0.722$ and PDMS: $K = 1.36 \cdot 10^{-4}$ dl/g, $\alpha = 0.69$.

2.4. Fourier transform infrared spectrometry

FT-IR spectra of the deposited copolymer fractions were obtained on a Mattson Polaris FT-IR spectrometer (Madison, WI, USA) with 16 scans at 4 cm^{-1} resolution. All copolymer film fractions were solvent annealed [16] with dichloromethane (J.T. Baker) vapor prior to FT-IR analysis. Quantitative calculations of copolymer fraction composition from FT-IR spectra were performed by a PLS-2 algorithm using GRAMS 386 software (Galactic Industries, Salem, NH, USA) and FT-IR calibration spectra of solvent-cast films of molecular mass 130 000 PMMA and 265 000 PDMS standards (American Polymer Standards).

3. Results and discussion

Considerable discussion has appeared in the literature concerning chemical composition separations of copolymers by HPLC dominated either by precipitation/redissolution or adsorption phenomena [18–20]. The general goal is to obtain copolymer resolution based on chemical composition with as little confounding molecular mass resolution as possible. It is therefore desirable to take advantage of both precipitation and adsorption retention in a synergistic manner to obtain the required separation [13].

Precipitation HPLC is performed with the use of a gradient from a non-solvent to increasing percentages of a good solvent on a stationary phase possessing weak adsorption interactions for the copolymer. In many cases the effect of copolymer molecular mass is mixed with that of chemical composition in a precipitation HPLC separation [21]. In contrast, adsorption retention controls separation when the copolymer molecules are soluble in all solvent compositions during a gradient elution HPLC separation. Strong adsorption interactions on small-pore column packings provide copolymer retention resulting in composition separations with very little molecular mass influence [22].

Usually a compromise between copolymer solubility and chromatographic solvent strength range is required to obtain copolymer separation over a broad chemical composition distribution. At best a synergistic combination may be obtained which allows initial retention of copolymer molecules by precipitation in a non-solvent-rich eluent and subsequent adsorption retention interactions after the solubility limit has been exceeded during the gradient [13]. Such a system was employed for the gradient HPLC separation of a PMMA–g-PDMS copolymer sample by chemical composition as shown in Fig. 1.

The ELS detector signal (Fig. 1) provides a convenient method of observing the elution of

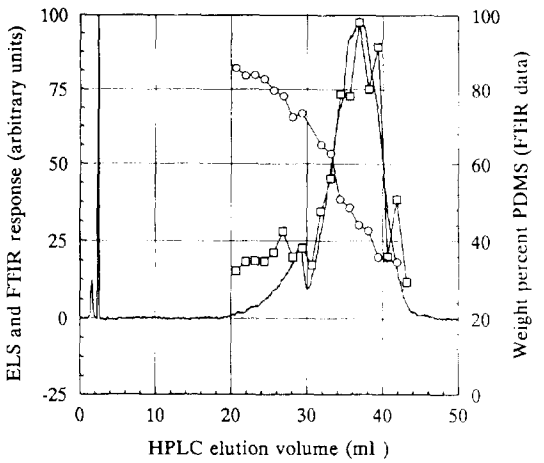

Fig. 1. Gradient elution HPLC chromatogram of a 1.0 mg injection of PMMA–g-PDMS copolymer. The evaporative light-scattering detection response (solid line) is overlayed on the total copolymer mass (□) (PMMA + PDMS) calculated from FT-IR spectra of solvent-evaporation interface deposited fractions. The weight percent PDMS incorporation values derived from the FT-IR spectra are shown as ○.

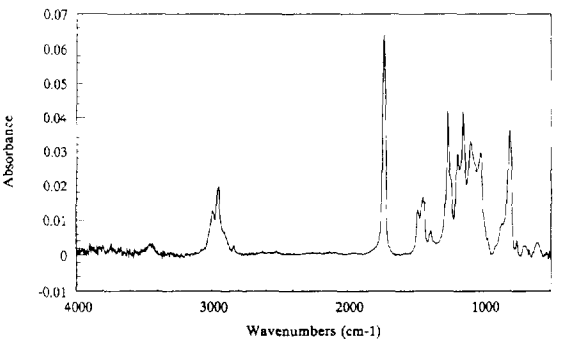

Fig. 2. FT-IR spectrum of a PMMA–g-PDMS HPLC fraction collected with the solvent-evaporation interface over 75 s elution time centered at 36.875 min (see Fig. 1). The spectrum was collected from 16 scans at 4 cm^{-1} resolution from less than 90 μg of copolymer after annealing with dichloromethane vapor.

non-volatile copolymer components during a gradient HPLC separation without regard to analyte or solvent chromophores. However, the ELS response is a complex function of analyte concentration and composition and is not easily calibrated [23,24]. An additional means of detection is required to provide chemical functional group information across the chromatogram, namely FT-IR spectrometry with a solvent-evaporation interface [14–16].

