Toward a More General Solution to the Band-Broadening Problem in Size Separation of Polymers

Dominik Konkolewicz,† James W. Taylor II,† Patrice Castignolles,† Angus Gray-Weale,‡ and Robert G. Gilbert*,§

Key Centre for Polymer Colloids, School of Chemistry F11, Sydney University, NSW 2006, Australia, School of Chemistry F11, Sydney University, NSW 2006, Australia, Hartley Teakle Building, University of Queensland, Brisbane, Qld 4072, Australia

Received December 31, 2006; Revised Manuscript Received February 26, 2007

ABSTRACT: The molecular weight distributions (MWDs) and hydrodynamic volume distributions of polymers can reveal considerable mechanistic information on the polymerization process, and have significant effects on physical properties such as viscosity. While the broadening function for a particular SEC setup can be found using ultranarrow standards, these are extremely difficult to obtain. The present paper implements and tests a suggested technique (*Aust. J. Chem.* **2005**, *58*, 178) to enable the deconvolution of size distributions using *broad* standards, synthesized under conditions which are expected to produce a number MWD $P(M)$ which is a single exponential. Broad standards with a wide range of $\bar{M}_n$ were synthesized for both styrene and methyl methacrylate (MMA), using low-conversion free-radical polymerization with appropriate choice of chain transfer agent (CTA) and initiator concentrations; standards with high $\bar{M}_n$were synthesized at 25 °C without added initiator. The broadening function was obtained by assuming a flexible functional form (exponential Gaussian hybrid) and least-squares fitting its parameters so that the "theoretical" exponential $P(M)$ curves for each sample, with exponents obtained experimentally, matched the experimental SEC distribution for styrene. The procedure was tested by using the same band-broadening function to deconvolute data for the original polystyrene "standards" and the polyMMA samples, using the Ishige deconvolution method. This method tends to amplify noise, and too tight a tolerance can lead to spurious structure in the deconvoluted distributions. Nevertheless, a tolerance range could be found which led to stable solutions, where the deconvoluted $P(M)$ curves for both were indeed single exponential over the range of molecular weights where data with acceptable accuracy could be obtained. This suggests that this is a generally applicable method to correct for band broadening for a wide range of systems, although improved deconvolution methods are needed to obtain truly converged and stable solutions.

Introduction

Techniques for characterizing polymers by their size in dilute solution include size-exclusion chromatography (SEC),[1] temperature-gradient interaction chromatography,[2] anionic and cationic-exchange chromatography,[3] capillary electrophoresis[4] and the various types of field-flow fractionation.[5] The separation principle has been shown for SEC[6−9] to be through the hydrodynamic volume V_h. This is a quantity with dimensions of volume and is proportional to the product $[\eta]w, \bar{M}_n$ where $[\eta]w$ and $\bar{M}_n$ are respectively the weight-average intrinsic viscosity and number-average molecular weight (the relationship between this quantity and the actual size of the molecule, as expressed by the radius of gyration, is straightforward for unbranched polymers[10] but not a fully solved problem for branched ones). If the polymer is linear or regularly branched, then there is a unique relation between hydrodynamic volume and molecular weight.

The number distribution of molecular weight or of hydrodynamic volume of a polymer sample can be expressed as $P(M)$ or $P(V_h)$,[11] respectively the number of chains with molecular weight M or hydrodynamic volume V_h. For notational simplicity, we shall henceforth only use M as dependent variable unless a particular point needs to be made for complex branched polymers. The number distribution is related to the SEC distribution $w(\log M)$ by[12,13]

$$w(\log M) = M^2 P(M) = M W(M) \tag{1}$$

Here $W(M) = M P(M)$ is the weight distribution.

Considerable information about polymer systems can be obtained from a knowledge of simple characteristics of the size distribution of a polymer sample: for example, (a) whether or not the system has a multimodal size distribution, and (b) from average quantities such as the weight- and number-average molecular weights.[14] However, useful information can also be obtained from the full molecular weight distribution (MWD), or, for complex branched polymers, from the hydrodynamic volume distribution (HVD).[11] For example, if some regions of the MWD of a linear polymer are governed by random chain growth and stoppage events, then $P(M)$ must be a single exponential (a particular case of the Flory−Schulz distribution[13,15,16]), in which case ln P would be linear in M in that region; hence a test of this hypothesis (random growth and stoppage) is that such linearity is observed over some range of M (a corresponding means of interpreting data for hyperbranched polymers has also recently been deduced[17]). In actuality,[18] however, this apparently simple test is vitiated by the effect of *band broadening* in the commonest means of finding MWDs and HVDs: size-exclusion chromatography, SEC.

Band broadening is the effect whereby chains with a given molecular weight elute over a significant range of elution times. Broadening is predominantly due to axial dispersion, caused by molecular diffusion, multiple flow paths along the column

* To whom correspondence should be addressed. Email: b.gilbert@uq.edu.au.
† Key Centre for Polymer Colloids, University of Sydney.
‡ School of Chemistry, University of Sydney.
§ University of Queensland.

10.1021/ma062973a CCC: $37.00
Published on Web 03/28/2007

and other mechanisms.[19,20] The asymmetric SEC traces observed from very narrow samples or ^{14}C labeled samples give evidence for other broadening mechanisms,[19,21] since the two mechanisms just listed suggest symmetric broadening.

Modern SEC equipment minimizes band broadening to the extent that this effect may be negligible for finding accurate values of average molecular weights or the bimodality of distributions (although MALDI−TOF MS and temperature-gradient chromatography data indicate that band broadening can be significant even in these cases[20,22]). Band broadening however causes a MWD which is truly a single exponential to yield a ln P which is concave-up, rather than a straight line.[18] It is clearly of importance to have means of eliminating band-broadening effects to use with the new methods being developed for obtaining information from the size distributions of polymers. The objective of the present paper is to do this by the experimental implementation of a technique recently suggested for this purpose[23] (discussed in detail later) which should be very widely applicable.

Band Broadening and the Convolution Equation. The basis of any size separation technique is the convolution equation:[11,24−26]

$$S(t_{el}) = \int_0^{\infty} G(t_{el},M)\, W(M)\, dM \qquad (2)$$

where t_{el} is the elution time, $S(t_{el})$ the detector signal for a differential refractive index detector, and $G(t_{el},M)$ the broadening function, which is specific for a given size-separation setup and solvent system. A generalization of eq 2 has been derived for any type of detector;[11] while this generalization will not be used here to avoid unduly complex notation, it is noted that the debroadening methodology derived in the present paper is applicable to data from any type of detector, including multidetection SEC.

In the hypothetical situation (a) where band broadening is absent, and also (b) where the SEC setup is such that a completely uniform (monodisperse) sample of molecular weight M elutes at a time t_{el} which is linear in ln M (a "linear calibration curve" given by the functional form $t_{el}(M) = a + b \ln M$), then $S(t_{el}(M)) = w(\log M)$.[13] This mathematical relation for the ideal case (which is never accurately applicable in practice) is the reason that $w(\log M)$ is called the "SEC distribution" .

The broadening function $G(t_{el},M)$ is the signal that would be observed for a series of perfectly uniform (monodisperse) standards of all molecular weights M. There are no means available to predict the form of this function a priori.[27] If one can evaluate $G(t_{el},M)$, then a number of methods exist[19] for inverting ("deconvoluting" or "debroadening") eq 2 to yield the true ("deconvoluted") MWD $W(M)$ and thus $P(M)$ (eq 1) from the signal observed with a given sample. Given that elution is determined only by V_h and not by the nature of the polymer, the $G(t_{el},M)$ determined for any polymer in a particular solvent and SEC setup will be valid for any polymer in the same system.[28]

Current Methods of Accounting for Band Broadening. The ultimate means of accounting for band broadening is to use a technique where it is negligible for the desired application, especially that of obtaining mechanistic information. One such technique is fluorophore-assisted capillary electrophoresis,[29−32] but this is limited by being only useful for low degrees of polymerization (∼100). Another technique is the use of ultranarrow standards[2,19,33−37] or even uniform (perfectly monodisperse) standards[38] whereby the broadening function can be determined directly as the signal, using eq 2. However, preparation of ultranarrow or uniform standards is extremely laborious, and none is available commercially. MALDI−TOF mass spectrometry can be used only for narrow MWD because of its bias in M.[39] Another means of determining G is the SEC/SEC two-dimensional method of Popovici et al.,[20,40] whereby successive fractions eluting through one SEC are then eluted through a second. If this is repeated, the signals will converge to the broadening function. While this is an elegant solution, it is hard to implement routinely because fractionation greatly diminishes the amount of material, and hence, the method is prone to signal-to-noise problems.

