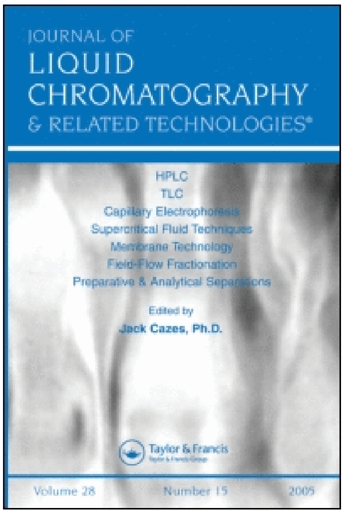

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CHARACTERIZATION OF CHEMICAL HETEROGENEITY OF GRAFT COPOLYMER BY CONVENTIONAL SEC

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ABSTRACT

Poly(methyl methacrylate) grafted with poly(dimethylsiloxane) was investigated by size exclusion chromatography coupled with refractometric and low-angle laser light scattering detectors. Using successively toluene and tetrahydrofuran as eluents, a variation in chemical composition and molecular weight of individual copolymer blocks as a function of hydrodynamic volume were measured. Chemical composition distribution and heterogeneity parameters of the copolymerization product were approximated and compared with the results obtained by supercritical fluid extraction fractionation and by fractionation in demixing solvents.

INTRODUCTION

Copolymers play an important role in many applications in practice. However, only a few studies of chemical composition distribution of graft copolymers have been reported.[1-6] On the basis of physical quantities measured by light scattering, which are influenced by both chemical composition distribution (CCD) and molar mass distribution (MMD), compositional heterogeneity parameters were obtained.[1,3,5]

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For the determination of CCD, supercritical fluid extraction (SCFE)[2] and fractionation in demixing solvents[3] (FDS) as well as adsorption high performance liquid chromatography (HPLC)[4,6] were used.

Size exclusion chromatography (SEC) with multidetection can provide information on CCD and MMD of graft copolymers as well. The comparison of graft copolymer heterogeneity characterization by SEC with results obtained by FDS and SCFE[7] is the subject of the present paper. Poly(methyl methacrylate) (PMMA) grafted with poly(dimethylsiloxane) (PDMS), i.e., PMMA-graft-PDMS,[7] served this purpose.

EXPERIMENTAL

Graft Copolymer and Solvents

PMMA-graft-PDMS was prepared by anionic copolymerization of PDMS macromonomer (component B) having the number-average molar mass $\langle M_B \rangle_n^* = 20000$ gmol^{-1} with methyl methacrylate (component A) in tetrahydrofuran (THF) at -78°C with 1,1-diphenylhexyllithium as initiator.[7] The average content of PMMA, $\langle X \rangle$, found by NMR was 66% (w/w).[7] The copolymer was considered to have a nonregular comb-like structure (with random position of nearly uniform, previously anionically prepared grafts on molecularly nonuniform backbone chain). Sample was characterized by mass average molar mass, $\langle M \rangle_w = (414 \pm 38) \times 10^3$ gmol^{-1}, determined by static light scattering in several solvents.[7] Toluene (Lachema, Czech Republic) and THF (Fluka, Switzerland) were distilled on a laboratory column.

Size Exclusion Chromatography

The chromatographic equipment consisted of a pump (HPP 5001), an injection valve LC-30 with a 100-μL-loop, a RIDK-102 differential refractometer (RI) (Laboratory Instruments, Czech Republic), and a low-angle laser light scattering (LALLS) detector (KMX-6, Chromatix, USA). Both detectors were connected via an A/D converter 2308 (Black* Star Ltd., England) to an IBM-compatible computer. The software used allows us on-line data collection as well as calculation of MMD and molar-mass averages. A commercial stainless steel column HP (7.5/600 mm) packed with PLGel 10 μm MIX (Polymer Laboratories, Inc., England) was used with THF/toluene as eluent. Under experimental conditions of SEC separation, the axial dispersion was negligible. SEC/LALLS and a broad polystyrene (PS) sample

