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► To cite this version:

Yohann Guillaneuf, Patrice Castignolles. Using apparent molecular weight from SEC in controlled/living polymerization and kinetics of polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, 2008, 46 (3), pp.897 - 911. <10.1002/pola.22433>. <hal-04037118>

HAL Id: hal-04037118

<https://hal.science/hal-04037118v1>

Submitted on 20 Mar 2023

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Using apparent Molecular Weight from SEC in controlled/living polymerization and kinetics of polymerization

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Abstract

Apparent molecular weights from size exclusion chromatography (SEC), that is molecular weights relative to standards of a nature different to that of the polymer sample being studied, are frequently used. We use calculations corresponding to realistic cases to provide guidelines for situations when, and to what extent, apparent molecular weights (MWs) can be meaningful. In controlled polymerization, we show how, without due care, use of apparent MW, could lead to the incorrect conclusion that the reaction was not controlled, whereas the true MWs would be close to theoretical values. We show here that the quality of the eluent as a solvent for the standard and the polymer sample is a good indication of the accuracy and the significance of the apparent polydispersity index. Accurate Mark-Houwink-Sakurada parameters are of limited availability, but the data about solvent quality available in handbooks or available from static light scattering measurements. Apparent M_n is of no use in controlled polymerization if simple simulations as performed in this work do not validate their use. The determination of transfer constants by the Mayo plot can be performed using apparent M_n without introducing any significant error, contrary to apparent weight-average molecular weight M_w or apparent ln number distribution.

Keywords:

Size Exclusion Chromatography (SEC), molecular weight distribution (MWD), Polydispersity Index (PDI), Controlled radical polymerization (CRP), Mark-Houwink-Kuhn-Sakurada parameters, Chain Length Distribution method, Transfer Constant.

INTRODUCTION

Size Exclusion Chromatography (SEC) is a widely used technique to analyze synthetic and natural polymers.^{1,2} SEC separates by hydrodynamic volume, not by molecular weight (MW). Various detection methods have been developed to determine MWs. The most reproducible is conventional calibration using narrow standards of same chemical nature and structure as the analyte, but the number of available standards (polystyrene (PS), poly(methyl methacrylate) (PMMA), pullulan, etc.) remains limited. To obtain true MWs even if no standards are available, it is possible to use universal calibration³⁻⁵ from narrow standards together with the Mark-Houwink-Kuhn-Sakurada (MHKS) parameters of the standards and the analyte. Benoit³⁻⁵ showed that SEC separates according to the product $[\eta] \times M$ (universal calibration principle), where $[\eta]$ is the intrinsic viscosity. Using the MHKS empirical relationship⁶ linking the MW to the intrinsic viscosity ($[\eta] = K \times M^a$), universal calibration can be used through the product $K \times M^{a+1}$. Knowing the parameters K and a for both the standards and the polymer sample allows a universal master curve to be built and used to determine the MW of the sample. One problem arises in this procedure in the use of universal calibration with the MHKS parameters: this empirical relationship is not generally valid for low MW^{7,8} and perhaps also for very high MWs;^{9,10} other problems are the large discrepancies between the reported values for the MHKS parameters.¹¹⁻¹³ Some alternatives to the MHKS parameters have been developed in attempts to improve the range of MW available but the limited data available for this purpose make these relationships difficult to use.¹⁴⁻¹⁸ The limitations and applicability of the universal calibration for complex branched polymers has also been extensively discussed.¹⁹⁻²⁴ When MHKS parameters are not available, unreliable or the relation is no longer valid, multiple detection techniques can be used,²⁵ including universal calibration using an online viscometer,²⁶ light scattering-based methods (low-angle laser light scattering,²⁷ multi-angle laser light scattering,²⁸ triple detection²⁹).

Recent advances in the control of ionic,^{30,31} radical,^{32,33} coordination³⁴⁻³⁶ polymerization and polycondensation^{37,38} allow the synthesis of well-defined macromolecules with various complex architectures (e.g. linear, functional, telechelic, gradient, tapered, block, branched, grafted, comb-like, star, cyclic, hyperbranched, etc. polymers).³⁹⁻⁴² These complex architectures lead to improved materials combining the properties of the different segments.^{39,43-45} Characterization of these architectures is crucial to know whether the assumed architecture is obtained or not but also to be able to relate the types of architecture to application properties (e.g. response to pH, temperature etc.). Nevertheless the characterization of such systems is difficult due to the complexity and the heterogeneity (in composition or/and shape), in addition to the inherent dispersity in molar masses.²⁵ For the complete characterization of complex polymer systems being disperse in more than one dimension, a combination of separation methods is needed,⁴⁶⁻⁴⁸ but is currently still too time-consuming and expensive to be used as often as it should. A good example is given by the elegant work of D'Agosto et al.⁴⁹ on the RAFT polymerization of dimethylaminoethyl methacrylate (DMAEMA). The PMMA equivalent MWs by THF SEC were half the theoretical value, whereas a longer and more complex procedure (in this case the polymer has to be acidified for viscosity purpose) using aqueous SEC multiangle laser light scattering detection showed a perfect accord between experimental and theoretical MW. Moreover the synthesis of new functional monomers to prepare specific materials such as the work of Hawker et al.⁵⁰, leads more and more researchers to synthesize new polymers whose physical properties (viscometric, etc) have not been fully determined. Developments of high-throughput technologies⁵¹⁻⁵⁵ speed up the macromolecular engineering and its applications, but at the same time increases the need for faster analysis, which then cannot be performed by current multi-dimensional HPLC techniques. These and other limitations exemplify why apparent MWs are commonly used in the literature, i.e. MWs are determined using standards and/or MHS parameters that do not correspond to the actual polymer being studied. For instance, if one examines the current issues (at the