An elegant technique for determining G is the peak variance method of Schnöll-Bitai and co-workers.[41−44] This quantifies the variance due to band broadening (rather than the broadening function itself), using relatively narrow standards whose distribution is close to Poisson. However, it is implicit in this treatment that the variance of the broadening function is constant. This assumption is acceptable over a moderate range of molecular weights but not over a wide range, because of evidence[19] for the dependence of the broadening on molecular weight.

The Present Method. The method used here is based on the following result.[18,23] If $P(M)$ is a single exponential, viz.

$$P(X) = \exp(\Lambda X) \qquad (3)$$

where X is the degree of polymerization and Λ is a (negative) constant for the particular sample, then it has been proved[18,23] the slope of the true (i.e., deconvoluted) ln P at the molecular weight corresponding to the maximum in the experimental (i.e., broadened) SEC distribution $w_{exp}(\log M)$ is the same as that which would be obtained using eq 1 without taking account of broadening. This result is expressed as

$$\frac{\ln P(M)}{\partial M}\Big|_{\text{max. in } w_{exp}(\log M)} = \frac{\partial \ln(m^{-2}\, w_{exp}(\log M))}{\partial M}\Big|_{\text{max. in } w_{exp}(\log M)} \qquad (4)$$

That is, broadening effects cancel at the maximum in the SEC distribution corresponding to a single-exponential $P(M)$.

Although various approximations are involved in its derivation, simulations[23] show that eq 4 is very accurate and robust, including for asymmetric forms of $G(t_{el},M)$ (i.e., when the variance of the band broadening function changes with molecular weight) and with amounts of band broadening significantly exceeding that of modern SEC equipment.

The deconvolution method suggested by Castro et al.[23] uses the fact that a truly single-exponential $P(M)$ can be obtained using free-radical polymerization with excess of chain-transfer agent A. In that case, the instantaneous number MWD is given by eq 3 with:

$$\Lambda = -\frac{k_{tr,CTA}\,[CTA]}{k_p\,[M]} \qquad (5)$$

where $k_{tr,CTA}$ and k_p are the rate coefficients for transfer to chain transfer agent (CTA) and for propagation respectively, and [CTA] and [M] are the concentrations of chain transfer agent and of monomer. If the reaction is stopped at a conversion sufficiently low so that consumption of both monomer and CTA is negligible, then the cumulative and instantaneous distributions will be essentially the same.

The process of finding $G(t_{el},M)$ in any size separation method used here is then as follows. One creates a series of *broad*

"standards" that have exponential $P(M)$s. We do this by free-radical polymerization in the presence of a range of concentrations of transfer agent in sufficient excess, and stopping the reaction at sufficiently low conversion, that the cumulative distribution should have the form given by eqs 3 and 5. Any monomer that does not produce a branched polymer may be used to make the broad "standards", e.g., styrene for organic-phase SEC and styrenesulfonate for aqueous-phase SEC. In the next step, these "standards" are injected into the SEC, and from the resulting data one determines the slopes of the resulting ln $P_{exp}(M)$ at the maximum in $w_{exp}(\log M)$. At this point, the method provides an internal consistency test through eq 4: for a given temperature and type of chain transfer agent, the slope for each "standard" found using eq 4 should be proportional to the concentration of chain-transfer agent used to prepare that sample. Taking the maximum in the SEC distribution also has the advantage of minimizing errors from baseline subtraction.[45]

The next step in the determination of the band broadening function is to choose a sufficiently flexible functional form of $G(t_{el},M)$, e.g., an exponentially modified Gaussian[36] or exponential-Gaussian hybrid (EGH)[46] (the functional form can be made as flexible as desired) and then to least-squares fit the parameters in this function to the observed SEC results over the whole range of broad "standards" . The fitting is through eqs 2 and 3, with the value of Λ for each "standard" obtained from the experimental SEC distribution for that "standard" using eq 4. The least-squares fit involves only a small number of parameters—depending on the form chosen for $G(t_{el},M)$—and it has been shown that convergence is readily obtained in a real system.[31] This results in the parameter values of $G(t_{el},M)$ for the particular functional form and SEC setup. Once $G(t_{el},M)$ is known, then the deconvoluted MWD for *any* polymer sample for that SEC setup can be obtained from the SEC trace for this sample using an appropriate deconvolution method.

Strategy for Synthesis of Broad "Standards". To be of practical use, it is important that the collection of exponential-distribution broad "standards" together cover a wide range of molecular weights for samples of interest, which might be $\sim 10^3-10^6$. This creates a problem, because the addition of a chain transfer agent of course results in a large reduction in molecular weight, and obtaining a truly exponential $P(M)$ requires large excess of chain transfer agent, leading perforce to a sample with relatively low $\bar{M}_n$. To have standards with single-exponential $P(M)$ having high values of $\bar{M}_n$ it is necessary to choose conditions such that the $\bar{M}_n$ in the absence of chain transfer agents is very high. In the present paper, single-exponential high- $\bar{M}_n$ standards were made by free-radical polymerization at low temperatures, minimizing radical—radical termination by using very low concentration of free-radical initiator. Indeed, it was found as part of the present work that, as first done by Stickler and Meyerhoff,[47] the best way of obtaining sufficiently high $\bar{M}_n$ for these standards was to perform the polymerization in the complete absence of added initiator; background radical generation (by spontaneous dissociation in the sample or from background radiation) creates enough radicals over a sufficiently long time period to enable appropriate standards to be obtained. For the present paper, these "standards" were synthesized using styrene as monomer and dodecyl mercaptan (DDM) as chain transfer agent.

For each individual broad "standard" , the value of Λ in eq 3 is then determined using eq 4, i.e., from the slope of the ln P at the maximum in the corresponding $w(\log M)$ without any broadening correction. Where the individual standard is one of a set synthesized at a single temperature with varying [CTA], then a consistency test for this set of "standards" is that Λ should be proportional to [CTA]. $G(t_{el},M)$ is then determined by choosing a suitably flexible functional form and least-squares fitting the parameters in this function to the entire set of "standards" using eq 2, with $P(M)$ given by eq 3 with the value of Λ found as just described.

Given $G(t_{el},M)$, the entire data set is then tested for consistency by deconvoluting each $w_{exp}(\log M)$ using eq 2 and an appropriate deconvolution algorithm; the Ishige algorithm,[48] a variant of the Picard method,[49] was chosen here for its simplicity. The resulting $P(M)$ for the single-exponential "standards" should all have a linear ln P.

A final test is then carried out by synthesizing what should be another set of polymer samples with linear ln P but with a different monomer, in this case using methyl methacrylate (MMA) with DDM. The $G(t_{el},M)$ found as above is then used to deconvolute each $w_{exp}(\log M)$ of each sample, using universal calibration:[7] i.e., converting the molecular weight of polystyrene into a hydrodynamic volume using the Mark—Houwink relationship with the Mark—Houwink parameters for polystyrene, and then finding the molecular weight of polyMMA with the same hydrodynamic volume using the Mark—Houwink parameters for polyMMA. The resulting deconvoluted polyMMA $P(M)$ should then have linear ln P. This then provides a further consistency test for the methodology.

Experimental Section

Chemicals. Styrene (Aldrich) was run through a *tert*-butyl catechol inhibitor removal column (Aldrich), distilled at 40 mbar and 60 °C, and finally was bubbled with oxygen and stored at 5 °C for up to 2 weeks prior to use. MMA (Aldrich) was run through a hydroquinone monomethyl ether inhibitor removal column (Aldrich), distilled at 35 mbar and 35 °C, bubbled with oxygen, and stored for up to 3 d at 5 °C. DDM was obtained from Aldrich. High-pressure liquid chromatography grade (99.9+%) toluene was obtained from Lab Scan. AIBN (2,2′-azodiisobutyronitrile) was dissolved in methanol at ~40 °C, filtered, and recrystallized by cooling with ice. High-purity argon was obtained from BOC gases.

Synthesis of Broad Standards. Reaction times, initiator concentrations, and concentrations of each component were chosen based on estimates calculated using classical free-radical polymerization kinetics at low conversion, to ensure that (a) chain stoppage was dominated by transfer to chain transfer agent and that (b) a sufficient amount of polymer would be formed for characterization purposes, (c) while at the same time ensuring that changes in monomer and DDM concentrations were sufficiently small over the chosen reaction time to be treated as constant in eq 5. Hydroquinone was used as an inhibitor. Details for each run are given in Table 1. Polymerization was done in a conventional Schlenk line. First, 50 mL reaction flasks equipped with a vacuum stopcock were charged with toluene (as the solvent), monomer, initiator, and DDM. The charged flask was first flushed with Ar, then subjected to three freeze—thaw cycles and (except for the high-polystyrene samples) then brought to the reaction temperature. At the end of the chosen reaction time, 1 mg of hydroquinone was added to inhibit further reaction. Conversions were measured gravimetrically.