($\langle M\rangle_w = 2.9\times10^5$ $gmol^{-1}$; $\langle M\rangle_w / \langle M_n\rangle \sim 6$) were used for calibration of the separation system in each of the eluents. To calculate the "universal" calibrations[1] dependences [relation of the hydrodynamic volume (product of intrinsic viscosity and molar mass $[\eta]M$) between elution volume, V] the Mark-Houwink-Sakurada equations for PS in THF (cf. ref. 8) and toluene,[9] $[\eta] = 1.17 \times 10^{-2}\ M^{0.717}$ and $[\eta] = 7.5 \times 10^{-3}\ M^{0.75}$, respectively, were used. These "universal" dependences, $\log[\eta]M$ vs. V, for individual eluents were linear and slightly differ within the range of elution volumes of interest.

Two runs of SEC analysis were made. In each of them, only one copolymer component was measured while the other was practically masked by isorefractivity with the eluent used. Consequently, the latter component was "invisible" for both detectors. Copolymer concentrations were selected in the range (1-2) $\times 10^{-3}$ g cm^{-3}. It is necessary to point out that eluents are good solvents both for PMMA[10,11] and for PDMS.[12] Hence, neither aggregation of graft copolymer, nor other undesirable effects (e.g., copolymer-column packing interaction), which could disturb the pure size exclusion mechanism, took place. Using the differential refractometry (Brice-Phoenix, Model BP-2000-V, USA), a non-zero refractive index increment of individual homopolymers [$(dn/dc)_{PMMA} = 0.087$ in THF, $(dn/dc)_{PDMS} = 0.085$ in toluene] and average content of PMMA in the sample, $\langle X\rangle = 67\%$ w/w, were found.

RESULTS

The concentration (RI response) and molar mass (LALLS response) profiles of PMMA in THF as well as those of PDMS in toluene were obtained independently in two SEC runs. (In the former eluent, PDMS was an isorefractive, "invisible", component whereas PMMA had anon-zero refractive index increment; the opposite was true for the latter eluent.) To obtain global mass fraction of the sample, both data sets were matched considering composition given by SEC separation on the basis of elution volume, $[\eta]M$. Hence, the elution volume as a variable in chromatograms was replaced by hydrodynamic volume of the sample as seen in Figure 1. Then, the differences in the hydrodynamic behaviour of the sample in individual eluents have to be corrected.

The intrinsic viscosity $[\eta]$ of the sample measured in toluene was by 12% lower than that in THF (Tab. 1). Assuming this hydrodynamic behaviour with all SEC fractions, their hydrodynamic volumes in toluene had to be increased by 12% to reach equivalent $[\eta]M$ values in THF. At the same time, the coefficients based on the average composition, ($\langle X\rangle$ determined independently) were applied to partial normalized (per unit area) distribution of $[\eta]M$.