time of the writing) of *Macromolecules* and *Journal of Polymer Science*, in the vol 40, issue 14 of *Macromolecules*, 13 articles were using SEC to characterize homo or copolymers and among them, 10 were using exclusively PS or PMMA equivalent MW for polymers having very different structures, i. e. polythiophene-*b*-polyisoprene, poly(arylene bicarbazole), poly(poly(ethylene glycol) methacrylate), poly(1'-octyloxy-4'-(6-methacryloxy)hexyloxy-5'-phenylmethaneone-(2-phenyl) azobenzene), hyperbranched polyurethane, etc. Vol 45, issue 15 of *Journal of Polymer Science, Polymer Chemistry*, contains 2 articles using multiple detection SEC, 1 article using polystyrene standards to characterize polystyrene and then 13 articles using apparent MWs and 3 articles not defining clearly the method to determine molecular weight (presumably apparent MW).

While apparent polydispersity index (PDI) was first proposed to be equal to the true PDI, Benoit et al. showed that the conventional calibration curve differs from one polymer to another not only by a translation (apparent PDI would be equal to the true one then) but also a rotation taking into account the MHKS exponents a of the two polymers (Scheme 1).^{4,5} A translation-only situation, with no change in PDI, is observed only if the MHKS exponents of the standard and the analyte are the same. Apparent MWs are commonly used without considering the effect of this rotation, or by implicitly assuming it is negligible for the determination of average MW or at least PDI. Discrepancies between apparent MW from SEC and MW determined by independent methods or expected (theoretical MW) are sometimes attributed to separation issues (adsorption etc.) implicitly considering the effect of the rotation as negligible (see for example discussion or reference ⁵⁶). Netopilik et al.⁵⁷ have discussed the effect of this rotation and the significance of polystyrene-equivalent MW. They showed that for a log – normal distribution function, the variation from the true MW is typically tens of percent and the maximum difference a factor of 3 in MW and a factor of 2 in PDI.

One of the objectives of the present paper is to examine apparent MW in practical cases and to provide recommendations for the conditions that allow apparent MW to be meaningful and what errors are introduced for typical cases. This is applied to several common situations for which apparent MWs are often used: to elucidate between polymerizations that are controlled or not, and to determine polymerization rate coefficients in transfer-dominated systems. Accurate determination of molecular weight is a requirement for all studies about kinetics of polymerization either conventional (e.g. ⁵⁸) or controlled (e.g. ⁵⁹). In the case of controlled polymerization, accurate determination of molecular weight is not necessary to determine whether or not a block copolymer is obtained. However, accurate determination of molecular weight is a requirement when the research aims at producing narrow molecular weight distributions⁶⁰ or to relate the structure of a complex polymer to its applications properties. We quantify the difference in both the whole MWD and average MW (M_n , M_w , PDI) for an apparent conventional calibration curve (obtained from standards different from the polymer sample), instead of the true calibration curve. This yields general guidelines about possible use of apparent MWs when the true MWs cannot be determined; these guidelines are directed toward important use of MW like: is a polymerization controlled? Is a kinetic constant determined accurately?

THEORETICAL MODELS AND PROCEDURES

This work applies to SEC separations, i.e. separation by hydrodynamic volume (no adsorption etc.). For linear polymers, SEC data can be expressed entirely in terms of the SEC MWD $w(\log M)$, which assuming no band broadening is given by:²²

$$S_{\text{DRI}}(V_e) \equiv \frac{d \log M}{dV_e} \times w(\log M) \quad (1)$$

where V_e is the elution volume and $S_{\text{DRI}}(V_e)$ the signal from the refractometer (or any mass-sensitive detector).

The SEC MWD relates to the number MWD $P(M)$, number of chains with molecular weight M , and the mass distribution $W(M)$, through the following equations:

$$P(M) = W(M) / M = w(\log M) / M^2 \quad (2)$$

We simulate realistic MWDs corresponding to two cases: conventional and controlled free radical polymerization. Realistic MWDs ($w(\log M)$ against $\log M$) for controlled radical polymerization were generated by using the PREDICI[®] software⁶¹ as discussed in detail in the supporting information. Realistic number average molecular weights, M_n , corresponding to different conversions are thus generated. The linear evolution of M_n with monomer conversion is one important indication that a polymerization is controlled. Ideally, living systems lead to polymers with degrees of polymerization predetermined by the ratio of concentrations of consumed monomer to initiator/controller $M_n = (M_0 \times [M]_0 \times \text{conversion}) / [\text{initiator}]_0$, with PDI close to that of a Poisson distribution ($\text{PDI} = M_w / M_n = 1 + M_0 / M_n$).

