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Determination of Molecular Weight and Compositional Heterogeneity of a Graft[†] Copolymer by a Combination of SEC and LALLS

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Introduction

Considerable effort is devoted to determine interdependent molecular weight distributions (MWDs) and chemical composition distributions (CCDs) of graft copolymers, i.e. branched macromolecules with a backbone composed of one type of polymer and side chain (grafts) of another. Size exclusion chromatography (SEC) is claimed to be a rapid, high-resolution method for determination of MWD.[1] Since the SEC separation mechanism is based on the effective hydrodynamic volume of macromolecules rather than on their molecular weight, application of this method to copolymer systems heterogeneous in composition and architecture is complicated because of an overlap of similar molecular sizes of various topology and composition. Hence, the use of two detectors sensitive to the polymer concentration and molecular weight detector is necessary for the success of a SEC experiment.[2] Generally, experimental determination of CCD seems to be unfeasible unless tedious fractionation techniques (cross-fractionation,[3−6] fractionation in demixing solvents,[7] supercritical fluid extraction fractionation,[8] and orthogonal chromatography[9,10]) are used.

This paper describes a very productive method for the determination of MWD and average chemical heterogeneity parameters. To analyze poly(methyl methacrylate) (PMMA) grafted with poly(dimethylsiloxane) (PDMS) (cf. ref 11), two SEC runs, in toluene and in THF, were performed with an on-line low-angle laser light-scattering (LALLS) detector.

Experimental Section

Graft Copolymer and Solvents. PMMA-*graft*-PDMS was prepared by free radical copolymerization of PDMS macromonomer (B), having the number-average molecular weight $\langle M_B \rangle_n^* = 1 \times 10^4$, with methyl methacrylate (A) in toluene.[10] The product of copolymerization was characterized by membrane osmometry and NMR, giving $\langle M \rangle_n = 1.26 \times 10^5$ and the average PMMA content $\langle X \rangle = 0.597$ w/w (cf. ref 7). Toluene (Lachema, Czech Republic) and tetrahydrofuran (THF, Fluka, AG, 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, an RIDK-102 differential refractometer (Laboratory Instruments, Prague, Czechoslovakia), an RI detector, and a LALLS detector (KMX-6, Chromatix, Sunnyvale, CA). Both detectors were connected via an A/D converter 2308 (Black*Star Ltd., St. Ives, Huntington, England) to an IBM-compatible computer. The software used allowed on-line data collection as well as calculation of *M*-distributions and *M*-averages. A commercial stainless steel HP column (7.5/600 mm) packed with PLGel 10 μm MIX (Polymer Laboratories, Inc., Shropshire, England) was used with THF/toluene as eluent. LALLS detection and a broad polystyrene (PS) sample ($\langle M \rangle_w = 2.9 \times 10^5$; $\langle M \rangle_w/\langle M \rangle_n \sim 6$) were used for calibration of the separation system in each of the eluents.

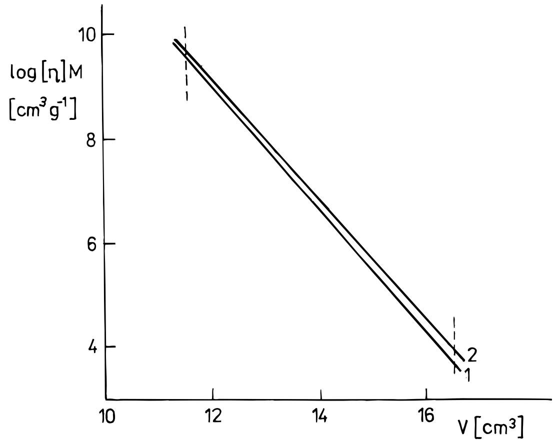

Figure 1. Universal dependence of hydrodynamic volume $[\eta]M$ on elution volume V for a separation system used in THF (1) and toluene (2).

In order to obtain a "universal calibration",[1] i.e. a relation between the hydrodynamic volume (expressed as the product of intrinsic viscosity and molecular weight $[\eta]M$) and the elution volume V, the Mark−Houwink−Sakurada equations for PS in THF[12] and toluene,[13] $[\eta] = (1.17 \times 10^{-2})M^{0.717}$ and $[\eta] = (7.5 \times 10^{-3})M^{0.75}$, respectively, were used. These "universal dependences", log $[\eta]M$ vs V, differ slightly for individual eluents within the range of elution volumes of interest (delimited by dashed lines in Figure 1). Two runs of SEC analysis were made: in THF and in toluene. In each of them, only one copolymer component was detected while the other was masked because of its isorefractivity with the eluent used. Consequently, the latter component was "invisible" for both detectors. Sample concentrations were selected in the range $(1-2) \times 10^{-3}$ g cm^{-3}. It is necessary to point out that the eluents used are good solvents for both PMMA[13,14] and PDMS.[15] 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.