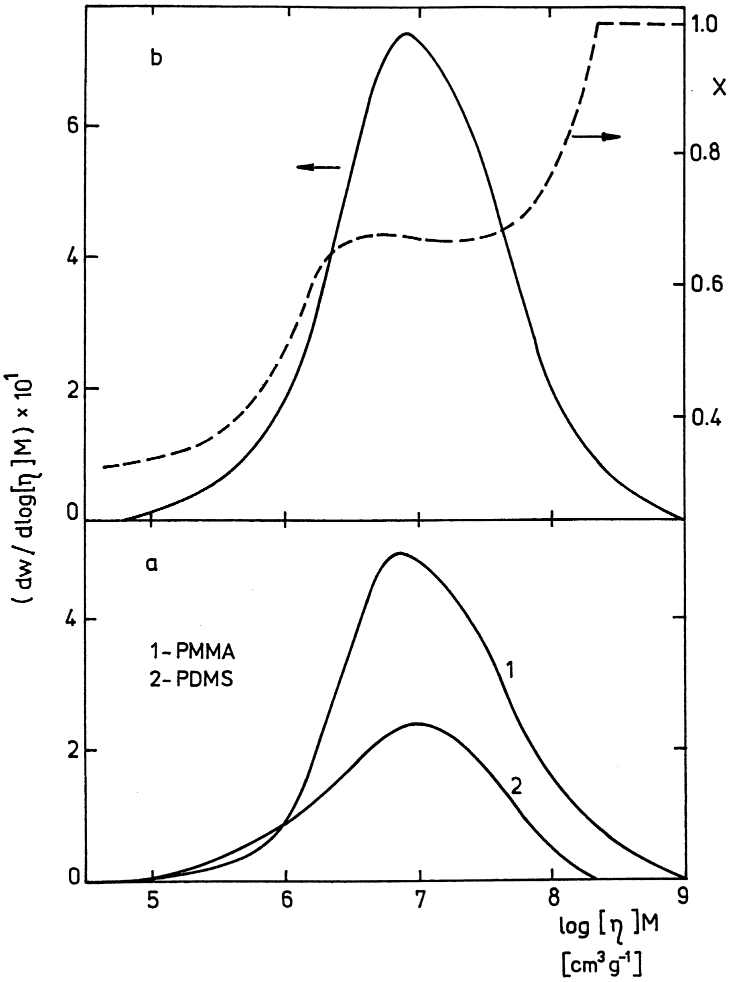

Figure 1. Dependence of mass fraction of [a] PMMA backbone, PDMS grafts; [b] the copolymer and PMMA content X in the sample on hydrodynamic volume [η]M in THF.

The summation of partial distributions modified in such a way afforded the global distribution of [η]M. Then, assuming a fraction of identical properties separated in each of the very good solvents used, mass fractions of both copolymer components at the same hydrodynamic volume, [η]M, were summed. This procedure approximated the distribution of hydrodynamic volume of the whole copolymerization product and the variation in chemical composition of that throughout the hydrodynamic volume range of interest (Figure 1b).

Some nonuniformity in chemical composition of the SEC fractions could be expected due to the influence of complexity of the graft copolymer system and the principle of separation mechanisms.

The technique used showed the sample considered earlier to be the neat copolymer[7] containing the PMMA homopolymer (Figure 1a). (For the components of the copolymerization product having the same molar mass, if present, the hydrodynamic volume decreases in the following order: PMMA-graft-PDMS, PMMA, PDMS.) The presence of free PDMS was not excluded either as follows from a dramatic drop in the PMMA content at small hydrodynamic volumes (Figure 1b).

Chemical Composition Distribution

The cumulative mass fraction vs. composition X (PMMA content, w/w) plot was compared with the published results[7] of two methods recommended exclusively for CCD determination (Figure 2a). SEC (curve 1) and fractionation in demixing solvent (FDS; curve 3) were found to exhibit the same efficiency. Both were capable of disclosing shoulders extending to both low and high PMMA contents.

Supercritical fluid extraction (SCFE; line 2) did not afford such shoulders; it was insensitive to small amounts of individual homopolymers present in the sample (cf. Figure 1). As expected, all the techniques observed the major part of anionically prepared sample having narrower CCD in comparison with the theoretical predicted CCD (Figure 2b).

The CCD-model was calculated according to Stejskal and Kratochvíl[12] for the neat (no homopolymer present) radically prepared graft copolymer with parameters of the sample under investigation given in Table 1 (e.g., number- and mass-average degrees of polymerization of the backbone chain, ratio of molar mass of monomer A and macromonomer B $\left(\langle M_A \rangle_0 / \langle M_B \rangle_n^*\right)$ and average chemical composition of copolymer $\langle X \rangle$).