Shulz-Flory distributions were used to simulate chain transfer-dominated polymerization. In a chain polymerization, when transfer is the main chain-stopping event, the PDI value is close to 2 and the number distribution $P(M)$ for high DP is described by the following equation:

$$\ln P(M) = \kappa - \Lambda \frac{M}{M_0} \quad (3)$$

where M_0 is the molecular weight of the monomer unit.

The details of the calculation are given in supporting information. The chain transfer rate constant can be determined by plotting the inverse of the slope of number chain length distribution $\Lambda = d \ln P(M) / dM$ versus the ratio $[X]/[M]$,⁶²⁻⁶⁴ where X is the chain transfer agent.

Procedure used to calculate apparent molecular weights

The calculations performed in this work are similar to the simulations carried out by Netopilik et al.⁵⁷ The apparent MW is determined using the MHKS parameters of the standards and of the polymer:⁵⁷

$$\log M^{\text{app}} = \frac{1}{a' + 1} \log \frac{K}{K'} + \frac{a + 1}{a' + 1} \log M \quad (4)$$

where M^{app} is the apparent MW, K' and a' are the MHKS parameters of the standards, K and a are the MHKS parameters of the studied polymer. In the case of controlled polymerization, PREDICI[®] yields the SEC distribution $w(\log M)$ against $\log M$, and $P(M)$ is determined using eq 2. The apparent MW is determined using eq 4. In the case of Flory-Schulz distributions, the number MWDs is directly obtained and the SEC chromatograms are computed using eq 2. From the simulated chromatograms, the apparent MWD and associated averages are obtained using the calibration curve given in eq 4.

For each application (controlled polymerization and determination of chain transfer constant) an example calculation is detailed in the supporting information. All the following results were obtained assuming that the calibration curve is linear. SEC calibration curves are commonly fitted with a third order polynomial function,¹ especially if one perform calculations on a broad range of MW, which is necessary to determine accurate average MWs. The shape of the calibration curve affects the shape of $w(\log M)$ (see eq 1). It was thus important to examine whether the shape of the calibration curve could induce a difference between the true and apparent $w(\log M)$. The equations taking this phenomenon into account have been examined (see supporting information) and show that the results and conclusions presented in this work are independent of the polynomial order of the calibration curve.

Choice of K and a values

To extract useful recommendations from the simulations, one first needs to determine what range of MHKS parameters is comprehensive and physically sensible. The exponent a in the MHKS equation can take values between 0 (spherical chains) and 2 (rod-like chains).⁶⁵ This work is focused on linear polymers which adopt a random coil conformation in solution, for which a varies between 0.5 for theta solvents and 0.8 for thermodynamically good solvents. The choice of K values is not so straightforward. First, K is related to the stiffness of the chains.⁶⁶ K and a are not independent and comparing different polymers and/or solvents the higher the exponent a , the lower the K value.⁶⁶⁻⁶⁸ The decrease of K while a increases could be associated with the uncoiling and straightening of the chain. Aharoni et al.⁶⁷ have collected data for different polymers and concluded that a linear relation:

$$\log K = C - B \times a \quad (5)$$

is obtained for all polymers with different C and B values according to the nature of the polymer. Another explanation for this phenomenon lies in statistics: during the fitting of $[\eta]$ versus M , a higher value of a would be compensated for by a lower value of K (likewise for fitting the Arrhenius equation to a data set of kinetic constants against temperature, a higher pre-exponential factor may be compensated for by a higher activation energy).

This work is focused on random coil conformation and in this case K typically varies over one decade.⁶⁷ Two limit cases are considered: $a = 0.5 / K = 30 \times 10^5 \text{ mL}\cdot\text{g}^{-1}$, applicable to a theta solvent) and $a = 0.8 / K = 3 \times 10^5 \text{ mL}\cdot\text{g}^{-1}$, applicable to a good solvent. These limit cases encompass K and a encountered for common polymers e.g. polystyrene, poly(alkyl methacrylates)⁶⁹ or poly(alkyl acrylates)¹².

RESULTS AND DISCUSSION

Determination of average molecular weight and PDI

Controlled Radical Polymerization

The accurate determination of the MW is necessary to conclude whether a polymerization is controlled or not. Two different types of SEC results were simulated. The first case corresponds to the eluent being a better solvent for the standard than for the studied polymer, e.g. polystyrene standards in THF and pullulan standards in most of the aqueous eluents are all in good solvent. The second case corresponds to the eluent being a better solvent for the studied polymer than for the standards. The K and a values used are $a = 0.5 / K = 30 \times 10^5 \text{ mL} \cdot \text{g}^{-1}$, applicable to a theta solvent) and $a = 0.8 / K = 3 \times 10^5 \text{ mL} \cdot \text{g}^{-1}$, applicable to a good solvent (see part “choice of K and a value” for more details). When the studied polymer is not in a thermodynamically good solvent ($a = 0.5$), the polymer chains are not fully extended and their separation suffers from a lower resolution than the separation of the standards ($a' = 0.8$, i. e. a thermodynamically good solvent for the standards), and thus the slope of the true calibration curve is higher than that obtained with the standards (the latter yields the apparent MW). The apparent separation then seems to be more efficient than it really is.