Fig. 2 shows the FT-IR spectrum obtained from a dried film of a 75-s HPLC fraction of PMMA–g-PDMS near the chromatogram peak maximum of Fig. 1. Excellent signal-to-noise and spectral band shapes are obtained for this fraction corresponding to less than 90 μg of copolymer. Quantitative FT-IR analysis of seventeen deposited film fractions across the HPLC chromatogram shown in Fig. 1 indicates a monotonic decrease in PDMS incorporation in the graft copolymer exceeding a range of 50% (w/w). The ELS and FT-IR chromatograms are in good agreement. Note that the ELS response decreases more rapidly with copolymer concentration in wings of the peak than does the FT-IR data. This is consistent with the usual non-linear ELS concentration response.

PDMS homopolymer is completely soluble in these gradient solvents and is unretained on the silica packing. However, since the majority of the PMMA–g-PDMS sample is insoluble in the starting eluent solvent of cyclohexane–toluene–ethanol (60:36:4, v/v/v), the mode of retention is in question. PMMA homopolymer was observed to have a solubility limit of cyclohexane–toluene–ethanol (40.3:53.73:5.97, v/v/v). Taking into account the gradient lag and column void volume, this corresponds to an elution volume of 22.1 ml. Fig. 1 clearly indicates that nearly all copolymer components are retained beyond this solubility limit even though increasing PDMS incorporation only increases copolymer solubility. Indeed, the observed elution volume of PMMA is shown in Fig. 3 to be at the end of the copolymer distribution for a molecular mass 49 700 standard. Note that although the copolymer chromatogram tails out to the elution time of PMMA, no resolved PMMA homopolymer was observed to be present from the graft copolymerization reaction.

The retention process for PMMA–g-PDMS in this solvent system on silica relies on initial precipitation of the copolymer followed by adsorption retention after redissolution in the sol-

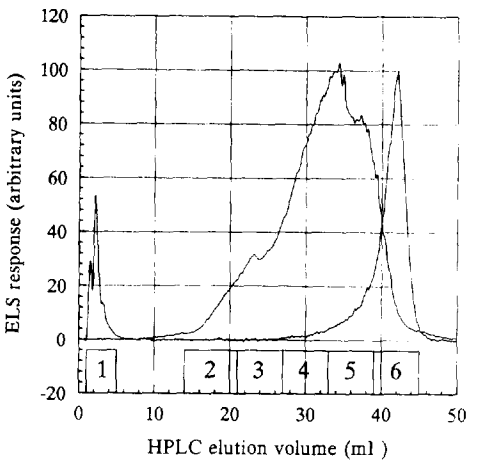

Fig. 3. Comparison of the gradient elution HPLC chromatograms of 10.0 mg of PMMA–g-PDMS and 0.5 mg of a molecular mass 49 700 PMMA. The intervals used for semi-preparative fraction collection of the graft copolymer are shown in the numbered boxes.

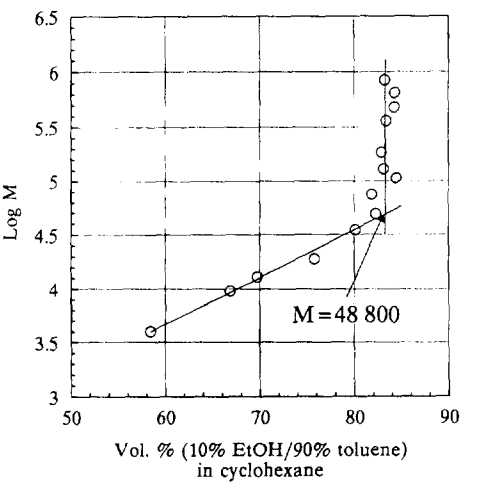

Fig. 4. Variation of solvent concentration required for PMMA elution from 100 Å pore silica as a function of polymer molecular mass.

vent gradient. PDMS has only weak adsorption interactions on silica; however PMMA cannot be eluted with toluene as the strong solvent [13]. Therefore, a low percentage of ethanol was added as a hydrogen-bond displacer [22], despite the fact that ethanol is a non-solvent for both graft copolymer components.

