Characterization of random copolymers by size exclusion chromatography with a light scattering detector

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Measurement of the molecular weight and molecular-weight distribution of copolymers by size exclusion chromatography (s.e.c.) can be difficult because of the lack of appropriate samples for calibration of the column. Comparison of copolymers of varying composition is even more problematic. The recent development of light scattering detectors for s.e.c. permits direct measurement of the molecular weight as the polymer elutes from the column, so that no calibration is necessary. A series of six copolymers of poly(4-(acetoxymethyl)styrene-*co*-4-(t-butyloxycarbonyloxy)styrene) have been measured, ranging in composition from 5 to 100 mol% of the poly(4-(acetoxymethyl)styrene). The differential refractive index increment varied linearly with composition. The weight-average molecular weights (M_w) determined by s.e.c. with the light scattering detector agree well with those determined with light scattering alone. Application of the technique to copolymers is discussed.

(Keywords: characterization; copolymers; light scattering; size exclusion chromatography)

INTRODUCTION

The characterization of the molecular weight and molecular-weight distribution of synthetic copolymers by size exclusion chromatography (s.e.c.) presents a problem owing to the lack of appropriate samples for calibration of the column. Frequently a series of molecular weights of an entirely different polymer (polystyrene, for example) is used for calibration, and molecular-weight averages are reported 'relative to polystyrene'. Comparison of a series of copolymers of varying functionality is even more difficult because even the relative molecular weights obtained with the polystyrene calibration will depend on the functionality. Absolute methods such as colligative methods or light scattering are time-consuming, require large amounts of sample, and give no information about the molecular-weight distribution.

Light scattering detectors that interface with an s.e.c. have been introduced in recent years to address these problems[1–4]. These instruments differ from the classical light scattering instrument design in several ways: (1) optics and detectors are usually fixed, (2) sample flows through the scattering cell, and (3) very small scattering volumes (as small as 0.1 μl) are used. The instruments are also useful for light scattering alone, where both the flow-through design and the small scattering volume aid in eliminating dust. When used with s.e.c., light scattering (l.s.) provides a direct measurement of the molecular weight from the scattered intensity of the eluting sample. Historically, intensity light scattering measurements were difficult, often plagued by contributions from dust or aggregates. The s.e.c./l.s. technique also addresses these difficulties in that the s.e.c. functions as an efficient filter, separating any very large particles that may dominate the scattering from the bulk of the sample. The most recent l.s. detector introduced commercially provides a range of as many as 15 scattering angles, so that as many as 16 individual chromatograms are obtained with each injection; one for each scattering angle plus the refractive index (or absorption) chromatogram[3]. With these data, the angular dependence of the scattered intensity may be determined at each elution volume. In principle, with multi-angle detectors, the root-mean-square radius of gyration (R_G) may then be obtained as a function of elution volume. This presents the appealing possibility of being able to measure R_G vs. M over a decade of M with as little as a few milligrams of sample for a broad distribution polymer.

The polymers studied (*Figure 1*) are precursors to poly(4-(acetoxymethyl)styrene-*co*-4-hydroxystyrene), a new negative resist based on the crosslinking of the phenolic group via an electrophillic aromatic substitution[5–8]. Synthesis of these copolymers is carried out with 4-(t-butyloxycarbonyloxy)styrene, to avoid competing reactions that occur with 4-hydroxystyrene. The phenolic group is then generated by removal of the protective t-BOC group from the copolymers shown in *Figure 1*. This copolymer is one of a group of 'chemically amplified' resists in which the initiating proton is regenerated at each step. The resists may be patterned by ultra-violet light, electron beam or synchrotron radiation. Details of the synthesis and lithographic applications have been reported previously[5–8]. In this study, six samples were studied, with the mole fraction of 4-vinylbenzylacetate units (X in *Figure 1*) varying from 0.05 to 1.0.