SEC. SEC traces were obtained on a Shimadzu SEC system with a Shimadzu RID-10A differential refractive index detector for polyMMA and a Shimadzu SPD-10A UV—vis detector set to record at 254 nm for polystyrene (the UV detector gives less noise than the DRI detector, so was preferred for polystyrene, but cannot be used for polyMMA). The column set consisted of two Polymer Labs PLgel Mixed-B Columns, with the column oven at 40 °C. The eluent was tetrahydrofuran (THF, 99%, Unilab) with a flow rate of 1.0 mL min^{-1}. The injection used was 50 μL in a 100 μL loop. The recording time was set to 35 min. Calibration was with 15 polystyrene standards (Polymer Standards Services), ranging in

Table 1. Reaction Conditions for Synthesis of Broad Polystyrene "Standards" and of PolyMMA Used for Testing the Consistency of the Whole Procedure[a]

sample number	[DDM]/mM	$x_{conv,M}$	$x_{conv,CTA}$
Styrene (0.5 w/w Fraction in Toluene), 70 °C, 0.1 mM AIBN Initiator, 8 h Reaction Time			
LMW1	2.15	0.0053	0.086
LMW2	0.60	0.0065	0.10
LMW3	2.54	0.0083	0.13
LMW4	0.779	0.0045	0.074
LMW5	2.15	0.0043	0.071
LMW6	1.41	0.0094	0.15
Styrene (0.5 w/w Fraction in Toluene), 25 °C, No Added Initiator, 6 d Reaction Time			
HMW1	0.459	0.0038	0.0076
HMW2	0.396	0.0029	0.0058
HMW3	5.25	0.0045	0.0090
MMA (0.5 w/w Fraction in Toluene), 60 °C, 0.1 mM AIBN Initiator, 3 h Reaction Time			
MMA1	5.4	0.022	0.0060
MMA2	1.78	0.018	0.0049
MMA3	13.1	0.042	0.0115

[a] $x_{conv,M}$ and $x_{conv,CTA}$ refer to the fraction conversion of monomer and of CTA respectively, the former measured by gravimetry and the second calculated from the chain-transfer constant.

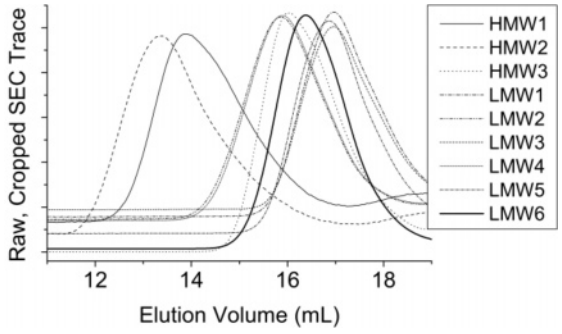

Figure 1. Raw SEC traces from polystyrene broad standards with varying temperatures, initiator amounts and amounts of DDM (Table 1).

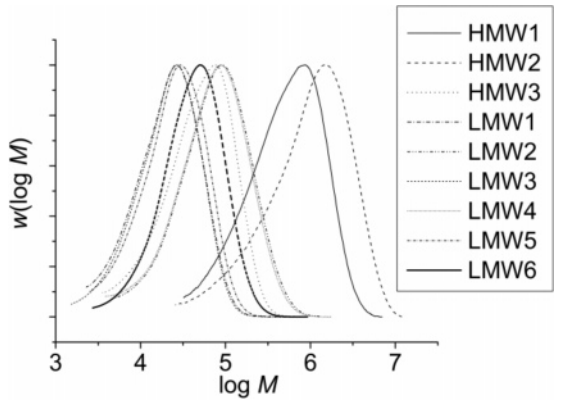

Figure 2. SEC distributions from polystyrene broad standards, processed from data of Figure 1.

molecular weight from 1820 to 5.15×10^6. A standardized method was used to correct for the baseline and to crop SEC traces. The baseline was drawn as close to each end of the chromatogram as possible, ensuring that it went through the middle of the noise as best possible on each side of the chromatogram. If there was a nonpolymer peak on the chromatogram, the polymer peak was cropped just inside the trough between the two peaks. Results for raw SEC traces and SEC distributions for the broad polystyrene "standards" are shown in Figures 1 and 2 (showing incidentally that one of the recipes at 25 °C designed to produce a high molecular weight in fact produced a sample with an average

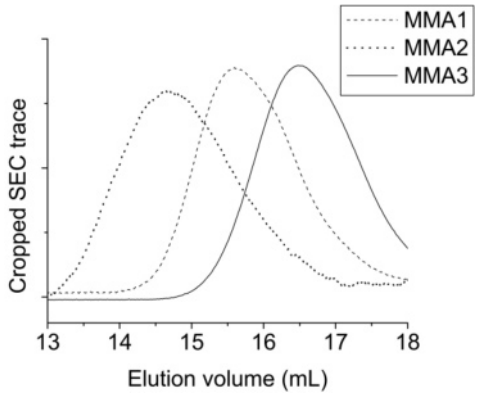

Figure 3. Raw SEC traces from polyMMA samples with various amounts of DDM (Table 1).

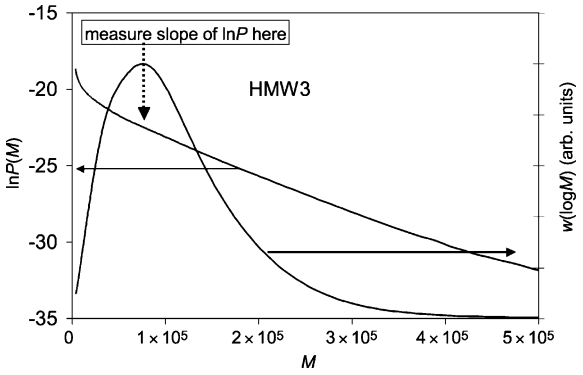

Figure 4. Typical data used for finding the slope of the true ln *P* using the theorem of eq 4. The data are for run HMW3. As expected, the undeconvoluted ln *P*(*M*) is concave-up.

molecular weight in the same range as those designed to produce lower molecular weight), and the raw SEC traces for polyMMA in Figure 3. Raw SEC data are presented in terms of elution volume, which is proportional to elution time.

The SEC distributions $w_{exp}(\log M)$ are then converted to "undebroadened" (i.e., from the experimental SEC distribution without broadening correction) $P_{exp}(M)$ using eq 1, and the value of Λ for each ln *P* then found as the slope of ln P_{exp} at the value of *M* corresponding to the maximum in $w_{exp}(\log M)$, as illustrated in Figure 4, i.e. using the theorem of eq 4.

Consistency Test of Dependence on [DDM]. One of the implications of the theorem on the cancellation of band-broadening effects at the maximum in $w_{exp}(\log M)$, eq 4, and for eqs 3 and 5 to be applicable, is as follows. For data with different concentrations of chain-transfer agent (at a given temperature), the slope of the experimental (i.e., broadened) ln *P* taken at the value of *M* corresponding to the maximum in $w_{exp}(\log M)$ should be proportional to chain transfer agent concentration. The results of this consistency test are shown in Figures 5, 6, and 7. It can be seen that these data can be adequately fitted by a straight line, consistent with the supposition.

A further consistency test is if the intercept of these data give the literature value of the transfer constants to monomer (k_{tr}/k_p) and to DDM: in the limit of low initiator concentration, a more complete version of eq 5 is that the slope is given by $\Lambda = -(k_{tr}/k_p + k_{tr,CTA}[CTA]/k_p[M])$. The intercepts of Figures 5−7 are respectively $(-3.1 \pm 0.4) \times 10^{-7}$, $(+3.8 \pm 3.9) \times 10^{-7}$ and $(+2.8 \pm 2.9) \times 10^{-6}$. This intercept should be the negative quantity $-k_{tr}/(M_0 k_p)$, where M_0 = molecular weight of monomer. Clearly no conclusions can be drawn from the (positive!) intercepts for styrene at 25 °C and for MMA at 70 °C because of the high uncertainty, and because these data sets contain only three concentrations of DDM. The intercept for styrene at 70 °C is in acceptable accord with the corresponding value calculated from the literature transfer constant for styrene,[50] which is -5.8×10^{-7}.