A perfectly controlled and living polymerization has been simulated: the computed evolution of the true M_n against conversion is linear (Figure 1, full circles). The plot of apparent M_n against conversion is however curved and levels off at high conversion (Figure 1, full squares). Experimental M_n values lower than that predicted by theoretical M_n may be explained by transfer.³² While this bulk polymerization is perfectly controlled, one could conclude from the apparent M_n that there was a significant transfer reaction. Applying the equation used by Zetterlund et al.⁷⁰ ($[\text{chains}]_{\text{tr}} = [M]_0 \times C_{\text{tr}} \times \text{conversion}$) can lead to a transfer constant to the monomer of 1.8×10^{-3} , which is a high but sensible value compared to literature.³³ When the

same evolution of apparent M_n is obtained for a solution polymerization ($[S]_0 = 5 \text{ mol}\cdot\text{L}^{-1}$), a transfer constant to solvent can be determined from the eq 6:^{71,72}

$$DP_n = \frac{[M]_0 \times \text{conversion}}{[I]_0 + [S]_0 \times (1 - (1 - \text{conversion})^{C_{tr}})} \quad (6)$$

leading to a transfer constant of 9.0×10^{-4} which would appear perfectly reasonable for a solvent transfer reaction comparing with literature values.³³ In this case, using apparent MWs could lead to the incorrect conclusion that the polymerization is not controlled because of a transfer reaction, whereas the control and the livingness were actually achieved. This may be well illustrated by the very recent work of Yuan et al.⁵⁶, in which they prepared dendritic star-block poly(L-lactide)-*b*-poly(2-*N,N*-dimethylaminoethyl methacrylate). They observed that the apparent MWs determined by SEC (polystyrene-equivalent) were much lower than those determined by ¹H NMR and the theoretic values. SEC results were attributed to some adsorption of the poly(2-*N,N*-dimethylaminoethyl methacrylate) block onto the SEC column and the fact that apparent Molecular weight are used is not taken into account. Moreover, the PDMAEMA is known to have apparent MW lower than the true one in THF.⁴⁹ The presence of branching leads to a contraction of hydrodynamic volume and thus apparent MW of branched polymers generally underestimates the true MW.^{73,74} The lower MW could be also explained by an overestimation of the SEC separation and not by any adsorption. The occurrence of adsorption can be experimentally tested by varying the quantity of polymer injected (injection concentration) and injecting at different concentrations and comparing the hydrodynamic volume distributions.²²

The examination of experimental and theoretical M_n when the latter is higher is commonly used to determine the efficiency of the initiation (the higher the theoretical M_n compared to experimental, the lower the efficiency). The initiator efficiency could have a critical importance when telechelic polymers are desired. The endgroup fidelity has to be checked before the preparation of complex architecture by hydrogen bonding⁷⁵ or by coupling reactions⁷⁶. Similarly, a controlled polymerization with a true initiating efficiency of only 80 % could appear perfectly controlled with an

apparent efficiency of 100 % (Figure 2, apparent M_n (empty square) compared to true M_n (empty circle), the detail of how the distribution has been generated is given in supporting information.

A poorly-controlled polymerization was simulated with significant occurrence of irreversible termination. This leads to a long tail in the oligomer region of the MWD (Figure 3, full line). The true PDI of this MWD is 1.79, reflecting the lack of control. However, the apparent PDI can be as low as 1.35, significantly lower than the true values obtained from conventional free radical polymerization, if the eluent is indeed a theta solvent of the studied polymer while the standards are in good solvent (Figure 3).

We now consider the case for which the eluent is a good solvent for the studied polymer ($a = 0.8$) and a theta solvent for the standards ($a' = 0.5$). The separation of studied polymer chains now exhibits a better resolution than the separation of the standards. The apparent PDI of the polymer is then higher than the true one. This case could be represented by a DMF SEC calibrated with PS standards to determine polyacrylonitrile MW.¹ The apparent M_n can then be higher than the true one. A quite living (67 % of living fraction for 82.5 % of conversion) and controlled (PDI = 1.25) polymerization was simulated. A short tail is due to some irreversible termination, especially during the early stages of the polymerization (Figure 4, full line). The apparent MWD can be significantly broader (PDI = 1.77) than the true one and the M_n significantly higher at 16,000 g.mol⁻¹ (Figure 4, dotted line and also scheme 1). From the apparent MWD, one may conclude that the polymerization is poorly controlled with a possible initiation problem, whereas the polymerization is actually controlled. In these conditions, apparent MWs of a perfectly controlled polymerization could be interpreted as a polymerization for which the initiation efficiency was only close to 80 % (see Figure 3, full symbols and supporting information for more details).

In the case described in Figures 3 and 4, the apparent (PDI 1.10) and true (PDI 1.05) MWDs were both narrow, and the apparent M_n was significantly higher than the true

one. One important question is whether apparent M_n s have still higher values, when the PDI becomes significantly greater than unity. We consider the case for which the evolution of true M_n against conversion levels off to yield values lower than the theoretical ones. These MWs (Figure 5, full circles) are simulated adding a transfer reaction to the solvent (see supporting information). The apparent M_n (Figure 5, full crosses) are in this case essentially the same as the true ones, unlike the previous results. M_n are not overestimated here because of the PDI is overestimated (true PDI is 1.22 while apparent PDI is 1.56). Thus, apparent M_n should not be used without a careful examination of solvent quality of the eluent for the standard and sample. The same simulations as presented here should then be performed in the different possible general cases; the simple software we used in this work is accessible free of charge on <http://www.uq.edu.au/gilbertgroup/>.