Compositional Heterogeneity Parameters

Parameters P and Q are used to quantify the compositional heterogeneity of the copolymer sample.[13] P describes interdependence of CCD and MMD, while Q primarily represents the broadness of the CCD. These parameters, usually measured using light scattering, are defined[13] as:

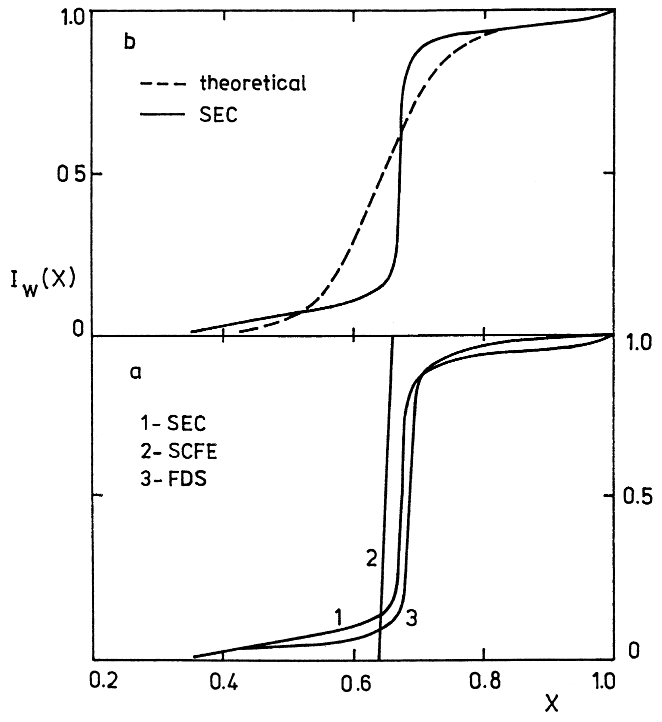

Figure 2. Cumulative mass fraction I (X) vs. composition (X - content of PMMA) as obtained by different methods.

$$P = \Sigma w_i M_i \, \Delta X_i \tag{1}$$

$$Q = \Sigma w_i M_i \, \Delta X_i^2 \tag{2}$$

where M_i is molar mass of SEC fraction having X_i content of A component. $\Delta X_i = X_i - \langle X \rangle$, where $\langle X \rangle$ is overall average content of A. To determine P and Q parameters, the MMD of the sample under study was required. After appropriate correction of toluene $[\eta]M$ data, as given above, the dependences M_A and M_B vs. $[\eta]M$ were plotted in the same graph. Then, assuming SEC fractions with low molar-mass nonuniformity, the molar mass of fraction of the whole copolymerization product M_i was approximated by the sum of molar masses of individual components measured by LALLS at the same hydrodynamic volume ($M_{A,i} + M_{B,i} = M_i$).

Table 1

Molecular Parameters of PMMA-Graft-PDMS Copolymer

Mass-Average Molar Mass, g/mol	
Copolymer, $10^{-5}\langle M\rangle_W$	4.78
PMMA backbone, $10^{-5}\langle M_A\rangle_W$	4.00
PDMS grafts, $10^{-5}\langle M_B\rangle_W$	1.16
Number-Average Molar Mass, g/mol	
Copolymer, $10^{-5}\langle M\rangle_n$	2.64
PMMA backbone, $10^{-5}\langle M_A\rangle_n$	2.18
PDMS grafts, $10^{-5}\langle M_B\rangle_n$	0.50
PDMS single graft, $10^{-5}\langle M_B\rangle_n$*	0.20
Other Characteristics	
Chemical composition $\langle X\rangle$ (PMMA mass fraction, w/w)	0.67
Heterogeneity parameter P (eq.(1))	54342
(eq.(3))	33600
Heterogeneity parameter Q (eq.(2))	15220
(eq.(4))	8398
Intrinsic viscosity [η], cm^3/g	
in toluene	68
in THF	77