EXPERIMENTAL METHODS

The differential refractive index increment (dn/dc) for each polymer in toluene was measured using a KMX-16 (LDC Milton Roy) laser differential refractometer with 623.8 nm light, at 25°C. The values measured were quite small, ranging from 0.0344 for 5% 4-vinylbenzylacetate

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units to 0.064 for the homopolymer poly(4-(acetoxymethyl)styrene), as listed in *Table 1*.

Low-angle light scattering (l.a.l.s.) measurements were carried out on three of the samples in toluene using a Chromatix KMX-6 light scattering photometer (LDC Milton Roy). Samples were dissolved in toluene and five concentrations ($5\ \mathrm{mg\ ml^{-1}} < c < 30\ \mathrm{mg\ ml^{-1}}$) were measured. In this instrument, the solution flows through a spacer (15 mm Teflon or 5 mm stainless steel) held between two polished silica windows. The scattered light is measured in a solid angle about the incident beam defined by one of a series of annuli. Samples were filtered directly into the 15 mm Teflon spacer through a 0.5 μm Fluoropore filter (Millipore Corp.) with the aid of a syringe pump. All measurements were done at ambient temperature (22–25°C), using the 6–7° annulus and 0.2 mm field stop.

S.e.c. measurements were done using a Waters GPC I equipped with a model 590 pump, a R401 refractive index detector and a WISP autoinjector. The mobile phase used was toluene; columns were a series of four 30 cm columns packed with a crosslinked polystyrene gel (10 μm particle size) (PLGel, Polymer Laboratories) with nominal porosities of 10^6, 10^5, 10^4 and 10^3 Å. The columns were housed in an oven maintained at 40°C. The eluant from the column was directed through a DAWN-F multi-angle light scattering detector (Wyatt Technology) and then through the R401 to avoid subjecting the fragile refractometer cell to high back-pressure. The outputs of the DAWN-F and the R401 were directed to an IBM AT and the output of the R401 was also directed to an IBM XT through an HPIB intelligent interface. Software from Wyatt Technology was used to perform calculations for s.e.c./l.s. ($M_v^{\mathrm{sec/ls}}$ at each elution volume v from the light scattering intensity). Software from Nelson Analytical was used to perform calculations for s.e.c. (M_v^{sec} at each elution volume v from the calibration curve obtained with PS standards). In some cases, s.e.c. measurements were also carried out using a Waters 150C liquid chromatograph with tetrahydrofuran (THF) as the mobile phase. The temperature, columns and data reduction were as described above for toluene.

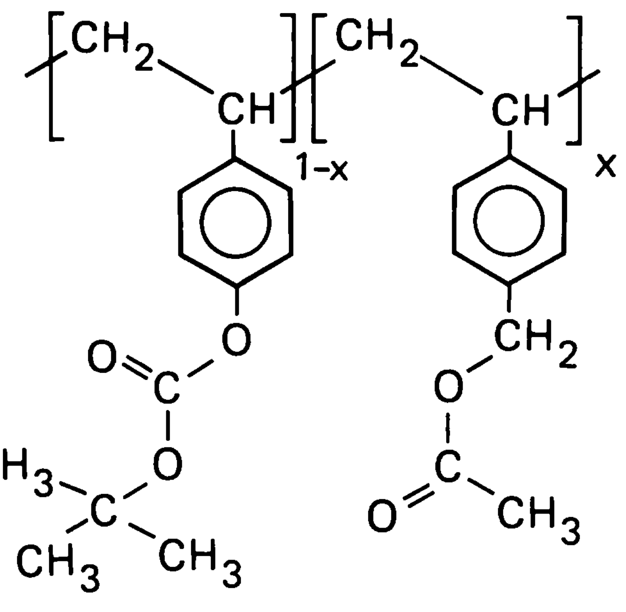

Figure 1 Structure of the poly(4-(acetoxymethyl)styrene-*co*-4-(t-butyloxycarbonyloxy)styrene) copolymer. *X* is the mole fraction of the 4-vinylbenzylacetate units