The results obtained in this section show that conclusions about controlled radical polymerization using apparent MW can be meaningful if they are used together with examination of solvent quality and possibly performing simulations. A controlled polymerization can be apparently non-controlled and vice versa. The apparent PDI value is not only related to the true PDI but also to the quality of the solvent for both the standards and the polymer, whereas the difference between apparent and true M_n is too complex to predict without performing simulations, since it is strongly dependent on both the MHKS parameters. If no standards and MW-sensitive detectors are available, one should first check in the range of SEC eluent available (new SEC conditions are being developed using eluents such as 1,1,1,3,3,3-Hexafluoroisopropanol⁷⁷ or dimethyl acetamide^{78,79}), if there is an eluent with the same quality as a solvent for both the apparent standards and the polymer sample. This is a particularly important consideration in aqueous SEC where an infinite range of eluents (varying the nature and concentration of salt, buffer and co-solvent) is available. This can be deduced not only from the parameter a , but also from many other tabulated values like 2nd virial coefficients,⁸⁰ polymer-solvent interaction

parameters⁸¹ or solubility parameters values (Hildebrand parameters) when the MHKS parameters are not available.^{82,83} 2nd virial coefficient can be determined from the colligative properties, by scattering methods (light, X-ray or neutron), and also from sedimentation. These useful values are tabulated in some publications, e.g. Penzel and Goetz work for poly(alkyl acrylates),⁸⁴ or in the Polymer Handbook.⁸⁰ For some monomer families, the MHKS parameters are not known for all the members but only for some of them. In this case, the MWs can not be calculated using MHKS parameters of the others members, but if the chemical structure is close enough (for example some alkyl (meth)acrylate derivatives⁶⁹), the quality of the solvent should be close and can give a good approximation for this monomer. When the eluent is a solvent of the same quality for both the polymer sample and the standards, then the apparent PDI is close to the true one and can be used safely to draw conclusions on the controlled character of a system. When the eluent is a better solvent for the standard than for the studied polymer, then the PDI is underestimated: a high apparent PDI is indicative for poor control, but a low PDI is meaningless. When the eluent is a better solvent for the studied polymer than for the standards, then the PDI is overestimated: a low apparent PDI is indicative for good control, but a high PDI is then meaningless. It is still common in the literature to encounter MW determined by absolute technique like static light scattering and apparent polydispersity index by SEC. While these authors don't use M_n or M_w , they still discuss the width of the MWD in term of apparent PDI (e.g. ⁷⁴). Our work shows that there could be significant differences between apparent PDI and true PDI in practical cases. Discussing the increase or decrease of apparent PDI when changing the structure or nature of a polymer (grafting, copolymerizing), one should take the solvent quality for the SEC into account. For example, copolymerization of styrene with sec-butenyl acetate in emulsion yields yields lower apparent polydispersity than corresponding homopolymerization of styrene.⁸⁵ This may be explained by a lower solubility of the

copolymer than the polymer in the eluent (THF) and not only the polymerization kinetics.

Using the Polymer Handbook,⁸⁰ one can for example deduce that in NaCl-based aqueous solution, pullulan-equivalent PDI of poly(glutamic acid) may be underestimating the true one, since NaCl-based aqueous eluent are better solvent for pullulan (the second virial coefficient A_2 ranges from 1.5 to $2.5 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$) than for poly(glutamic acid) (A_2 ranges from 0.3 to $0.9 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$). It is important to compare ranges of values of A_2 available in the literature and not single values since this parameter is also temperature and MW-dependent. The same conclusion may be valid for polystyrene-equivalent or poly(methyl methacrylate)-equivalent PDI for poly(vinyl acetate) in tetrahydrofuran (A_2 ranges from 1 to $5 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$, from 1 to $10 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$, from 0.16 to $0.28 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$ respectively for poly(methyl methacrylate), polystyrene, poly(vinyl acetate)). In dimethyl formamide, poly(ethylene oxide) standards are in good solvent (A_2 ranges from 30 to $50 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$) and poly(ethylene oxide)-equivalent PDI will underestimate the true PDI of many other polymers (e. g. A_2 ranges from 3 to $4 \times 10^{-4} \text{ mol}\cdot\text{cm}^3\cdot\text{g}^{-2}$ for poly(acrylonitrile)). In order to determine apparent PDI close to the true value, one could tune the quality of the eluent as a solvent by including additives. For example, the quality of water as a solvent for polyelectrolytes can vary from very good to bad solvent by addition of salts and buffers. In this case, one has to find appropriate conditions in the literature for standard and sample and then to check that the separation still occurs by a SEC mechanism (no adsorption etc.).

Case of transfer-dominated polymerization

As just shown, the apparent MW can be significantly different from the true one. The occurrence of transfer leads to a decrease of the true MW. Transfer has been regularly considered to explain unusually low MW, with cases like the free radical

polymerization of dialkyl itaconates, where low PMMA-equivalent MW were first incorrectly attributed to transfer before Velickovic et al.⁸⁶ showed that the true MWs are actually higher than the apparent ones.