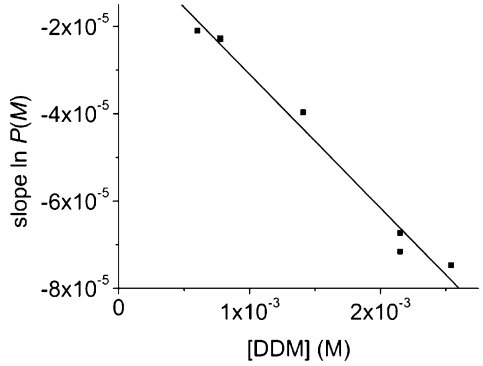

Figure 5. Dependence of slope of (broadened) ln *P* at *M* corresponding to maximum in $w_{exp}(\log M)$ on concentration of DDM, for styrene at 70 °C.

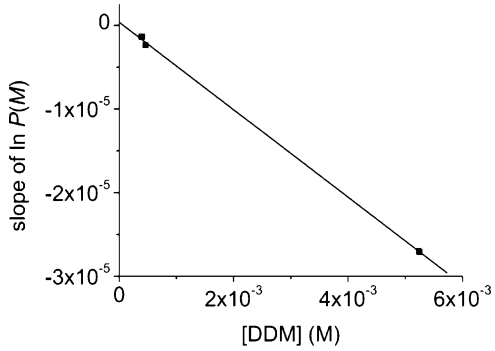

Figure 6. Dependence of slope of (broadened) ln *P* at *M* corresponding to maximum in $w_{exp}(\log M)$ on concentration of DDM, for styrene at 25 °C.

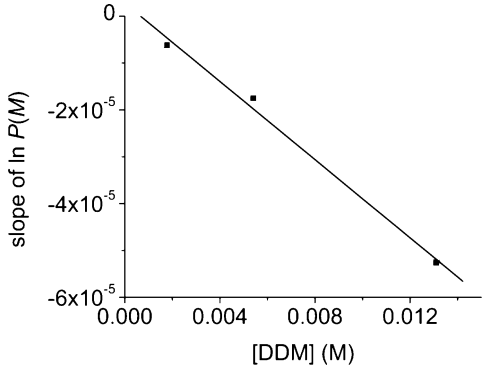

Figure 7. Dependence of slope of (broadened) ln *P* at *M* corresponding to maximum in $w_{exp}(\log M)$ on concentration of DDM, for MMA at 70 °C.

The slopes of these plots give the transfer constant to DDM, $k_{tr,CTA}/k_{p;}$ these slopes yield the following values for the transfer constant: 12 ± 1 (styrene/DDM, 70 °C), 2.0 ± 0.2 (styrene/DDM, 25 °C) and 0.27 ± 0.02 (MMA/DDM, 70 °C). The only corresponding reliable data in the literature are for styrene/DDM at 70 °C,[51] viz., 19 (no uncertainty being quoted); the consistency is taken to be acceptable.

Determining the Band-Broadening Function

To solve Tung's dispersion equation, eq 2, it is necessary to assume a functional form for the broadening function $G(t_{el},M)$. It is convenient[23,31] to change the integration variable in eq 2 from molecular weight M to a time variable t_c given by the SEC calibration curve $\ln\tilde{M}(t_c)$; this is the functional form of the conventional calibration curve obtained from a plot of the maxima in *narrow* standards of given molecular weight M against elution time. Equation 2 is thus expressed in terms ofthe corresponding broadening function $G(t_{el},t_c)$:

$$S(t_{el}) = \int_0^\infty G(t_{el},t_c)\, W(\tilde{M}(t_c))\, dt_c \qquad (6)$$

To capture the asymmetric nature of the spreading,[19] the functional form of is chosen here as the EGH function:[46]

$$G(t_{el},t_c|\sigma,\tau) = \left\{ \begin{array}{ll} \dfrac{1}{\Omega}\exp\left(\dfrac{-(t_{el}-t_c)^2}{2\sigma^2+(t_{el}-t_c)\,\tau}\right), & 2\sigma^2+(t_{el}-t_c)\,\tau > 0 \\ 0, & 2\sigma^2+(t_{el}-t_c)\,\tau \le 0 \end{array} \right\} \qquad (7)$$

σ describes the time range over which a monodisperse sample is expected to elute, while τ determines the extent to which the signal is skewed; this functional form allows for the variance of the spreading to change with molecular weight. Other functional forms are possible, including the simple expedient of allowing σ and τ to vary with molecular weight,[31] but as will be seen later, the joint confidence intervals obtain from fitting the present set of data are such that such extensions are not justified in the present work. The normalization constant Ω is given by[31]

$$\Omega = \int_\infty^{-\infty} G(t_{el},t_c)\, dt_c \qquad (8)$$

The parameters σ and τ are determined by fitting the theoretical unbroadened signal, S_{th}, which is given by eq 3 with the value of Λ obtained using eq 4, to experimental SEC data, viz., an SEC trace S_{exp}. This fit is by minimizing the value of χ^2 defined as

$$\chi^2(\sigma,\tau) = \sum_{j=1}^{N} \left(S_{exp}(t_{el_j} \mid \Lambda) - S_{th}(t_{el_j} \mid \sigma,\tau,\Lambda)\right)^2 \qquad (9)$$

where t_{el_j} is the set of elution times over which the experimental data are collected. Because of poor signal-to-noise ratio away from the peak of $w(\log M)$, a single SEC trace is unlikely to be an adequate description of the broadening in the SEC system over a useful range of molecular weight. To overcome this problem, all transfer-dominated systems for styrene with different values of Λ were minimized together as a global sum of squares with respect to σ and τ over the whole range of molecular weights.

The technique chosen to minimize χ^2 was the Powell direction set method.[52] The experimental SEC distribution of each broad "standard" is plotted in Figure 8, alongside the corresponding fitted S_{th} for each standard from the least-squares fit. The broadening function is characterized by $\sigma = 0.411$ min and $\tau = -2.93 \times 10^{-2}$ min. The experimental data are well fitted for the low molecular weight standards, but the high molecular weight samples show poorer fit; however the fit is still of sufficient quality to proceed, since the discrepancies do not appear systematic, and may be due to experimental error, or poor signal-to-noise ratio. An area for future development is to use alternative functional forms for G to see if this fit could be improved.

The shape of χ^2 near the minimum determines the range over which the parameters σ and τ are expected to vary between similar samples. To determine this, the 95% confidence interval was constructed, as the set of (σ, τ) where the value of χ^2 is 5% greater than that at the minimum. This joint confidence interval is given in Figure 9, and suggests that the error in

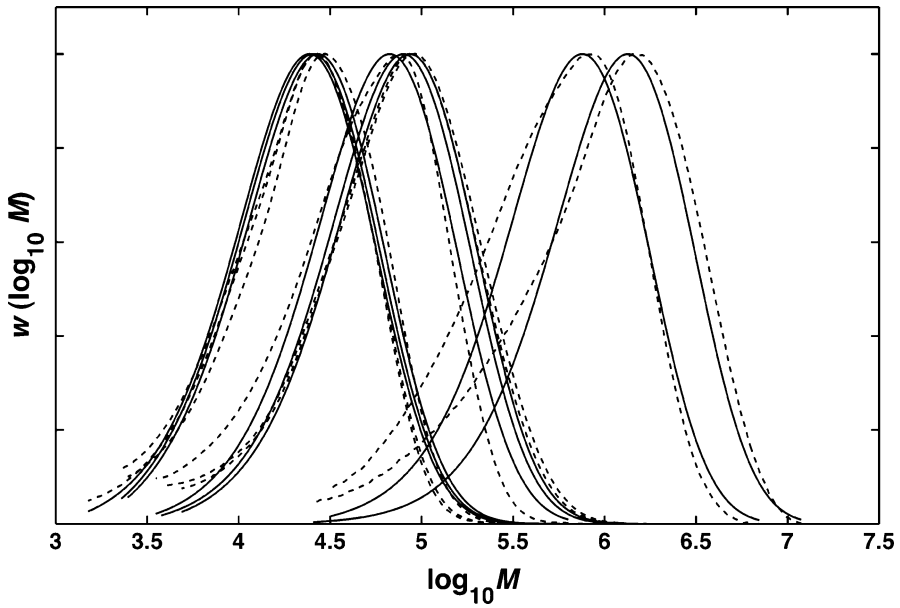

Figure 8. Experimental SEC distributions (broken lines), and the fitted broadened SEC distributions from global least-squares fitting of the broadening function *G* (solid lines).