The molecular mass resolution of this separation was evaluated with a series of narrow PMMA standards. The data for PMMA elution volume converted to the corresponding solvent composition at elution is shown in Fig. 4. The small pores (nominal 100 Å) of the silica column packing provide exclusion and nearly molecular mass independent elution for PMMA in excess of 48 800. The effect of low-molecular-mass resolution is shown in the fronting peak shape of the 49 700 PMMA in Fig. 3. Similar results have been observed previously for a different solvent system on this type of silica adsorbent [13]. Molecular-mass-independent separations under adsorption conditions have also been reported by Mori [22] for styrene–alkyl methacrylate copolymers. Unfortunately, a narrow-composition molecular mass series of graft copolymers was not available to determine the generality of this phenomenon for the current study.

The compositional heterogeneity observed across the SEC molecular size separation of the whole PMMA–g-PDMS sample (Fig. 5) was also determined using the solvent-evaporation FT-IR interface. Since the PDMS copolymer component is isorefractive with the THF SEC mobile phase, the molecular size distributions given by

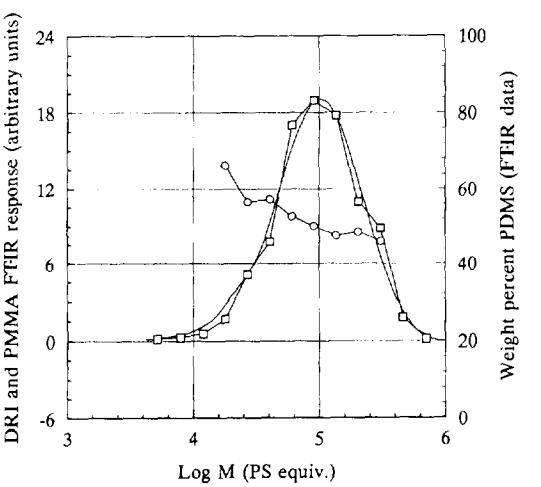

Fig. 5. Comparison of the PS equivalent molecular mass distributions from DRI response (solid line) and mass of PMMA (□) determined from FT-IR spectra from the solvent-evaporation interface for 0.6 mg of a whole PMMA–g-PDMS sample. Variation in the FT-IR determined weight percent PDMS is shown as ○.

the DRI detector is compared with that of the PMMA portion of the copolymer calculated from the FT-IR spectra. The agreement is quite good. Note that, although the average values of PDMS obtained from HPLC (55.0%, w/w) and SEC (52.5%, w/w) are in good agreement, the range of compositions observed across the chromatogram is dramatically reduced in SEC by the overlap of various compositions of similar molecular size. In addition, the average composition values from the FT-IR data for both HPLC and SEC appear biased toward prediction of high PDMS incorporation relative to NMR analysis. This most likely results from the use of homopolymer standards for the PLS-2 calibration set despite linear calibration results. Copolymer standards are not currently available and alternatives are being investigated.

Additional information regarding the joint composition and molecular mass distributions of graft copolymers may be obtained by orthogonal separations. Augenstein and Stickler [24] presented a detailed experimental investigation of the precipitation HPLC separation of terpolymers produced by methyl methacrylate grafting-from ethylene–propene–diene copolymer. HPLC was performed on weakly adsorbing cyanopropyl-bonded silica with a THF–2,2,4-trimethylpentane gradient subsequent to SEC fractionation. ELS detection of the HPLC chromatograms clearly showed the compositional heterogeneity present in the graft copolymer as a function of molecular size, but was unable to quantify the actual copolymer composition due to the lack of ELS detector selectivity.