The historical way to determine the transfer constant to a species X, $C_{tr,X}$, was developed by Mayo⁸⁷ and consists in plotting the inverse of the initial kinetic chain length (which is estimated from the initial DP_n) against the ratio between the initial concentration of the transfer species [X] over the initial concentration of the monomer [M] (eq 7).

$$\frac{1}{DP_n} = \frac{k_t R_p}{k_p^2 [M]^2} + C_{tr,M} + C_{tr,X} \frac{[X]}{[M]} \quad (7)$$

The values obtained in the literature with this method are often scattered because of several well-known but not always appreciated limitations of the method:⁸⁸ impurity level leading to significant inhibition or retardation should be negligible, only low conversion should be used to limit the occurrence of transfer to polymer, the rate coefficient k_p and especially k_t , have to be chain-length independent over the DP range of interest. Another significant source of error is the determination of the DP_n by SEC; this is very sensitive to the baseline determination and peak selection, and is indeed the least reproducible data yielded by SEC.^{64,89,90} When transfer is the only significant event stopping the growth of the chains, the theoretical PDI is 2 (Flory-Schulz distribution) and DP_n is more precisely estimated as $DP_w/2$.^{33,90} The determination of the transfer constant using Mayo equation has been thoroughly discussed in the literature and a number of useful guidelines have been proposed.⁸⁸ However, no guideline has ever been given regarding the use of apparent MW together with Mayo equation. The differences observed between the apparent and true M_n in the case of controlled polymerization would seem to vitiate the use of Mayo equation, at least using DP_n .

To investigate this issue, true number MWDs applicable to the bulk polymerization of styrene at 60 °C with different concentrations of 1-butanethiol as transfer agent ($C_{tr} =$

21)⁹¹ were simulated using eq 3. Apparent number MWDs were then calculated considering the two extreme types of separation: (i) standard in good solvent, while the studied polymer is in theta solvent; (ii) studied polymer in good solvent, while the standard is in theta solvent. The K and a values used are given in the part “choice of K and a value”. True and apparent Mayo plots and C_{tr} from these simulations are compared in Figure 6a and in Table 1. The apparent DP_n is significantly lower than the true DP_n in case (i) and significantly higher in case (ii). However, the three Mayo plots are “pseudo” linear (a sharp examination of the Figure 6, showed a slight curvature for high MW polymers) and the apparent C_{tr} values are in good agreement with the theoretical one ($C_{tr} = 21.1$ for case (i) and $C_{tr} = 21.2$ for case (ii), while the true C_{tr} is 21.0). This unexpected result could be explained by the huge weight put on low MW polymers in the Mayo plot (inverse DP_n Vs $[X]/[M]$ plot). As depicted in Scheme 1, Figure 2 and according to eq. 4, the higher the MW, the bigger the difference between true and apparent MW. The value of apparent C_{tr} for low MW is therefore not so different from the true one and due to this result, the Mayo plot is quite accurate. Contrary to the case of controlled polymerization, apparent DP_n values can be used reliably in a Mayo plot to determine the transfer constant. Using a single apparent DP_n leads to incorrect transfer constants for any concentration of transfer agent (Table 2), and so the range of determined DP_n should be broad to ensure an accurate determination, which is indeed also the case, when true DP_n are used. However it is important to note the trends in the difference between apparent and true DP_n depending on the SEC system. In case (i), this difference decreases with MW even at low MW; using apparent DP_n , it is highly recommended to include low DP_n in the Mayo plot. On the other hand, in case (ii), at very low MW the difference increases with MW (due to the difference between apparent and true PDI, the same holds for case (ii) applied to controlled polymerization). In this case, the plot leads to accurate transfer constants once very low MWs are discarded.

The reproducibility of the DP_w determined by SEC is usually far higher than the reproducibility of the DP_n ,⁸⁹ mainly because of the uncertainty in baseline determination and the presence of low MW tails. Indeed, in the case of transfer dominated system, the PDI value is equal to a value close to 2 (the band broadening and the presence of impurities can increase the PDI), $DP_w/2$ has been proved to represent a more accurate value for the initial kinetic chain length than the DP_n .⁶³ The situation would then be the same for apparent MW and at first sight it would seem that more accurate transfer constants would be obtained using $DP_w/2$ for the Mayo plot. To test this, the simulated MWDs were used to calculate these Mayo plots for case (i) and are displayed on Figure 6b. The apparent Mayo plot is still linear (see Table 1), but surprisingly yields an apparent transfer constant significantly different from the true one. This suggests that Mayo plots should not be used with apparent DP_w . The explanation of these unexpected results may be that the difference between apparent and true M_w is more important than in the case of the M_n , however, it is not possible to extract a systematic trend. The principal reason for this result is more probably that the apparent PDI of these distributions significantly differs from 2, with apparent PDI of 1.5 (case (i)) or 3.4 (case (ii)); therefore assuming $DP_n = DP_w/2$, the theoretical Flory-Schulz distribution result, thus the main hypothesis does not hold. Apparent DP_w values obtained from SEC should be the more reproducible values, but with a systematic and likely stronger deviation to the true value than DP_n values; the Mayo plot can lead to a meaningful transfer constant only using apparent DP_n (and including very low MW or not depending on the type of SEC separation). $DP_w/2$ should only be used for the Mayo plot if the PDI value is equal to 2, and this guideline is true whatever true or apparent MW are used.