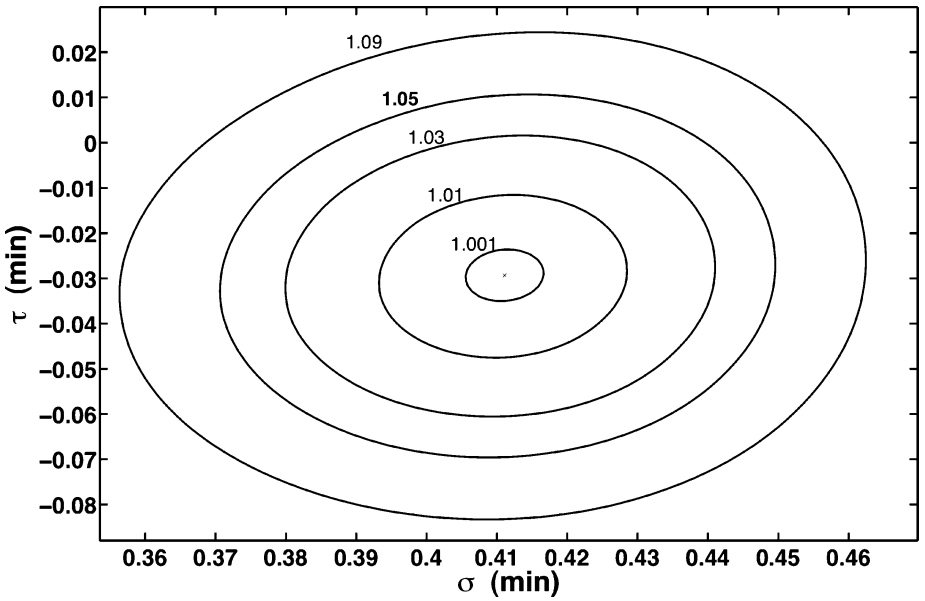

Figure 9. Behavior of the global χ^2 function near the minimum, used to obtain the 95% joint confidence interval for the broadening function parameters σ and τ.

calculating σ is less than 10%, while the range of variation in τ is quite broad, although it is likely that its numerical value is negative. The contour lines are not exactly along the *x* and *y* axes, indicating that errors in σ and τ are correlated. It is noted that the value of τ, being significantly less than zero within this joint confidence interval, suggests that broadening width varies significantly with molecular weight, as also seen from studies of ultranarrow standards.[19]

In principle it is possible to compare the values of σ and τ with those reported by Baumgarten et al.,[19] who used a similar set of columns, and who deduced molecular weight dependences of these quantities (although no joint confidence interval of these values was provided). However, in practice such comparison is hard because broadening depends not only on the column but also flow rate, column temperature and other parameters specific to a particular SEC setup. The only meaningful way to compare results from different set-ups is to compare the distributions obtained by deconvoluting the same sample in each setup.

Deconvolution Procedure and Results. Given an SEC trace and the broadening function *G*, the Ishige algorithm[48] was used to invert the axial dispersion relation, eq 2, to obtain the true weight distribution. In the present notation, this algorithm is as follows for the *i*th iteration:

$$W'_i(t_{el}) = S_{i-1}(t_{el}) \tag{10}$$

$$S_i(t_{el}) = \int_0^\infty G(t_{el},t_c)\, W'_i(t_{el})\, dt_c \tag{11}$$

$$W'_{i+1}(t_{el}) = W'_i(t_{el}) + \frac{S_{i-1}(t_{el}) - S_i(t_{el})}{S_i(t_{el})}\, W'_i(t_{el}) \tag{12}$$

Iteration is continued until a set convergence criterion is satisfied, which in the present case is that the least-squares

difference in the signal-weighted weight distribution is less than a prescribed tolerance. That used here is the tolerance given by

$$\text{tolerance} = \frac{\int_0^\infty |S_i(t_{el}) - S_{i-1}(t_{el})|\, dt_{el}}{\int_0^\infty S_i(t_{el})\, dt_{el}} \qquad (13)$$

When this algorithm is applied to raw SEC data, experimental noise was found to be amplified, as seen in Figure 10, where the prescribed tolerance was set as 10^{-3}. The ln P plot has the correct linear trend with randomly scattered noise about the trend, except at very low M.

This figure and extensive calculations of this type show that small, rapid oscillations in the SEC trace lead to large oscillations in the inverted solution after 150 iterations and failed convergence at 0.1%. It was deemed necessary to determine the stability of the Ishige algorithm with respect to oscillations in the input trace. The stability was tested on a simulated trace with exponent $\Lambda = -2.383 \times 10^{-5}$ and EGH broadening function G with $\sigma = 0.411$ min and $\tau = -2.93 \times 10^{-2}$ min (the values obtained using the present polystyrene standards). Small perturbations were applied to the SEC trace to test whether the algorithm converges to the true weight distribution. The perturbations were introduced in the following way

$$S_{pert}(\log M) = S_{unpert}(\log M)\,(1 + \delta S(\log M)) \qquad (14)$$

where $\delta S(\log M) = \Gamma \sin(\omega(\log M))$. The quantity Γ determines the magnitude of the perturbation, while the sine term allows the frequency ω of the perturbation to vary, thus simulating noise. The extent of smoothing necessary to remove instability was determined by the value of ω above which the inversion led to a noisy solution. The results indicate that the Ishige algorithm introduces errors that prevent convergence to a tolerance of $\sim 10^{-6}$ or less. This is of concern, since the algorithm converges to the correct solution initially. As the algorithm is iterated further to improve the tolerance, errors are introduced and divergence from the correct solution is seen. This may arise from the Ishige algorithm itself, since the method gives approximately the correct solution before it diverges. It is well-known that the solution of this type of integral equation is very hard to implement numerically; more powerful algorithms should hopefully solve these problems for the particular case of SEC data.

Despite the problem with the numerical convergence of the algorithm, perturbations outlined above were applied to the test SEC trace. These perturbations reveal the effect of experimental noise on the convergence and behavior of the solutions. These results are only semiquantitative due to the problems with convergence, but indicate that the solution is not destroyed with slow oscillations where $\omega = 3$, and the correct ln P plot is obtained. Furthermore, perturbations with $\omega \geq 9$ amplify the noise significantly. Smoothing procedures were found to mitigate this noise amplification problem, but can introduce artifacts. It was therefore decided to avoid smoothing and to let the tolerance vary, to see if stable solutions can be found. The results of applying this procedure to experimental data are given in the following subsection.

Deconvolution of Broad "Standards". The deconvolution algorithm was first applied to the broad "standards" used in determining the broadening function. Results are shown in Figures 11 (lower molecular weight polystyrene), 12 (intermediate molecular weight polystyrene), and 13 (higher molecular weight polystyrene). Data are presented as both $w(\log M)$ and ln $P(M)$, for the undebroadened experimental data, and debroadening distributions obtained with two tolerances (0.05 and 0.01) in the debroadening procedure.

The debroadened $w(\log M)$ are narrower than the undebroadened ones: a trivial result because convolution always produces a broader distribution. There are three significant observations from these figures.

- The slope of the experimental and debroadened ln P curves at the maximum in $w(\log M)$ are virtually the same, thereby supporting the applicability and accuracy of eq 4.
- The tighter tolerance produces distributions which are similar to those produced with a looser tolerance, except that in some cases the tighter tolerance leads to distributions showing structure at low molecular weights. From the model calculations above, this structure may an artifact of the noise amplification to which the Ishige algorithm is prone (a phenomenon also observed by Castro et al.[31]), although as discussed below it cannot be ruled out that the shoulder seen clearly with the tighter

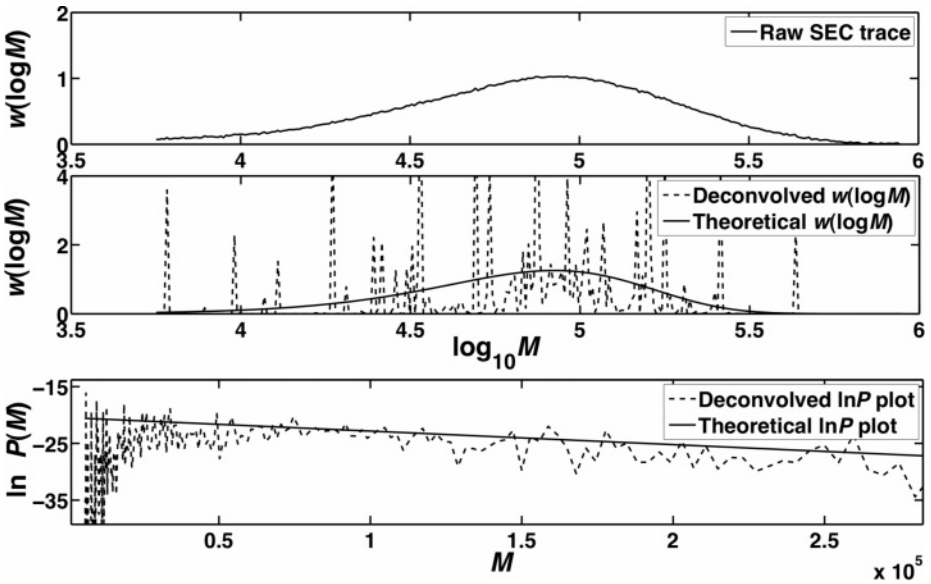

Figure 10. Noise in the deconvolution process. Top panel: ("undebroadened", i.e., from the experimental SEC distribution without broadening correction) SEC distribution $w_{exp}(\log M)$. Middle panel: true distribution $w(\log M)$ (i.e., calculated from the appropriate single-exponential $P(M)$ (solid line) and the results of the deconvolution of the noisy data series. Bottom panel: the true slope and the ln $P(M)$ from deconvolution.