RESULTS AND DISCUSSION

The d*n*/d*c* of a copolymer may be expressed as:

$$\left(\frac{dn}{dc}\right) = w_A\left(\frac{dn}{dc}\right)_A + (1 - w_A)\left(\frac{dn}{dc}\right)_B \qquad (1)$$

where w_A is the weight fraction of polymer A, and A and B refer to the acetate and t-BOC portions respectively[9–11]. *Figure 2* is a plot of d*n*/d*c* as a function of w_A, and a linear regression fit to equation (1) yields $(dn/dc)_B$ of the homopolymer poly(4-(butyloxycarbonyloxy)styrene) equal to 0.0342 in toluene.

Low-angle light scattering measurements independent of the s.e.c. were carried out as described above. Values for the weight-average molecular weight M_w and the second virial coefficient A_2 were determined by measurement of the Rayleigh factor R_θ at several concentrations c and use of a square-root plot of $(Kc/R_{\theta=4})^{1/2}$ *versus* c. Truncating the expansion of the reciprocal scattering

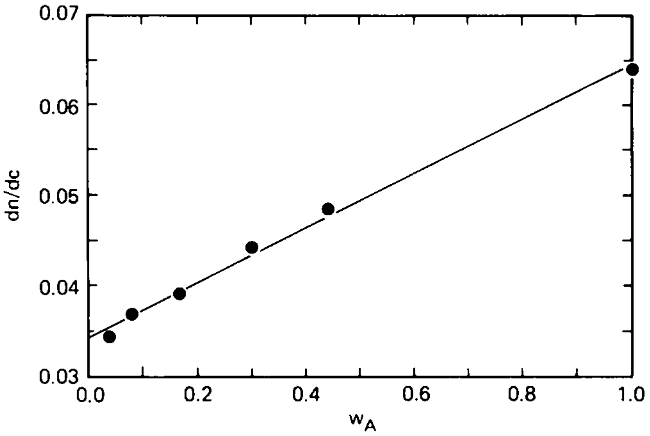

Figure 2 The differential refractive index increment (d*n*/d*c*) as a function of the weight per cent of 4-vinylbenzylacetate, w_A

Table 1 Summary of l.s. and s.e.c./l.s. results in toluene

Sample	X	d*n*/d*c* (ml g^{-1})	M_w^{ls} (g mol^{-1})	$10^4 A_2$ (ml mol g^{-2})	$M_w^{\mathrm{sec/ls}}$ (g mol^{-1})	M_w/M_n	M_w^{sec} (g mol^{-1})
7	0.05	0.0344	–	–	106 000	2.0	65 000
8	0.10	0.0368	99 200	2.88	102 000	2.1	64 500
9	0.20	0.0391	–	–	98 400	2.1	61 800
10	0.35	0.0443	–	–	94 900	1.9	56 000
11	0.50	0.0486	70 800	3.27	72 900	2.1	48 000
12	1.0	0.0643	58 600	0.74	–	1.9	39 300[a]

[a] In THF

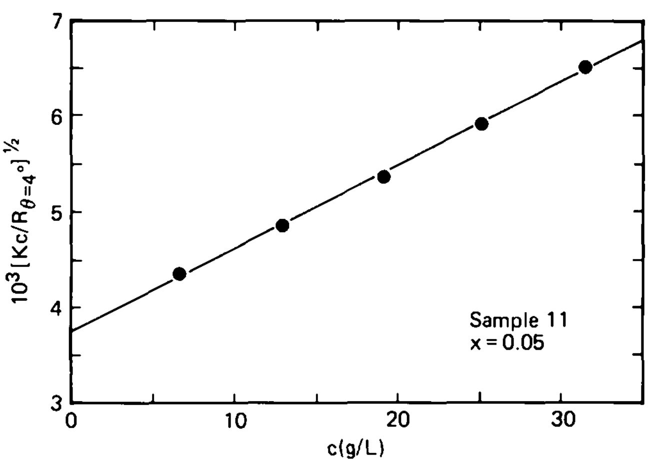

Figure 3 $(Kc/R_{\theta=4})^{1/2}$ as a function of the concentration c for the $X=0.50$ sample