Results and Discussion

The concentration and molecular weight data of PMMA (component A) in THF as well as those of PDMS (component B) in toluene were obtained as a function of elution volume. To gain as much information as possible about the whole graft copolymer, the principle of "universal calibration" was used and the data obtained were presented as a function of hydrodynamic volume. It was necessary to take into account any possible difference in the hydrodynamic behavior of the copolymer in each solvent. The measured $[\eta]$ values for the original sample were 48.5 and 50 cm^3 g^{-1} in toluene and THF, respectively. Consequently, the overall hydrodynamic volumes ($[\eta]M$) of the copolymer in individual solvents are nearly identical. Assuming the individual copolymer fractions separated in both eluents have the same properties, an approximation was made by summing up concentration fractions dw/d log $[\eta]M$ determined in individual eluents (Figure 2a). Thus the distribution of hydrodynamic volumes, $[\eta]M$) of graft copolymer and the compositional variation (X-weight fraction of PMMA) throughout the whole range of hydrodynamic volumes were obtained (Figure 2a). The molecular weights of SEC fractions of the backbone part $\langle M_{A,i} \rangle_w$ and the graft part $\langle M_{B,i} \rangle_w$ of the copolymer (measured by LALLS) and their sum on $[\eta]M$ were plotted in the same graph (Figure 2b).

[†] Preliminary results were presented at the 34th IUPAC International Symposium on Macromolecules, Prague, 13−18 July 1992.

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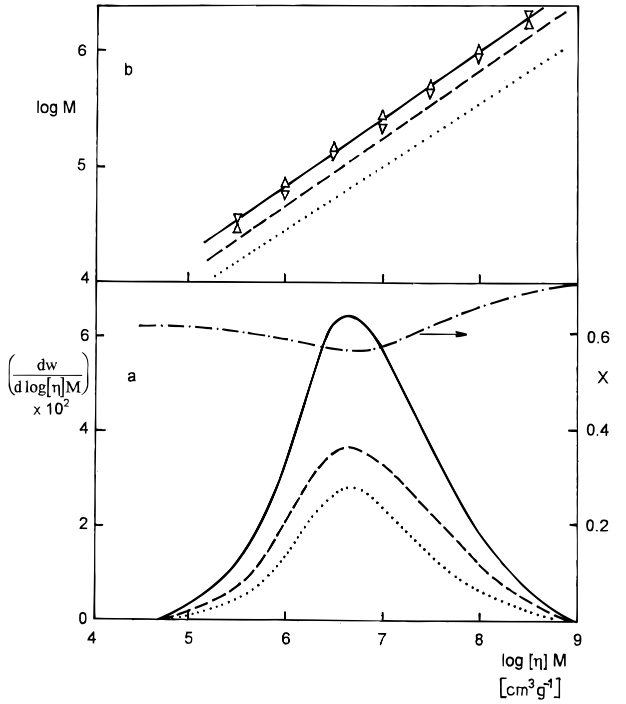

Figure 2. (a) Dependence of the weight fraction of the copolymer (—), the PMMA backbone (A) (– – –), the PDMS graft (B) (···), and the weight fraction of A in the copolymer (X) (—•—•—) on hydrodynamic volume $[\eta]M$. (b) Dependence of the molecular weight on $[\eta]M$: ··· M_B; (– – –) M_A; (—) ($M_A + M_B$); (△) M_A/X; (▽) $M_B/(1 - X)$.

Molecular Weight Distribution. The investigated graft copolymer was considered to be a heterogeneous comb-like type (i.e., the position of fairly identical grafts on the nonuniform backbone chain was random). Regarding the separation mechanism, nonuniformity in structural composition and molecular weight for each copolymer fraction of defined $[\eta]M$ could be expected. As a check of the molecular uniformity of fractions separated by SEC, the following relations[7] were applied

$$M_i = M_{A,i} + M_{B,i} = M_{A,i}/X_i = M_{B,i}/(1 - X_i) \qquad (1)$$

where X_i is the composition expressed by the weight fraction of component A (PMMA). The relations given in eq 1 (cf. ref 7) hold for number-average molecular weights ($\langle M_i \rangle_n$, $\langle M_{A,i} \rangle_n$, $\langle M_{B,i} \rangle_n$). Using RI and LALLS data, the following inequalities were found $\langle M_{A,i} \rangle_w/X_i > \langle M_{A,i} \rangle_w + \langle M_{B,i} \rangle_w > \langle M_{B,i} \rangle_w/(1 - X_i)$. In the vicinity of the chromatographic peak, the difference between ($\langle M_{A,i} \rangle_w + \langle M_{B,i} \rangle_w$) and $\langle M_{A,i} \rangle_w/X_i$ or $\langle M_{A,i} \rangle_w/(1 - X_i)$ was as high as ±11% (cf. Figure 2b; $\langle M_{A,i} \rangle/X_i$ and $\langle M_{B,i} \rangle/(1 - X_i)$ are denoted by (△) and (▽), respectively). In this fashion, the copolymer fractions were shown to be quite narrow and the MWD of the graft copolymer was calculated using $M_i = M_{A,i} + M_{B,i}$. In addition to the MWD of the whole copolymer, the MWDs of its backbone and graft part are shown in Figure 3a. All accessible molecular weight averages calculated from SEC data in an appropriate manner are given in Table 1.