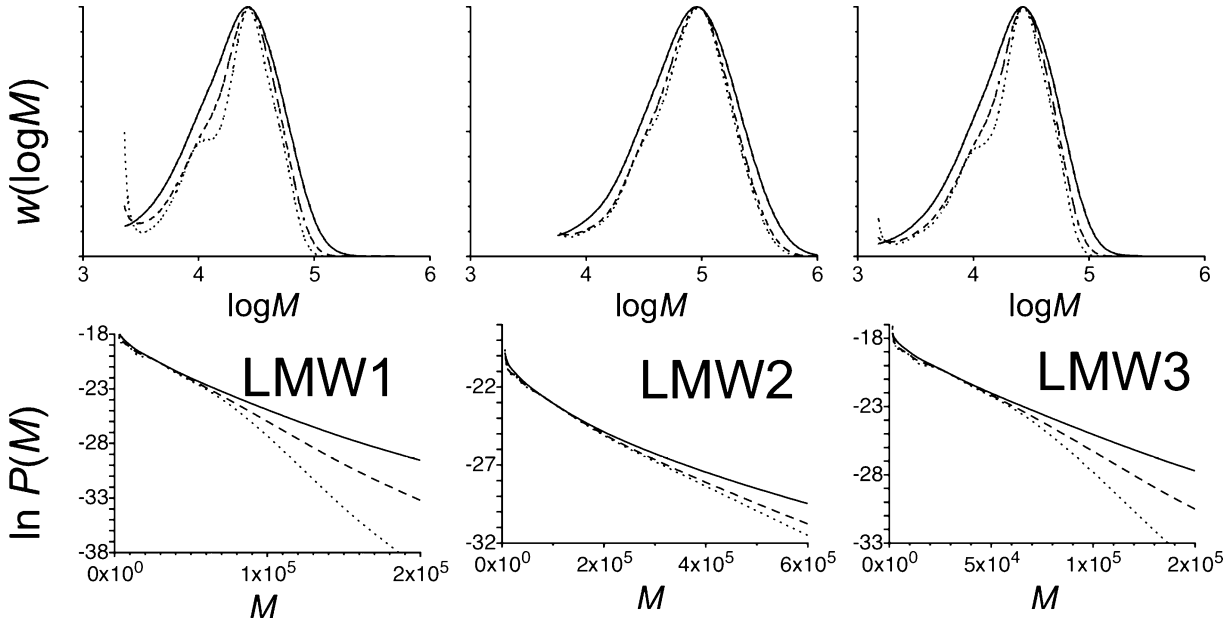

Figure 11. Deconvoluted $w(\log M)$ and ln P plots for the lower molecular weight polystyrene samples of Table 1. Key: full line, undebroadened experimental data; long dashes, debroadened with tolerance 0.05; short dashes, debroadened with tolerance 0.01.

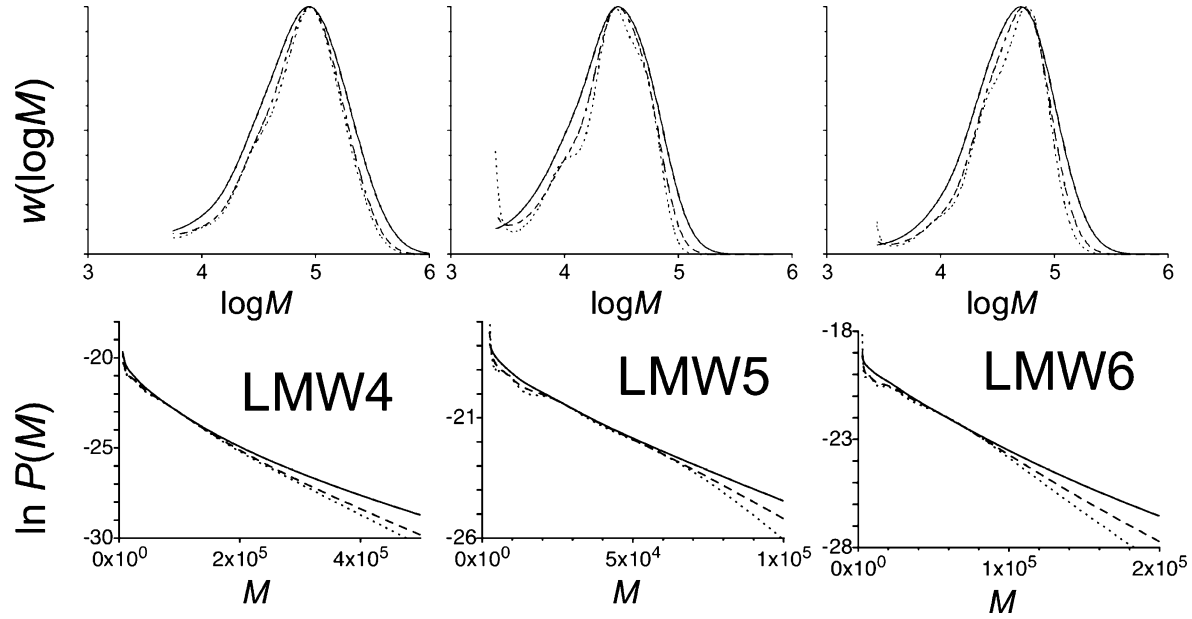

Figure 12. Deconvoluted $w(\log M)$ and ln P plots for the intermediate molecular weight polystyrene samples of Table 1. Key: full line, undebroadened experimental data; long dashes, debroadened with tolerance 0.05; short dashes, debroadened with tolerance 0.01.

tolerance is in fact genuine. That low-M noise is amplified is not unexpected, because of the relation between $P(M)$ and $w(\log M)$, eq 1: it can be seen that dividing the experiment SEC MWD, $w(\log M)$, by M^2 will give greater emphasis to experimental error/noise at lower M (arising mainly from baseline subtraction and low signal).

• At a tolerance of 0.05, when the deconvoluted distribution seems to be always well behaved, the deconvoluted ln P is always more linear than that obtained from the undebroadened (experimental) $w_{exp}(\log M)$ using $P_{exp}(M) = M^{-2}\, w_{exp}(\log M)$. This linearity holds over the range where the parent experimental (broadened) distribution has reasonable signal-to-noise.

The reason that the shoulder appearing in $w(\log M)$ at tighter tolerances may in fact be real is that it could possibly be a component resulting from termination. This result is seen most strongly with highest amounts of chain transfer agents, when the growing radicals are short and hence more mobile, and thus having an increased termination rate coefficient.[53−57] However, as tolerance is reduced below that used in Figure 11, this shoulder, while still present over the same range of molecular weights, is accompanied by other, clearly artifactual, peaks which change with tolerance.

From these results, it is concluded that the deconvoluted results are all consistent with the applicability of the deconvolution procedure which is the subject of this paper. There is clearly a problem with divergence (noise amplification) of the deconvolution procedure as the tolerance is made tighter. This is a real difficulty, because a true solution to eq 2 should converge to a stable distribution as tolerance is made increasingly small. That is, although the results of applying the Ishige algorithm at moderate but not very tight tolerance are physically reasonable, they cannot be a truly accurate solution of the deconvolution equation. Alternative deconvolution methods to the Ishige algorithm[19] may eliminate this problem in the future.