Further characterization of the graft copolymer structure of PMMA–g-PDMS was pursued in the current experimental study after having established that a chemical composition separation could be efficiently performed by adsorption HPLC with presumably minimal molecular mass influence. SEC with molecular-mass-sensitive detection (LALLS, differential viscometry and DRI [17]) provided an attractive approach to obtaining detailed information about both the mass of the whole copolymer molecule and that of the PMMA backbone by use of a mobile phase solvent (THF) isorefractive with the PDMS side chains. As discussed below, the narrow composition fractions provided by HPLC separation were better suited to molecular-mass-sensitive detection methods than the whole copolymer by minimizing errors introduced by the effect of copolymer composition heterogeneity on refractive index and hydrodynamic size.

It is difficult to obtain accurate molecular mass data from SEC of a compositionally heterogeneous copolymer primarily due to the lack of accurate concentration detector response. Calculation of molecular mass by universal calibration using differential viscometry (DV) and DRI detection is performed by calculation of the local intrinsic viscosity at each retention volume according to Eq. 1 [25].

$$[\eta]_i = \frac{\eta_{sp,i}}{c_i} \tag{1}$$

The local intrinsic viscosity, $[\eta]_i$, at each elution volume data point is calculated from the specific viscosity, $\eta_{sp,i}$, measured by the DV and the local concentration, c_i. The c_i at each elution volume data point is conventionally obtained from the injected sample mass, m, with the DRI response normalized across the entire chromatogram of n data points, where W_i is the DRI response at each volume increment Δv as shown in Eq. 2.

$$c_i = \frac{W_i}{\sum_{i=1}^{n} W_i \, \Delta v} \cdot m \tag{2}$$

A fit to the universal calibration data determined for the SEC column set using narrow polymer standards then yields the molecular mass distribution plot.

$$[\eta]_1 M_1 = [\eta]_2 M_2 \tag{3}$$

If the copolymer sample is heterogeneous in composition across the SEC chromatogram, then the DRI response varies with copolymer refractive index yielding inaccurate local concentration values. In turn Eq. 1 provides inaccurate local intrinsic viscosity values and thereby Eq. 3 yields incorrect molecular masses, M_i.

The variation in PMMA–g-PDMS copolymer

composition across the SEC profile was determined from FT-IR spectra of deposited fractions and is shown in Fig. 5. Correction of the DRI response for local copolymer refractive index variation [26] using the FT-IR determined copolymer composition might yield an improved molecular mass distribution using universal calibration. However, the propagation of error through this series of data corrections is not likely to yield accurate results beyond the center of the copolymer distribution.

Despite the copolymer compositional heterogeneity overlapping the SEC molecular size separation, an alternative exists for molecular mass determination using LALLS detection. SEC in a solvent isorefractive with the PDMS side chains of the graft copolymer allows accurate molecular mass determination of the PMMA backbone [27]. Eq. 4 gives the relationship between the excess Rayleigh scattering, $\bar{R}_{\theta i}$, and M_i at each elution volume.

$$\frac{K^* c_i}{\bar{R}_{\theta i}} = \frac{1}{M_i} + 2A_{2i}c_i \tag{4}$$

The instrumental constant, K^*, is given by Eq. 5 from the solvent refractive index, n_0, the polymer refractive index increment, $(\partial n/\partial c)$, the laser wavelength in vacuum, λ_0, and Avogadro's number, N_A.

$$K^* = \frac{4\pi^2 \bar{n}_0^2 (\partial n/\partial c)^2}{N_A \lambda_0^4} \tag{5}$$

The second virial coefficient term, $2A_{2i}c_i$, in Eq. 4 has little contribution at the low concentrations employed in SEC and is usually ignored. For a copolymer of segregated comonomer units, such as the current graft copolymer, the refractive index increment can be accurately replaced by the average refractive index given by Eq. 6.

$$\overline{(\partial n/\partial c)} = (\partial n/\partial c)_A \bar{x}_A + (\partial n/\partial c)_B \bar{x}_B \tag{6}$$

The average refractive index increment of the copolymer, $\overline{(\partial n/\partial c)}$, is related to those of the corresponding homopolymers $[(\partial n/\partial c)_A$ and $(\partial n/\partial c)_B]$ by their respective weight fractions of comonomer incorporation, ($\bar{x}_A$ and $\bar{x}_B$). In THF $(\partial n/\partial c)_{PDMS} \approx 0$ and therefore $(\partial n/\partial c) = (\partial n/\partial c)_{PMMA}\bar{x}_{PMMA}$. In addition, the concentration of the PMMA backbone at each elution volume data point is accurately given by Eq. 2 provided m is replaced with the injected sample mass of PMMA in the copolymer. The molecular mass distribution of the PMMA backbone of the graft copolymer shown in Fig. 6 is thereby obtained directly from Eq. 4. This isorefractive solvent approach has also been discussed by Prud'homme and Bywater [28] for the characterization of block copolymers.