Light scattering can also be used in conjunction with "universal calibration dependence" to obtain an estimate of the intrinsic viscosity of the sample. This approach gave the dependence of $[\eta]$ vs M, as presented in Figure 3b. To our knowledge, this is the first presentation of this dependence for a copolymer with nearly identical long chain grafts. Owing to the architecture of copolymer chains, the values of $[\eta]$ significantly dropped in comparison with those of linear PMMA chains (cf. Figure 3b).

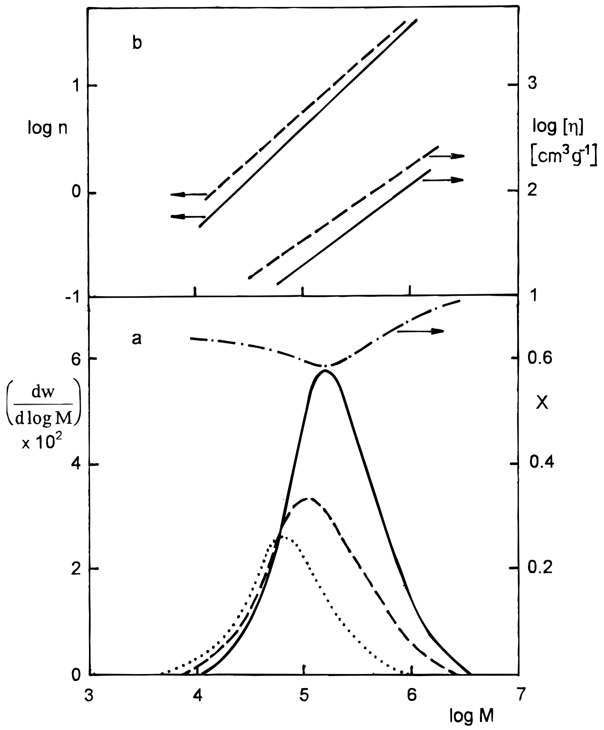

Figure 3. (a) Molecular weight distribution of the copolymer (—), the PMMA backbone (– – –) and the PDMS graft (···), and the weight fraction of PMMA in the copolymer (—•—•—). (b) Dependence of log$[\eta]$ on log M of the copolymer (—) and free PMMA (– – –). Number of grafts, n, in dependence on ($M_A + M_B$) (—) and on M_A (– – –).

Table 1. Molecular Parameters of the PMMA-*g*-PDMS Copolymer

	this work	ref[7]
weight-average molecular weight		
whole copolymer, $10^{-5}\langle M \rangle_w$	3.15	3.65
PMMA backbone, $10^{-5}\langle M_A \rangle_w$	2.33	2.60
PDMS graft, $10^{-5}\langle M_B \rangle_w$	1.03	1.35
number-average molecular weight		
whole copolymer, $10^{-5}\langle M \rangle_n$	1.17	1.26
PMMA backbone, $10^{-5}\langle M_A \rangle_n$	0.70	0.75
PDMS graft, $10^{-5}\langle M_B \rangle_n$	0.47	0.51
PDMS single graft, $10^{-5}\langle M_B \rangle_n$	0.10	0.10
other characteristics		
chemical composition $\langle X \rangle$ (wt PMMA fraction)	0.595	0.597
heterogeneity parameter P (light scattering)		14970
(eq 2)	8250	
(eq 4)	18530	
(eq 6)	26510	
heterogeneity parameter Q (light scattering)		6940
(eq 3)	680	
(eq 5)	5060	
(eq 7)	23880	
intrinsic viscosity $[\eta]$, cm^3 g^{-1} in toluene	48.5	
in THF	50.0	

Compositional Heterogeneity. The integral chemical composition distribution (CCD) has been calculated from the copolymer concentration profile and composition data (Figure 2a) by the procedure recommended for evaluation of data from classical fractionation. In Figure 4 the experimental integral CCD is compared with that calculated according to Stejskal and Kratochvíl.[16] Our CCD turns out to be narrower than theoretically predicted. The reliability of the CCD determination depends on whether the SEC separation has actually proceeded on the basis of M. As shown above, this condition has been fulfilled satisfactorily.