Determination of the molecular weight distribution

To avoid some of the drawbacks described previously for the Mayo technique in the determination of transfer constants (presence of low MW impurities altering M_n

value, baseline determination, assumption of chain-length independent termination etc.), Gilbert et al.⁶² proposed the use of the logarithm of the number distribution $\ln P$, and eq 3 to determine transfer constants and named this method the chain length distribution (CLD) method.

This method has been widely used to study the kinetics of emulsion polymerization,⁶² to determine transfer constants in conventional free radical polymerization,⁹²⁻⁹⁴ catalytic chain transfer,⁹⁵ termination rate coefficients⁹⁶ and recombination constants k_c between nitroxides and macroradicals.⁵⁹ Guidelines have been given regarding the use of this method, as follows. The part of the $\ln P(M)$ Vs M plot (called $\ln P$ plot) used to determine the transfer constant should have its slope insensitive to different initiator concentrations.^{62,63} Band-broadening, even using modern SEC columns and equipment, induces a curvature of the linear parts of the $\ln P$ plots⁹⁷ and either one needs to correct for band broadening^{98,99} or to determine the slope of the $\ln P$ at the maximum of the SEC distribution, where the band-broadening has been proved to have no effect.^{97,100,101} No guidelines have been given towards the use of apparent $\ln P$ plots. It is first possible to examine the relation between the apparent $\ln P$ plots and the true ones. Combining eq 3 and 4 leads to:

$$\ln P^{app}(M^{app}) = \kappa + \frac{2}{a+1} \ln \frac{K'}{K} + 2 \frac{(a' - a)}{a+1} \ln(M^{app}) + \frac{\Lambda}{M_0} \left(\frac{K'}{K} \right)^{1/a+1} (M^{app})^{a'+1} \quad (8)$$

$\ln P^{app}$ is not a linear function of M^{app} . However, the two first terms, κ and $\frac{2}{a+1} \ln \frac{K'}{K}$ are constant, i.e. do not affect the slope. The third term, $\ln(M^{app})$ is small and negligible (because $a'-a$ is small) as long as the apparent MW is low enough. Finally the last term contains M^{app} to the power $(a'+1)/(a+1)$, which can have values between 0.83 and 1.2, i.e. relatively close to unity. To test the sensitivity of this method to the use of apparent MWs, we simulate apparent $\ln P$ obtained for different SEC conditions.

The same MWDs as used in the previous section have been studied and the apparent $\ln P$ plots actually look linear in all cases. The true and apparent A values were determined and are plotted against the ratio $[X]/[M]$ on Figure 7. This plot of is also linear but the resulting apparent C_{tr} (Tables 2 and 3) are different from the theoretical ones. The main reason for this discrepancy lies in the term $(K'/K)^{1/(a+1)}$. Apparent MW should thus not be used to determine transfer constants using the $\ln P$ method (chain length distribution method).

CONCLUSIONS

Apparent MWs (i.e. polystyrene- or pullulan-equivalent MWs) are very widely used in the literature. It is well known, but still often unappreciated, that apparent MWs are generally different from the true MWs and should be used carefully, but, practical and concrete guidelines to assist in this care have hitherto been missing. In this work, we propose guidelines mainly based on the quality of the eluent as solvent for the studied polymer and for the used standards, using simulations. When the MHKS parameters are not available, other well-known accessible data like second virial coefficient A_2 or Hildebrand parameters can thus help in the interpretation of SEC data. While constant improvement of light scattering and viscometric detectors for SEC makes the use of apparent MWs less necessary, progress in macromolecular engineering leads to the synthesis and analysis of more and more complex architectures and copolymers, for which the Mark-Houwink-Sakurada relation is invalid, refractive index increment varies with molecular size etc. The use of apparent MWs is still necessary. Our results show that numerous “old-fashioned” characterization methods which determine solvent quality without fractionation (osmometry, light scattering, but also other measure of colligative properties etc.) have still indeed a strong potential, not only to determine average MW, but also to make it possible to understand SEC results without using time-consuming and expensive multiple detection techniques. The

common practice of measuring M_w by static light scattering and the apparent polydispersity index from SEC should be accompanied by a discussion of the validity of this apparent polydispersity index using the A_2 values determined by Static Light Scattering (and literature data).

When analyzing controlled radical polymerization or transfer-dominated polymerization, the simulations here show that if the sample and standards have similar interactions with the solvent (similar MHKS exponents or second virial coefficient etc.), the apparent PDI is close to the true one and can be safely used to draw conclusions about the controlled character of the polymerization. While the apparent PDI can be meaningful and useful due to these guidelines, one has to be even more careful using apparent M_n . The apparent and true M_n can be significantly different even if the eluent has the same solvent quality for both the polymer studied and the standard. One should thus use apparent M_n only after applying to their particular case the same kind of simulation performed here.