The difficultly of erroneous concentration detector (DRI) response due to compositional heterogeneity can be resolved by the prior HPLC separation of the graft copolymer into narrow composition fractions. However, application of SEC to HPLC fractions was limited by requiring sufficient mass of HPLC fractions to obtain accurate concentration solutions for SEC molecular-mass-sensitive detector calculations. The semipreparative-scale HPLC chromatogram of the PMMA–g-PDMS sample was shown in Fig. 3 in comparison to a PMMA standard of similar M to the cutoff value of Fig. 4. Overload HPLC shows only moderate peak distortion consistent with an adsorption copolymer retention mechanism [29].

The somewhat overloaded HPLC composition separation prior to SEC provides more uniform chemical composition fractions despite only moderate narrowing in molecular mass distribution. This is shown in Fig. 7 for SEC–FT-IR of a HPLC fraction collected near the peak maximum of Fig. 3. The minimal resolution loss due to HPLC overload is indicated by comparison of the average PMDS value for the two HPLC spectra covering the same elution range of Fig. 1 (39.2%, w/w) and the overall average across the entire peak of Fig. 7 (39.7%, w/w). In addition, these more narrow composition fractions allowed increased accuracy in the normalized DRI concentration response for use with differential viscometry and universal calibration molecular mass calculations.

SEC with molecular-mass-sensitive detection was applied to each HPLC composition fraction

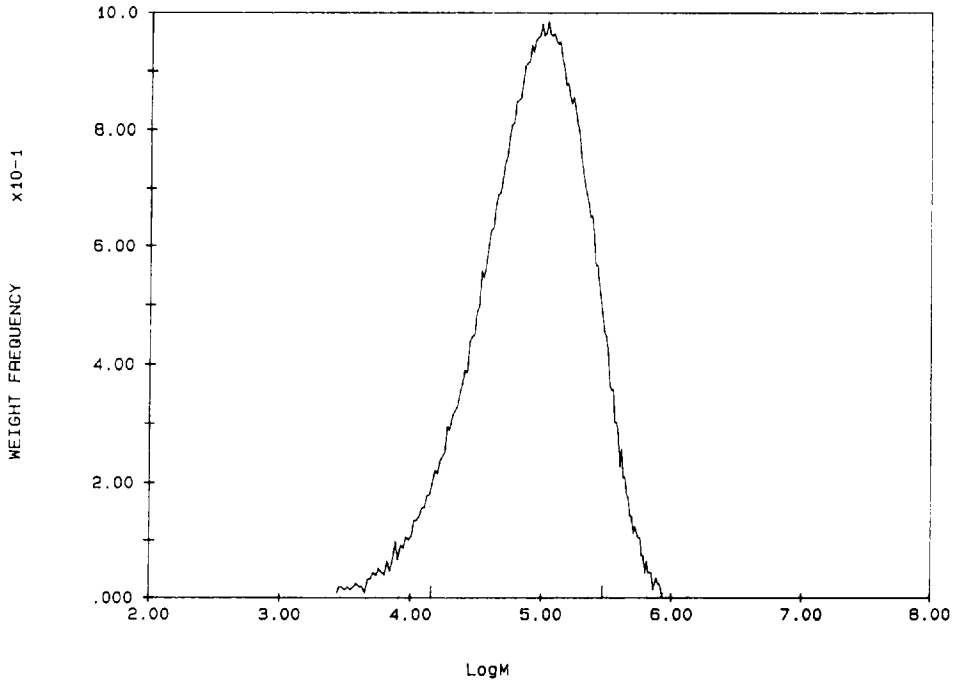

Fig. 6. Low-angle laser-light scattering molecular mass distribution of 0.4 mg PMMA–g-PDMS using the PMMA-corrected sample concentration and refractive index increment. $M_n = 43\,500$; $M_w = 125\,000$; M_z (z average molecular weight) 228 000; $M_w/M_n = 2.87$. Ticks (at 4.2 and 5.0 of the log M axis) denote extrapolation.