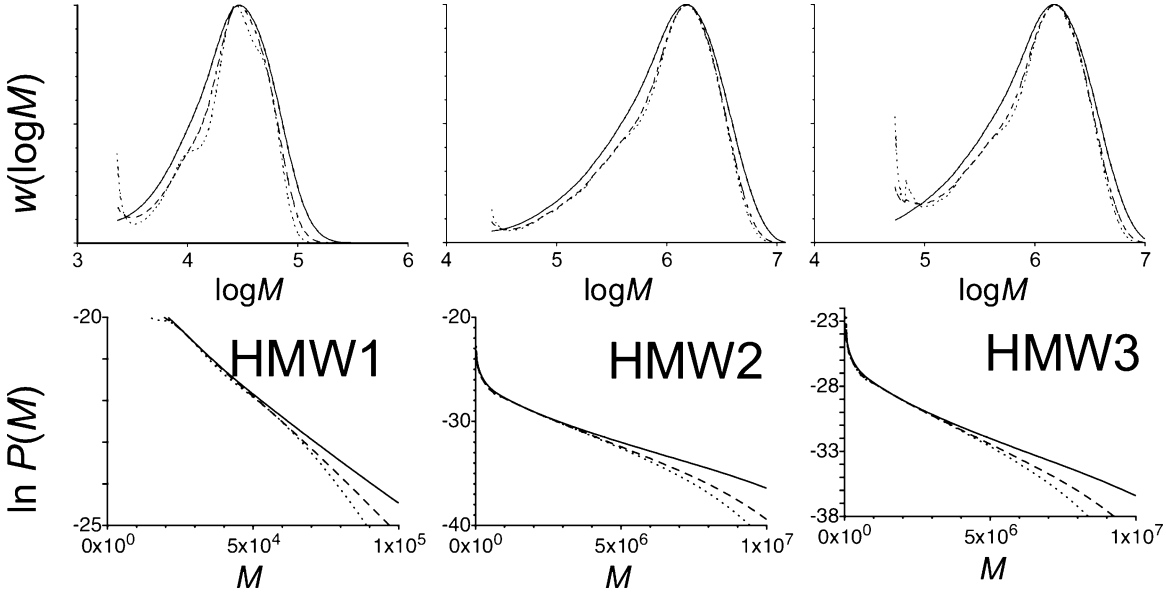

Figure 13. Deconvoluted $w(\log M)$ and $\ln P$ plots for the higher molecular weight polystyrene samples of Table 1. Key: full line, undebroadened experimental data; long dashes, debroadened with tolerance 0.05; short dashes, debroadened with tolerance 0.01.

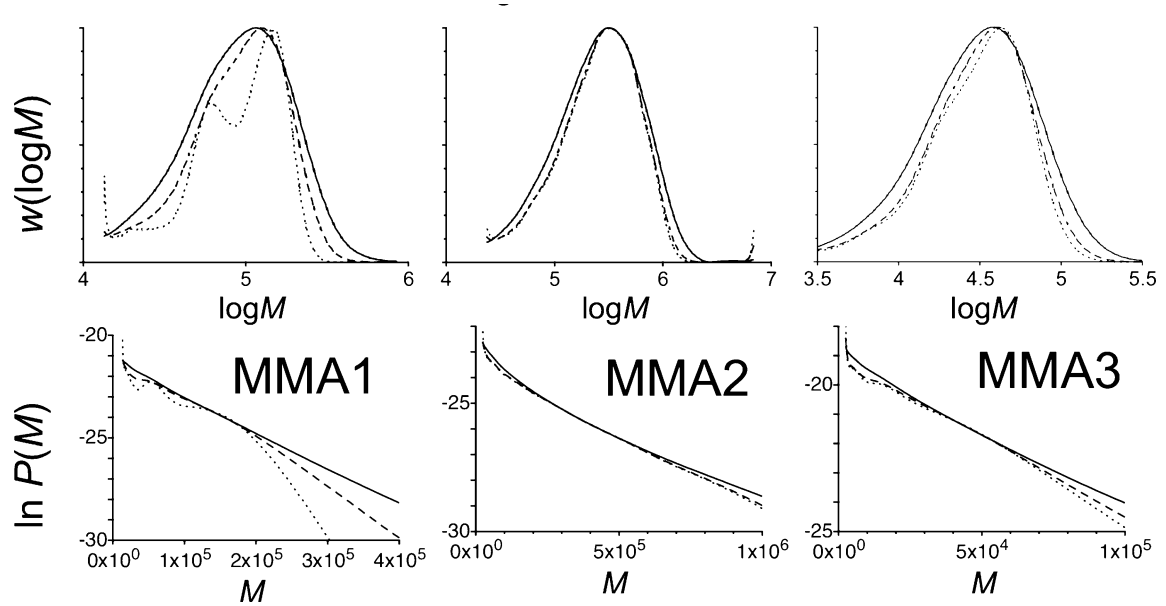

Figure 14. Deconvoluted $w(\log M)$ and $\ln P$ plots for the intermediate molecular weight poly(MMA) samples of Table 1. Key: full line, undebroadened experimental data; long dashes, debroadened with tolerance 0.05; short dashes, debroadened with tolerance 0.01.

Deconvolution of Poly(methyl methacrylate) Data. The deconvolution method was then used to correct for broadening in the pMMA samples obtained with excess of DDM (Table 1), which would be expected to have a linear debroadened ln *P*. Universal calibration and Mark−Houwink-Sakaruda parameters *K* and *a* were used for this purpose: $K = 11.4 \times 10^{-5}$ and 9.44×10^{-5} dL g^{-1} for polystyrene and pMMA respectively, and $a = 0.716$ and 0.719 for polystyrene and pMMA respectively.[58,59] As shown in Figure 7, the Λ obtained from the deconvolution was proportional to the amount of transfer agent (DDM). Debroadened distributions are shown in Figure 14.

These results show that the ln *P* for the looser tolerance are linear over an acceptable range (in particular, over the range of *M* where there is significant SEC signal), as expected. The general behavior is similar to that seen above for polystyrene. However, the results for the lowest molecular weight sample (MMA1) show a shoulder at lower molecular weight, visible also in the experimental undebroadened distribution; the deconvoluted distribution for MMA1 clearly becomes unstable with tighter tolerance. As for the styrene results, the shoulder may in fact be a real effect arising from termination, but this is certainly not a firm conclusion.

The fact that the polyMMA results deconvoluted using the broadening function obtained from polystyrene show a linear ln *P* supports the general applicability of the deconvolution procedure developed here.

Conclusions

This paper gives the experimental and computational implementation of the method for correcting SEC data for band broadening suggested by Castro et al.[23] This method uses broad standards which have been synthesized under conditions such that the number molecular weight distribution is expected to be a single exponential. Such "standards" can readily be

synthesized using free-radical polymerization with appropriate amounts of chain transfer agent. The method uses the simple result that, for such single-exponential distributions, band-broadening corrections cancel (to a high degree of accuracy) in the slope of a plot of ln(number distribution), ln $P(M)$, provided that this slope is taken at the molecular weight corresponding to the maximum in the experimental SEC distribution (without any correction for band broadening). Because the slope of this plot should be proportional to the concentration of added chain transfer agent for a set of runs wherein only this quantity is changed, the method provides an internal consistency test of the validity of the foregoing hypothesis about the MWD of these broad standards. The broadening function can then be ascertained for a particular SEC setup by least-squares fitting the calculated SEC distribution from the "theoretical" exponential $P(M)$ to that observed experimentally, with a wide range of broad standards; the fit yields the parameters in an appropriate functional form for the broadening function. Given this function, standard numerical techniques are used to solve the convolution equation for a new sample, yielding the true distribution, corrected for band broadening, from an observed SEC distribution.

This methodology has been applied by synthesizing a series of broad polystyrene "standards" using appropriate values of the amounts of added chain transfer agent (dodecyl mercaptan), of temperature and of initiator concentrations. This requires "standards" with MWDs which should have an exponential $P(M)$ whose $\bar{M}_n$ values cover a sufficiently wide range so as to be useful for deconvoluting samples with higher molecular weight. The high $\bar{M}_n$ "standards" were synthesized at room temperature in the absence of added initiator, with the very slow spontaneous radical generation ensuing under these conditions ensuring minimal radical−radical termination and thus optimal conditions for a transfer-dominated exponential $P(M)$. All these "standards" satisfied the internal consistency test.

SEC traces for these "standards" were used to determine the parameters for an exponential Gaussian hybrid functional form for the band-broadening function. The methodology was then tested by using these parameters to debroaden another set of samples, this time of poly(methyl methacrylate), again synthesized under conditions such that an exponential $P(M)$ should have been obtained. The debroadened molecular weight distributions for these polyMMA samples indeed had the expected single-exponential form over an appropriate range of molecular weight. This provides a proof of principle that band broadening may be corrected using the new methodology.

A major problem with the present implementation of the deconvolution procedure is the deconvolution algorithm, which amplifies noise when the tolerance becomes very tight: this effect is seen in model simulations with synthetic noise as well as in application to experiment. While what seem to be well behaved solutions are obtained for less severe tolerances, the fact that the solution does not converge as tolerance is tightened beyond a certain range implies that a truly converged, accurate, solution of the broadening equation has not been found with the algorithm used here. For any given case, the reasonableness of the solution over the range of stable tolerance can be examined by simulations with synthetic noise, but nevertheless, this situation is unsatisfactory. There is certainly room for improvement in the methodology through an improved deconvolution algorithm, such as a Newton−Raphson method[49] or maximum entropy.[60]

It is noted that the numerical instability in deconvolution can always be avoided by using the $G(t_{el},M)$ obtained as described here and comparing the *convoluted* SEC distribution for an assumed form of $P(M)$ with that observed experimentally. While this is less satisfactory than deconvolution (e.g., it cannot reveal unambiguously if an experimental ln $P(M)$ is linear), it completely avoids the issue of numerical instability.