(osmotic compressibility) in terms of c after the third term we obtain:

$$Kc/R_0 = 1/M_w + 2A_2c + 3A_3c^2 \qquad (2a)$$

or

$$(Kc/R_0)^{1/2} = 1/M_w^{1/2} + A_2 M_w^{1/2} c \qquad (2b)$$

where the substitution $A_3 = \frac{1}{3}A_2^2M$ has been made, and the subscript 0 indicates extrapolation of R_θ to 0° scattering angle. The 6–7° annulus corresponds to a scattering angle $\theta = 4°$ when corrected for the refractive index of the solution, and the Rayleigh factor at 4° scattering angle is taken as equal to R_0. The constant K denotes $4\pi^2n^2(dn/dc)^2/\lambda^4N_A$, where n is the refractive index of the solution, λ is the wavelength of the incident light (632.8 nm) and N_A is Avogadro's number. Light scattering measurements of copolymers can be complicated by a heterogeneous distribution of the composition, and theories have been developed to interpret the parameters measured[9–11]. When the composition is heterogeneous, the apparent M_w measured by light scattering, M_w^*, is dependent on the refractive index of the solvent, n_0. An extreme case occurs when the measured $dn/dc = 0$ and the n_0 lies between n_A and n_B where n_A and n_B are the refractive indices of the respective homopolymers A and B. Then individual molecules that differ in composition from the average may still have a non-zero dn/dc and scatter light, leading to infinite values of M_w^*. The M_w^* determined by light scattering will approach the M_w of the copolymer when the distribution of the composition is homogeneous, and/or the refractive indices n_A and n_B of the homopolymers are similar and far from n_0 (refs. 9–11). Determination of these copolymer compositions at low conversion as a function of the monomer feed ratio indicated that the incremental composition is nearly identical to the monomer feed; thus the copolymers are expected to have a random distribution of composition[8]. For random copolymers, it is expected that M_w measured by light scattering should be independent of n_0 (refs. 9–11). The data obtained for sample 11 with $X=0.50$ are shown in *Figure 3*. In the concentration range measured ($5\ \mathrm{mg\ ml^{-1}} < c < 30\ \mathrm{mg\ ml^{-1}}$) the excess scattering is approximately twice that of the toluene. In contrast, the concentration range detected in s.e.c./l.s. is at least an order of magnitude smaller. The values for M_w^{ls} and A_2 for samples 8 and 11, with $X=0.10$ and 0.50, respectively, are listed in *Table 1*.

The measured values of A_2 are only about 20–30% smaller than those observed for polystyrene in toluene; thus toluene is also expected to be a good solvent for these copolymers. The measured values of M_w^{ls} and A_2 for the homopolymer, poly(4-(acetoxymethyl)styrene) are also listed in *Table 1*. The A_2 value is significantly smaller than those reported for the copolymers, indicating that the toluene is thermodynamically a less favourable solvent for the homopolymer. As discussed below, the s.e.c. chromatogram of the homopolymer was also anomalous in shape in toluene, which may be related to the less favourable polymer–solvent interaction. Measurement of R_G of copolymers by light scattering is also complicated by the possibility of heterogeneous composition. In some cases the apparent radius of gyration, R_G^*, may even be negative. Measurement of R_G by light scattering requires that the angular dependence be experimentally measurable, generally $R_G \geqslant \lambda/20$, where λ is the wavelength of the light. For polystyrene in toluene, with $\lambda = 632.8$ nm, this requires $M \geqslant 500\,000$. The R_G of these copolymers is too small to be measured by light scattering, consistent with the negligible angular dependence observed for both l.s. and s.e.c./l.s. measurements.