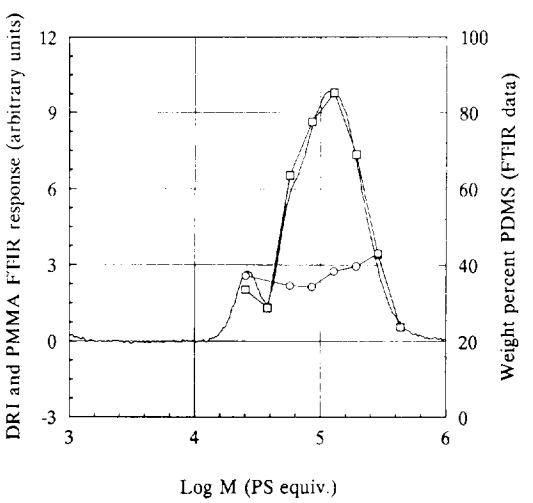

Fig. 7. SEC analysis of a 2.0-ml fraction centered at 38 min elution time for a gradient elution HPLC separation of 10.0 mg of PMMA–g-PDMS (see Fig. 3). The PS equivalent molecular mass distributions are shown for DRI response (solid line) and mass of PMMA (□) determined from FT-IR spectra from the solvent-evaporation interface for 0.6 mg of copolymer. Variation in the FT-IR-determined weight percent PDMS is shown as ○.

Table 1
Gradient HPLC fractions of PMMA–g-PDMS copolymer

HPLC fraction No.	Mass of fraction isolated (mg)	True SEC injected concentration (mg/ml)	DRI calculated PDMS (%, w/w)
1	Insufficient mass for analysis		
2	2.67	1.60	58.6
3	6.12	1.83	43.0
4	14.60	1.64	28.1
5	17.00	1.91	27.0
6	4.12	1.85	17.9
Whole sample	–	1.77	32

Fractions combined from five repeat HPLC separations totalling 50 mg.

listed in Table 1. The calibrated DRI response was used to determine the concentration of PMMA in each sample and by difference the weight percent PDMS. The PMMA-corrected concentration and PMMA ($\partial n/\partial c$) was then used to calculate the molecular mass distribution from the LALLS response. The true concentration

Table 2
SEC results for gradient HPLC composition fractions of PMMA–g-PDMS copolymer

HPLC fraction No.	Universal calibration $\bar{M}_w$	LALLS $\bar{M}_w$ of PMMA backbone	Calculated weight-average PDMS branches per copolymer molecule
2	78 500	26 800	3.95
3	90 800	47 800	3.28
4	136 000	91 000	3.44
5	202 000	144 000	4.43
6	199 000	164 000	2.67

and normalized DRI response was used with the differential viscometry detector to calculate the universal calibration molecular-mass distribution for each copolymer fraction. Thereby SEC of each HPLC fraction resulted in two molecular mass values as listed in Table 2, the molecular mass of the whole copolymer molecule and that of the PMMA backbone. The difference between these values was then divided by the molecular mass of the PDMS macromonomer

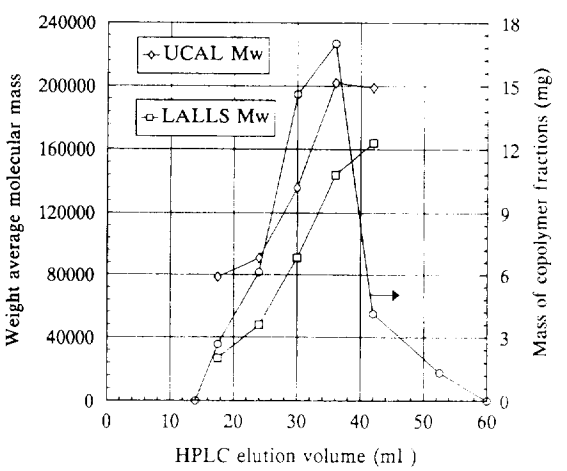

Fig. 8. Comparison of the universal calibration (UCAL, ◇) and low-angle laser-light scattering (LALLS, □) weight-average molecular masses determined for HPLC fractions (Fig. 3) of PMMA–g-PDMS. The mass of copolymer fractions (○) isolated from gradient elution HPLC indicates the composition separation profile. Data from Tables 1 and 2.