With improved numerical methods for solving the deconvolution equation, this new treatment will prove of considerable use in situations where fine detail is needed from SEC data: for example, if the precise shape of the observed distribution is consistent with a particular mechanistic hypothesis. Although the implementation, testing, and verification of the methodology in the present paper has employed UV and DRI detectors and a linear polymer, the methodology will prove equally useful for more complex polymers and detectors, e.g., branched polymers and in-line viscometric detection.[11] The same methodology is also applicable to other size-separation techniques such as field-flow fractionation.

Acknowledgment. We gratefully acknowledge the assistance of Dr Hank de Bruyn in synthetic work. The financial support of a Discovery and LIEF Grants from the Australian Research Council are gratefully acknowledged, as is an Australian Postdoctoral Fellowship (AAGW). The Key Centre For Polymer Colloids was established and supported by the Australian Research Council's Research Centres Program.

References and Notes

(1) Trathnigg, B., in *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; Wiley: Chichester, U.K., 2000; pp 8008−8034.
(2) Chang, T.; Lee, H. C.; Lee, W.; Park, S.; Ko, C. *Macromol. Chem. Phys.* **1999**, *200*, 2188−2204.
(3) Haddad, P. R.; Jackson, P. E. *Ion Chromatography - Principles and Applications*; Elsevier: Amsterdam, Oxford, U.K., New York, and Tokyo, 1990.
(4) Cottet, H.; Simo, C.; Vayaboury, W.; Cifuentes, A. *J. Chromatogr. A* **2005**, *1068*, 59−73.
(5) Giddings, J. *Science* **1993**, *260*, 1456−1465.
(6) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D.; Ziolliox, J.-G. *J. Chim. Phys.* **1966**, *63*, 1507−1514.
(7) Gallot-Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753−759.
(8) Hamielec, A. E.; Ouano, A. C.; Nebenzahl, L. L. *J. Liq. Chromatogr.* **1978**, *1*, 527−554.
(9) Kostanski, L. K.; Keller, D. M.; Hamielec, A. E. *J. Biochem. Biophys. Methods* **2004**, *58*, 159−186.
(10) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(11) Gaborieau, M.; Gilbert, R. G.; Gray-Weale, A.; Hernandez, J. M.; Castignolles, P. *Macromol. Theory Simul.* **2007**, *16*, 13−28.
(12) Shortt, D. W. *J. Liq. Chromatogr.* **1993**, *16*, 3371−3391.
(13) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552−569.
(14) Schnöll-Bitai, I.; Mader, C. *J. Chromatogr. A* **2006**, *1137*, 198−206.
(15) Lichti, G.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A:* **1980**, *18*, 1297−1323.
(16) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133−1137.
(17) Watts, C. J. C.; Gray-Weale, A.; Gilbert, R. G. *Biomacromolecules* **2007**, *8*, 455−463.
(18) van Berkel, K. Y.; Russell, G. T.; Gilbert, R. G. *Macromolecules* **2005**, *38*, 3214−3224.
(19) Baumgarten, J. L.; Busnel, J. P.; Meira, G. R. *J. Liq. Chromatogr. Relat. Technol.* **2002**, *25*, 1967−2001.
(20) Popovici, S.-T.; Kok, W. T.; Schoenmakers, P. J. *J. Chromatogr. A* **2004**, *1060*, 237−252.
(21) Berger, K. C. *Makromol. Chem.* **1975**, *176*, 399−410.
(22) Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2000**, *33*, 5111−5115.
(23) Castro, J. V.; van Berkel, K. Y.; Russell, G. T.; Gilbert, R. G. *Aust. J. Chem.* **2005**, *58*, 178−181.
(24) Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 375−385.
(25) Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 1271−1283.
(26) Tung, L. H.; Moore, J. C.; Knight, G. W. *J. Appl. Polym. Sci.* **1966**, *10*, 1261−1270.
(27) Netopilik, M. *J. Chromatogr. A* **2006**, *1133*, 95−103.

(28) Tung, L. H.; Runyon, J. R. *J. Appl. Polym. Sci.* **1969**, *13*, 2397−2409.
(29) Morell, M. K.; Samuel, M. S.; O'Shea, M. G. *Electrophoresis* **1998**, *19*, 2603−2611.
(30) O'Shea, M. G.; Samuel, M. S.; Konik, C. M.; Morell, M. K. *Carbohydr. Res.* **1998**, *307*, 1−12.
(31) Castro, J. V.; Ward, R. M.; Gilbert, R. G.; Fitzgerald, M. A. *Biomacromolecules* **2005**, *6*, 2260−2270.
(32) Castro, J. V.; Dumas, C.; Chiou, H.; Fitzgerald, M. A.; Gilbert, R. G. *Biomacromolecules* **2005**, *6*, 2248−2259.
(33) Lee, H. C.; Chang, T.; Harville, S.; Mays, J. W. *Macromolecules* **1998**, *31*, 690−694.
(34) Lee, H. C.; Lee, W.; Chang, T.; Yoon, J. S.; Frater, D. J.; Mays, J. W. *Macromolecules* **1998**, *31*, 4114−4119.
(35) Busnel, J. P.; Foucault, F.; Denis, L.; Lee, W.; Chang, T. *J. Chromatogr. A* **2001**, *930*, 61−71.
(36) Grushka, E. *Anal. Chem.* **1972**, *44*, 1733−1738.
(37) Yossen, M. M.; Vega, J. R.; Meira, G. R. *J. Chromatogr. A* **2006**, *1128*, 171−180.
(38) Hatada, K.; Kitayama, T.; Ute, K.; Nishiura, T. *Macromol. Rapid Commun.* **2004**, *25*, 1447−1477.
(39) Nielen, M. W. F. *Mass Spectrom. Rev.* **1999**, *18*, 309−344.
(40) Popovici, S. T.; van der Horst, A.; Schoenmakers, P. J. *J. Separation Sci.* **2005**, *28*, 1457−1466.
(41) Schnöll-Bitai, I. *Macromol. Symp.* **2005**, *215−7*, 357−363.
(42) Vega, J. R.; Schnoell-Bitai, I. *J. Chromatogr. A* **2005**, *1095*, 102−112.
(43) Schnoell-Bitai, I. *J. Chromatogr. A* **2005**, *1084*, 160−166.
(44) Mader, C.; Schnoell-Bitai, I. *Macromol. Chem. Phys.* **2005**, *206*, 649−657.
(45) Moad, G.; Moad, C. L. *Macromolecules* **1996**, *29*, 7727−7733.
(46) Lan, K.; Jorgenson, J. W. *J. Chromatogr., A* **2001**, *915*, 1−13.
(47) Stickler, M.; Meyerhoff, G. *Makromol. Chem.* **1978**, *179*, 2729−2745.
(48) Ishige, T.; Lee, S.-I.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1971**, *15*, 1607−1622.
(49) Hansen, J. P.; McDonald, I. R. *Theory of simple liquids*, 2nd ed.; Academic Press: London, 1990.
(50) Tobolsky, A. V.; Offenbach, J. *J. Polym. Sci.* **1955**, *16*, 311−314.
(51) Vidal, F.; Guyot, A.; Gilbert, R. G. *Macromol. Chem. Phys.* **1996**, *197*, 1835−1840.
(52) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992.
(53) Russell, G. T. *Aust. J. Chem.* **2002**, *55*, 399−414.
(54) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 2459−2469.
(55) Russell, G. T. *Macromol. Theory Simul.* **1995**, *4*, 497−517.
(56) Russell, G. T. *Macromol. Theory Simul.* **1995**, *4*, 519−548.
(57) Russell, G. T. *Macromol. Theory Simul.* **1995**, *4*, 549−576.
(58) Hutchinson, R. A.; Beuermann, S.; Paquet, D. A.; McMinn, J. H. *Macromolecules* **1997**, *30*, 3490−3493.
(59) Hutchinson, R. A.; McMinn, J. H.; Paquet, D. A.; Beuermann, S.; Jackson, C. *Ind. Eng. Chem. Res.* **1997**, *36*, 1103−1113.
(60) Frieden, B. R. *J. Opt. Soc. Am.* **1972**, *62*, 511−518.

MA062973A