Using an appropriate mass fraction shown in Fig. 1b, the MMD was constructed (Figure 3b). Heterogeneity parameters, which followed from SEC separation, were calculated using eqs (1) and (2) (cf. Table 1). The P and Q parameters for the neat copolymer can be obtained as functions of molar mass averages.[13]

$$P = 1/2\left(1-\langle X\rangle\right)\left(\langle M\rangle_w - \langle M_B\rangle_w\right) - 1/2\langle X\rangle\left(\langle M\rangle_w - \langle M_A\rangle_w\right) \qquad (3)$$

$$Q = \langle X\rangle\left(1-\langle X\rangle\right)\left(\langle M_A\rangle_w + \langle M_B\rangle_w - \langle M\rangle_w\right) \qquad (4)$$

Knowing MMDs of both components (Figure 3a) and of the whole copolymer under study (Figure 3b), molar mass averages (Table 1) required for determination P and Q parameters were calculated in an appropriate way. The approximated value of $\langle M\rangle_w$ (cf. Table 1) was in good accordance with that

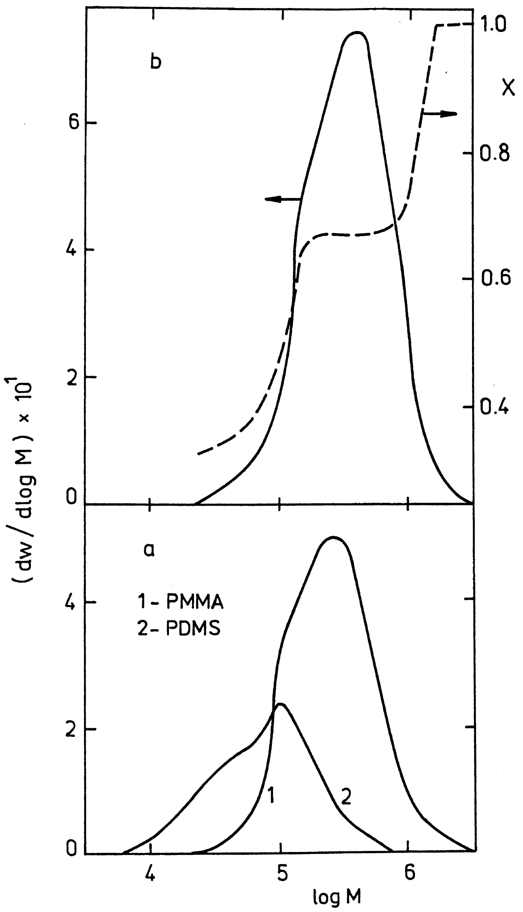

Figure 3. Molar mass distribution of [a] PMMA backbone, PDMS grafts, [b] the copolymer with PMMA content X in the sample.

value determined by stand-alone static light scattering (see Experimental Part) and this is the legitimacy of the presented experimental data evaluation. Using eqs (3) and (4), very low values of P and Q parameters were obtained as compared with the former method based on SEC separation (Table 1). Since the broad range of composition was observed by SEC, including the homopolymers present (Figure 2), the P and Q parameters calculated according to eqs (1) and (2) could be considered more likely.

Nevertheless, these parameters could be lower than real ones due to some distortion of compositional variation across the SEC chromatogram by the overlap of various compositions of similar molecular size (hydrodynamic volume).

CONCLUSION

SEC with two eluents (THF and toluene) and two detectors (RI and LALLS) proved to be comparable in estimation of the CCD with fractionation in demixing solvent; the method exclusively recommended for the purpose. Moreover, the MMD and heterogeneity parameters of the product of copolymerization were approximated. Choosing a proper method for determining the CCD of the nonuniform graft copolymer system, one has to compromise always between the high accuracy (if any) [6] of the obtained data on the one hand, and the speed, facility, and costs on the other. In a paper published recently,[6] the average SEC composition of graft copolymer of the same type needs correction according to the given experimental data. Then the correct PDMS content will conform to the NMR result as well, and both these values will contradict the average composition coming from the superior HPLC method based on adsorption and precipitation.

The present method is shown very productive especially for combination of the comonomers used. It is a successful compromise between the more rigorous but costly and tedious two-dimensional chromatography (HPLC-SEC)[6,14] and a simple combination of SEC and off-line light scattering.[5]

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