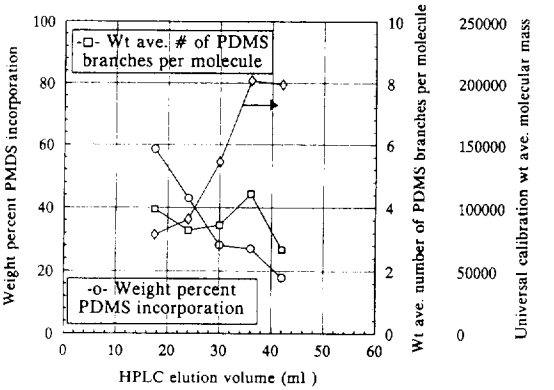

Fig. 9. Comparison of the universal calibration weight-average molecular mass (◇) of each HPLC composition fraction with the DRI-determined weight percent PDMS incorporation (○) and the estimated weight-average number of PDMS side chains per copolymer molecule (□). Data from Tables 1 and 2.

$\bar{M}_w$ = 13 100 to obtain an estimate of the weight-average number of PDMS side chains per copolymer molecule.

The data of Tables 1 and 2 are plotted in Figs. 8 and 9. The universal calibration molecular mass of the whole copolymer molecule and the LALLS determined molecular mass of the PMMA backbone are nearly parallel across the HPLC elution range as shown in Fig. 8. The mass of the isolated HPLC fractions gives an indication of the HPLC chromatogram consistent with Fig. 3. The DRI calculated weight percent PDMS is seen to decrease monotonically across the series of HPLC fractions in Fig. 9. In comparison with the steadily increasing molecular mass of the copolymer molecules, the estimate of the weight-average number of PDMS branches per graft copolymer molecule is relatively constant.

4. Conclusions

HPLC composition separation of PMMA–g-PDMS copolymer was achieved by adsorption

retention after initial precipitation. Relative to the observed retention behavior of PMMA, the HPLC separation was expected to be nearly independent of molecular mass for polymer molecules in excess of 48 800. FT-IR detection using a solvent-evaporation interface indicated a broad range of copolymer compositions present in a radical-polymerized PMMA–g-PMDS copolymer prepared from methyl methacrylate monomer and a 13 100 PDMS macromonomer. The same degree of compositional heterogeneity was not directly observable by SEC–FT-IR due to the coelution of a range of different copolymer compositions with similar molecular size in solution.

Semipreparative HPLC of the graft copolymer sample allowed preparation of more narrow composition fractions for subsequent SEC characterization. SEC with molecular-mass-sensitive detection (differential viscometry and LALLS) allowed estimation of both the whole copolymer molecular mass and that of the PMMA backbone in each HPLC composition fraction. Comparison of these results with the molecular mass of the starting PDMS macromonomer allowed calculation of the weight average number of PDMS branches per copolymer molecule. These results indicated a narrow range of the number of branches per molecule, but a steadily decreasing weight percent incorporation of PDMS with increasing copolymer molecular mass.

These experimental studies establish that gradient elution adsorption HPLC can be an efficient means of resolving broad composition heterogeneity in graft copolymers. Isolated narrow composition fractions from an HPLC separation can then be characterized by SEC with molecular-mass-sensitive detection to provide detailed structural information. The solvent-evaporation FT-IR interface was shown to be a powerful tool for obtaining quantitative composition information across both SEC and gradient HPLC separations. As essentially a microfraction collection device, the solvent-evaporation interface lends the possibility of performing subsequent analyses, such as SEC with molecular-mass-sensitive detection, on HPLC fractions whose composition has been quantitatively determined by FT-IR spectrometry. These approaches are under continuing investigation.

Acknowledgements

The authors would like to acknowledge the assistance of T.H. Mourey and S.M. Miller (Eastman Kodak) with performing the multi-detector SEC experiments.