SIZE EXCLUSION CHROMATOGRAPHY/LIGHT SCATTERING

Light scattering (90° scattering angle) and refractive index chromatograms for sample 7 with $X=0.05$ and for sample 11 with $X=0.50$ are shown in *Figure 4*. Typically, 300–400 'slices' or data points are collected across the distribution. All samples with the exception of the homopolymer, sample 12, exhibited similar chromatograms. The homopolymer chromatogram showed a nearly vertical leading edge, indicating separation mechanisms unrelated to the size distribution. Normal chromatograms were observed in THF. As discussed above, the l.s. chromatograms obtained for these copolymers were independent of scattering angle, with the exception that the lower angles were more noisy. Molecular weights at each elution volume were calculated as described below by averaging over all the scattering angles measured. The scattered intensity is proportional to cM so that the intensity is larger in the high-M portion of the distribution. In fact, the s.e.c./l.s. technique is very advantageous in detection of very small fractions of high-M species, such as aggregates or branched molecules, which are not detectable by any other solution technique[12]. Conversely, intensity in the low-M portion of the distribution can be quite small, and molecular-weight averages that primarily reflect the low-M contribution, such as M_n, may be erroneously large. The scattered intensities shown in *Figure 4* are quite small when compared with those measured using l.s. alone as shown in *Figure 3*. At the maxima of the l.s. chromatograms in *Figure 4*, the scattered intensity is only 7% larger than the baseline scattering from the eluting solvent (toluene). The molecular weight M_v at each elution volume v is then given by:

$$M_v = R_{0,v}/Kc_v \qquad (3)$$

neglecting any contribution from the second- or higher-order virial coefficients. At the high dilutions encountered in s.e.c., these terms constitute only a few per cent of the scattering from the polymer, well within the uncertainty of

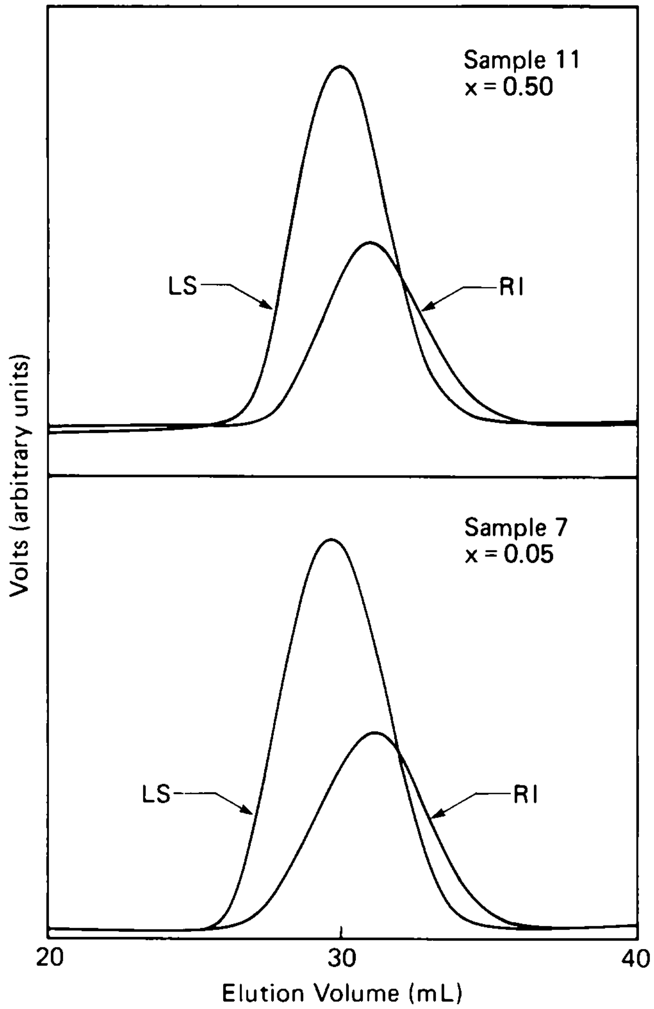

Figure 4 S.e.c./l.s. chromatograms for samples with $X=0.05$ and $X=0.50$. The curves labelled RI are the refractive index signals and the curves labelled LS are the light scattering intensities at 90° scattering angle