The parameters P and Q are used to quantify the compositional heterogeneity of the copolymer.[17] P de-

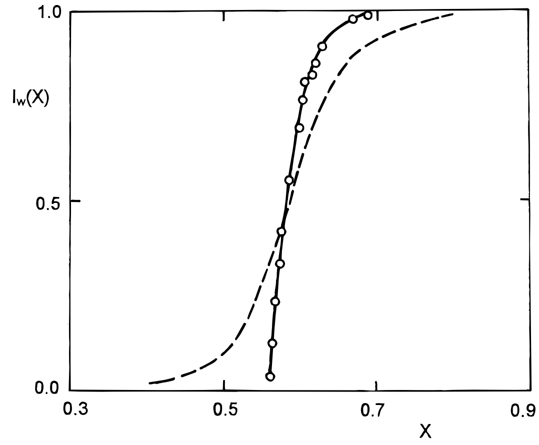

Figure 4. Cumulative weight fraction vs composition *X*: (—) experimental; (— — —) predicted.[16]

scribes the interdependence of the CCD and the MWD, while *Q* primarily represents the broadness of the CCD. Usually measured using light scattering, these parameters are defined[17] as

$$P = \sum w_i M_i \Delta X_i \qquad (2)$$

$$Q = \sum w_i M_i \Delta X_i^{\,2} \qquad (3)$$

$\Delta X_i = X_i - \langle X \rangle$ where $\langle X \rangle$ is the overall average composition of component A. *P* and *Q* parameters can be obtained as a function of molecular weight averages[17] (cf. Table 1)

$$P = {}^1/_2(1 - \langle X \rangle)(\langle M \rangle_w - \langle M_B \rangle_w) - {}^1/_2\langle X \rangle(\langle M \rangle_w - \langle M_A \rangle_w) \qquad (4)$$

$$Q = \langle X \rangle(1 - \langle X \rangle)(\langle M_A \rangle_w + \langle M_B \rangle_w - \langle M \rangle_w) \qquad (5)$$

In the special case of a graft copolymer, the number and branch nonuniformity of which are independent on the nonuniformity of the chain formed by the other monomer, one can use calculate *P* and *Q* with:

$$P = \langle X \rangle(1 - \langle X \rangle)[(\langle M_A \rangle_w - \langle M_A \rangle_n) - (\langle M_B \rangle_w - \langle M_B \rangle_n)] \qquad (6)$$

$$Q = \langle X \rangle(1 - \langle X \rangle)[(1 - \langle X \rangle)(\langle M_A \rangle_w - \langle M_A \rangle_n) + \langle X \rangle(\langle M_B \rangle_w - \langle M_B \rangle_n)] \qquad (7)$$

As a result of SEC separation (the SEC fractions could be nonuniform in chemical composition, and then only their average composition would be found), very low values of *P* and *Q* (Table 1) were calculated using eqs 2 and 3. In accordance a narrow CCD (parameter *Q*) is shown in Figure 4. The proportionality of the number of grafts, *n*, to $\langle M_{A,i} \rangle_w$ (dashed line) and to $\langle M_i \rangle_w$ (full line; slope ~ 1), shown in Figure 3a, demonstrated a weak correlation between the CCD and the MWD (parameter *P*), so that the SEC fractions differ only little in composition. On the other hand, higher values of *P* and *Q* parameters were obtained by means of eqs 4 and 5 using molecular weight averages determined from SEC data. These values seemed to be more likely (Table 1), since they are comparable with results from stand-alone light scattering.[7] Finally, the highest values of *P* and *Q* are obtained from eqs 6 and 7; however, the resulting considerable broadness of of CCD (parameter *Q*) is considered unlikely.

Conclusion

The graft copolymer studied had properties which are especially suited for the presented experimental approach. The use of two eluents (toluene and THF) and two detectors (RI, LALLS) enabled us to examine separately each copolymer component as to its molecular weight and its concentration in copolymer. The insight provided by SEC yielded the MWDs of both the whole copolymer and the individual copolymer components as well as the variation of [η] with the molecular weight of the graft copolymer. In addition to average compositional parameters, a rough estimate of the compositional variation along the SEC chromatogram could be gained. It is common for SEC with selective detection to provide a less precise characterization of the whole copolymer due to the dependence of copolymer hydrodynamic volume on chemical composition. Nevertheless, the recommended separation by SEC of fractions previously separated by composition was not shown to be more successful in the characterization of the same type of graft copolymer. The average value of the PDMS content corrected using the published SEC data[10] (34−36% w/w) conforms to NMR results (32−40% w/w), and both contradict the average composition resulting from a HPLC method based on adsorption and precipitation (55% w/w). In this respect, two-dimensional chromatography (HPLC-SEC), which requires very expensive and sophisticated equipment, would probably not be more precise. On the other hand, the present method provided a more comprehensive description of the graft copolymer in comparison with a simple combination of stand-alone light scattering and osmometry[7] (cf. Table 1).

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