References

[1] P. Remp and P. Lutz, in G. Allen and J. Bevington (Editors), *Comprehensive Polymer Science*, Vol. 6, Pergamon, New York, 1989, pp. 404–405.
[2] R. Milkovich and M.T. Chang, CPC International, *US Pat.*, 3 786 116 (1974); *US Pat.*, 3 842 059 (1974); *US Pat.*, 3 862 101 (1975).
[3] S.D. Smith, G. York, D.W. Dwight, J.E. McGrath, J. Stejskal and P. Kratochvíl, *Polym. Prepr., ACS Div. Polym. Chem.*, 28 (1987) 458.
[4] G. Meijs and E. Rizzardo, *Rev. Macromol. Chem. Phys.*, C30 (1990) 305.
[5] R. Milkovich, in J.E. McGrath (Editor), *Anionic Polymerization —Kinetics, Mechanisms, and Synthesis* (*ACS Symposium Series*, Vol. 166), American Chemical Society, Washington, DC, 1981, p. 41.
[6] R. Young, R. Quirk and L. Fetters, *Adv. Polym. Sci.*, 56 (1984) 1.
[7] P. Dreyfuss and R. Quirk, in J. Kroschwitz (Editor), *Encyclopedia of Polymer Science and Engineering*, Vol. 7, Wiley, New York, 1987, p. 552.
[8] R.J. Ceresa, *Block and Graft Copolymerization*, Vol. 2, Wiley, New York, 1976.
[9] Y. Ikada, in H.J. Cantow (Editor), *Structure and Properties of Polymers* (*Advances in Polymer Science*, Vol. 29), Springer, New York, 1978, p. 47.
[10] Z. Tuzar and P. Kratochvíl, *Adv. Colloid Interface Sci.*, 6 (1976) 201.
[11] Z. Tuzar, A. Sikora, D. Straková, J. Podešva, J. Stejskal and P. Kratochvíl, *Collect. Czech. Chem. Commun.*, 50 (1985) 2588.
[12] J. Stejskal, D. Straková, P. Kratochvíl, S.D. Smith and J.E. McGrath, *Macromolecules*, 22 (1989) 861.
[13] T.C. Schunk, *J. Chromatogr. A*, 661 (1994) 215.
[14] A.H. Dekmezian, T. Morioka and C.E. Camp, *J. Polym. Sci. Part B Polym. Phys.*, 28 (1990) 1903.

[15] P. Cheung, S.T. Balke and T.C. Schunk, in T. Provder, H.G.Barth and M.W. Urban (Editors), *Hyphenated Techniques in Polymer Characterization (ACS Advances in Chemistry Series)*, American Chemical Society, Washington, DC, in press.
[16] P. Cheung, S.T. Balke, T.C. Schunk and T.H. Mourey, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, 52 (1993) 105.
[17] T.H. Mourey and S.T. Balke, in T. Provder (Editor), *Chromatography of Polymers Characterization by SEC and FFF (ACS Symposium Series*, Vol. 521), American Chemical Society, Washington, DC, 1993, Ch. 12.
[18] G. Glöckner, *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*, Springer, New York, 1991.
[19] T.H. Mourey and T.C. Schunk, in E. Heftmann (Editor), *Chromatography (Journal of Chromatography Library*, Vol. 51B), Elsevier, Amsterdam, 1992, Ch. 22.
[20] T.C. Schunk, *J. Chromatogr. A.*, 656 (1993) 591.
[21] G. Glöckner, M. Stickler and W. Wunderlich, *Fresenius' Z. Anal. Chem.*, 330 (1988) 46.
[22] S. Mori, *Polymer*, 32 (1991) 2230.
[23] T.H. Mourey and L.H. Oppenheimer, *Anal. Chem.*, 56 (1984) 2427.
[24] M. Augenstein and M. Stickler, *Makromol. Chem.*, 191 (1990) 415.
[25] R. Lew, P. Cheung, S.T. Balke and T.H. Mourey, *J. Appl. Polym. Sci.*, 47 (1993) 1685.
[26] D.-C. Lee, T.A. Speckhard, A.D. Sorensen and S.L. Cooper, *Macromolecules*, 19 (1986) 2383.
[27] J.S. Lindner and S.S. Huang, in H.G. Barth and J.W. Mays (Editors), *Modern Methods of Polymer Characterization*, Wiley, New York, 1991, Ch. 9.
[28] J. Prud'homme and S. Bywater, *Macromolecules*, 4 (1971) 543.
[29] H. Engelhardt, M. Czok, R. Schultz and E. Schweinheim, *J. Chromatogr.*, 458 (1988) 79.