the measurement. $R_{0,v}$ may be obtained by extrapolation of $R_{\theta,v}$ to $\theta=0°$ for each elution volume v. For these samples, with $R_G<200$ Å, $R_{\theta,v}$ was independent of θ, and the values of $R_{\theta,v}$ were averaged. The concentration at each elution volume, c_v, is given by:

$$c_v = wh_v/A \tag{4}$$

where w is the total mass of the polymer injected, A is the integrated area of the refractive index peak in volt × ml, and h_v is the refractometer signal in volts at elution volume v. Alternatively, the dn/dc of the polymer may be used with the calibration of the differential refractometer to measure c_v. Most differential refractometers used as detectors for s.e.c. (such as the R401) use a broadband white light source (tungsten), but instruments using red light are available. Moments of the molecular-weight distribution, such as the number-average, M_n, the weight-average, M_w, and the z-average, M_z, molecular weights, are calculated from the concentration (weight fraction) c_v at each elution volume (or slice) v and the corresponding molecular weight, either M_v^{sec} from the PS calibration, or $M_v^{\text{sec/ls}}$ from the DAWN-F light scattering intensity:

$$M_n^{\text{sec}} = \frac{\sum c_v}{\sum c_v/M_v^{\text{sec}}} \tag{5a}$$

and

$$M_w^{\text{sec/ls}} = \frac{\sum c_v M_v^{\text{sec/ls}}}{\sum c_v} \tag{5b}$$

with the other averages calculated in a similar manner. The results in *Table 1* are a clear indication that even these low scattering intensities are sufficient for accurate measurement of both the M_w and the polydispersity M_w/M_n. The values of $M_w^{\text{sec/ls}}$ agree well with those measured using l.s. alone (M_w^{ls}). Values of $(M_w/M_n)^{\text{sec}}$ are also in agreement with $(M_w/M_n)^{\text{sec/ls}}$ and are reported in *Table 1* simply as M_w/M_n. The shape and width of the distribution are similar to the Schulz–Flory distribution (the 'most probable' distribution), with $h=1$:

$$w(M_i) = \left(\frac{h+1}{M_w}\right)^{h+1} \frac{M_i^h}{\Gamma(h+1)} \exp\left(\frac{-(h+1)M_i}{M_w}\right) \tag{6a}$$

with

$$h^{-1} = (M_w/M_n) - 1 \tag{6b}$$

so that $M_w/M_n=(h+1)/h$, $M_z/M_w=(h+2)/(h+1)$, etc.

A calibration curve for each sample may be constructed as shown in *Figure 5*, where the $M_v^{\text{sec/ls}}$ measured at each elution volume v is plotted as a function of v. A molecular-weight range from 20 000 to 500 000 is easily obtained from a single injection of a few milligrams of polymer. Much larger ranges of molecular weight may be obtained by combining samples of varying M. In some cases, more accurate determinations of M_n may be obtained using such a calibration than from the direct measurement of the light scattering intensity at the low-M portion of the distribution[13].

The backbone structure of the copolymer shown in *Figure 1* is that of polystyrene, so that the hydrodynamic volume is expected to be similar for similar degrees of polymerization. However, the substituents increase the molecular weight per repeat unit by nearly a factor of 2 from that of polystyrene. Thus, the copolymers elute at volumes corresponding to polystyrenes of lower M. This may be seen in the comparison of the values of M_w^{sec} obtained from the PS calibration with the values of $M_w^{\text{sec/ls}}$ listed in *Table 1*. The 'polystyrene equivalent' molecular weights, M_w^{sec}, differ from the M_w^{ls} or $M_w^{\text{sec/ls}}$ by a factor of about 1.5–1.6. This factor appears to decrease slightly as the weight fraction of the acetate portion increases. Values of M_w^{sec} obtained using a polystyrene calibration

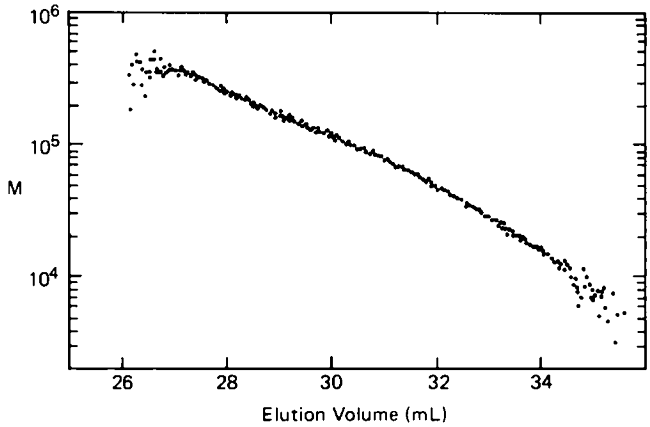

Figure 5 Molecular weight from s.e.c./l.s. as a function of elution volume for the $X=0.50$ sample

are frequently corrected with the 'universal calibration', in which polymers of varying structure are assumed to elute according to their hydrodynamic volume, expressed as the product $[\eta]M$ (ref. 14). Then the molecular weight of polymer A, M_A, may be related to the molecular weight of the polystyrene, M_{PS}, that elutes at the same volume through their respective Mark–Houwink–Sakurada (MHS) constants, K and a, where for a given polymer A:

$$[\eta]_A = K_A M_A^{a_A} \tag{7a}$$

so that at a given elution volume v:

$$[\eta]_A M_A = [\eta]_{PS} M_{PS} \tag{7b}$$

or

$$M_A = \left(\frac{K_{PS}}{K_A}\right) M_{PS}^{(a_{PS}+1)/(a_A+1)} \tag{7c}$$

When the MHS exponents a_A and a_{PS} are nearly equal (as is expected for flexible polymers in good solvents), then the correction may be simplified to a factor $(K_{PS}/K_A)^{1/(1+a)}$, where $a = a_A = a_{PS}$. The validity of the universal calibration procedure is still unproven; however, when the polymers are quite similar in structure, as are these copolymers and polystyrene, most reported results confirm the universal calibration[15]. When M is measured directly with a light scattering detector, then the universal calibration procedure may be used in reverse to predict the MHS constants[16]. For polystyrene in toluene:

$$[\eta] = 1.069 \times 10^{-2} M^{0.724} \tag{8}$$

has been reported by Meyerhoff and Appelt[17], with $[\eta]$ in ml g^{-1}. Based on the assumption of the validity of the universal calibration, we would expect an approximate Mark–Houwink–Sakurada relation for these copolymers of:

$$[\eta] = 0.53 \times 10^{-2} M^{0.72} \tag{9}$$

in toluene. The copolymers do not span an adequate range of M to assess the validity of equation (8). The $[\eta]$ of sample 11 with $X = 0.5$ was measured in toluene to be 19.3 ml g^{-1}, which is within 15% of the value estimated from equation (9).

The technique of s.e.c./l.s. has been used to determine M_w and M_w/M_n of a series of copolymers with as little as 3 mg of sample. These materials represent an unusually demanding application in that $M_w \simeq 100\,000$ and the values of dn/dc are quite low, so that scattered intensities were not even 10% larger than that of toluene alone. Despite these limitations, $M_w^{sec/ls}$ were in good agreement with M_w^{ls} obtained from light scattering alone.

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