Surprisingly enough, apparent M_n can still be useful in a transfer-dominated system to measure transfer constant using a Mayo plot. In this case, apparent transfer constants can have values very close to the actual ones. The same conclusion cannot be drawn about the newest method used to determine transfer constants: the chain length distribution method using the \ln (number distribution), $\ln P(M)$. While actual and apparent $\ln P$ plots are qualitatively the same (both linear plots), their slope and thus the determined transfer constant differ significantly. Even if the Mayo plot using M_n has been shown in the literature to suffer from limitations independent from the SEC calibration and Mayo plot using $M_w/2$ or the $\ln P$ plot has been shown to lead to more reliable results, the situation is different when one has to use apparent MWs.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support of an ARC Discovery Grant DP0556963. We are grateful to Prof. Robert G. Gilbert for his scientific support. YG thanks Profs Denis Bertin and Paul Tordo for using the PREDICI[®] software.

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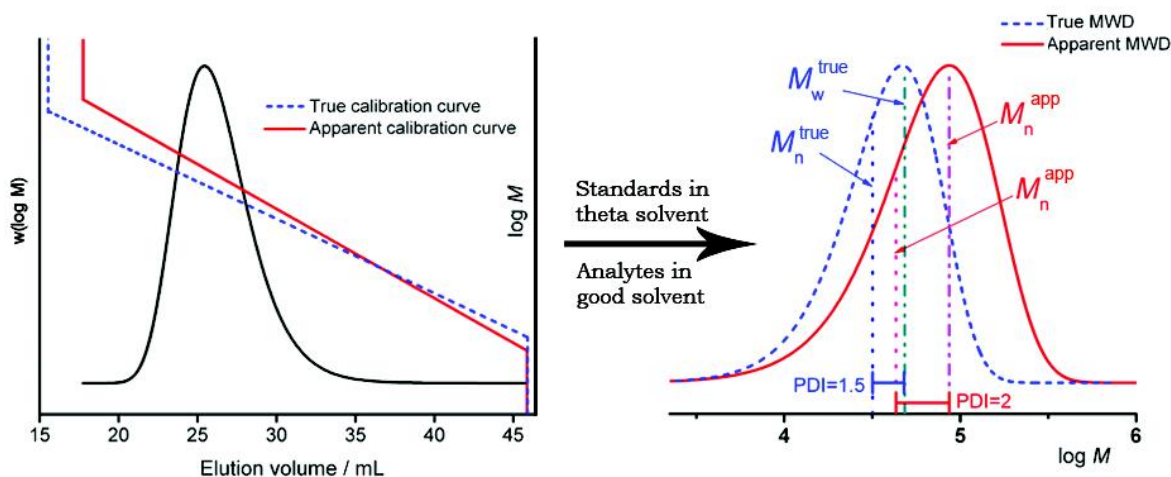
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SCHEMES, FIGURES, TABLES



Scheme 1: Comparison of the M_n , M_w and PDI values obtained with two different calibration curves.

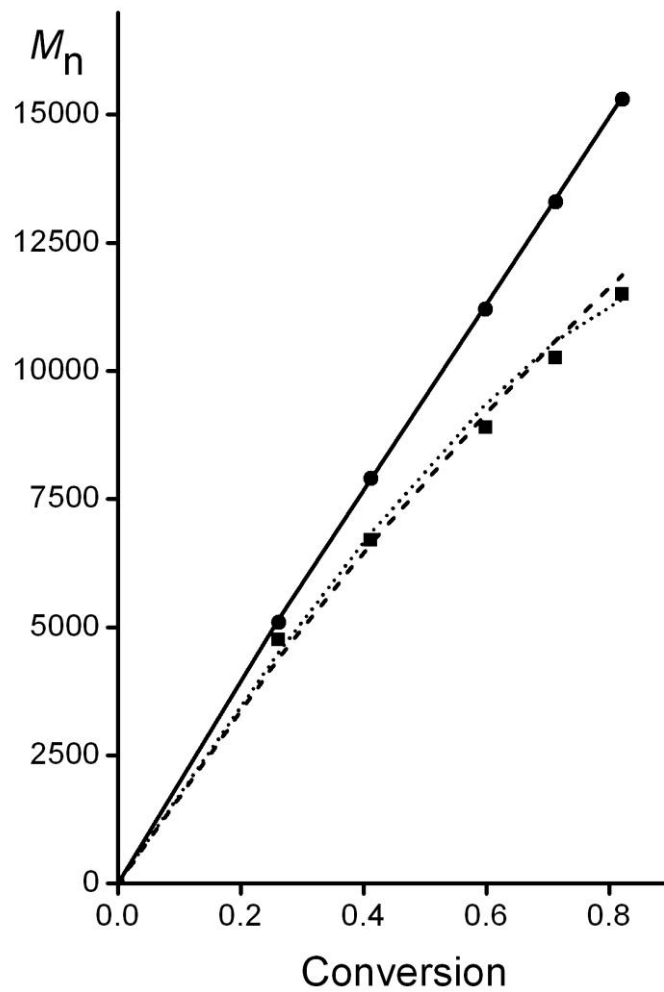


Figure 1: M_n vs Conversion plot. (●) True M_n for simulated perfectly controlled polymerization (Table 1 entry 2). (■) Apparent M_n ($K = 30$, $a = 0.5$ for the polymer sample and $K' = 3$, $a' = 0.8$ for the standard). (—) Theoretical M_n . (...) Theoretical M_n assuming transfer to solvent using eq 6. (---) Theoretical M_n assuming transfer to monomer and using the equations from Zetterlund et al.⁷⁰

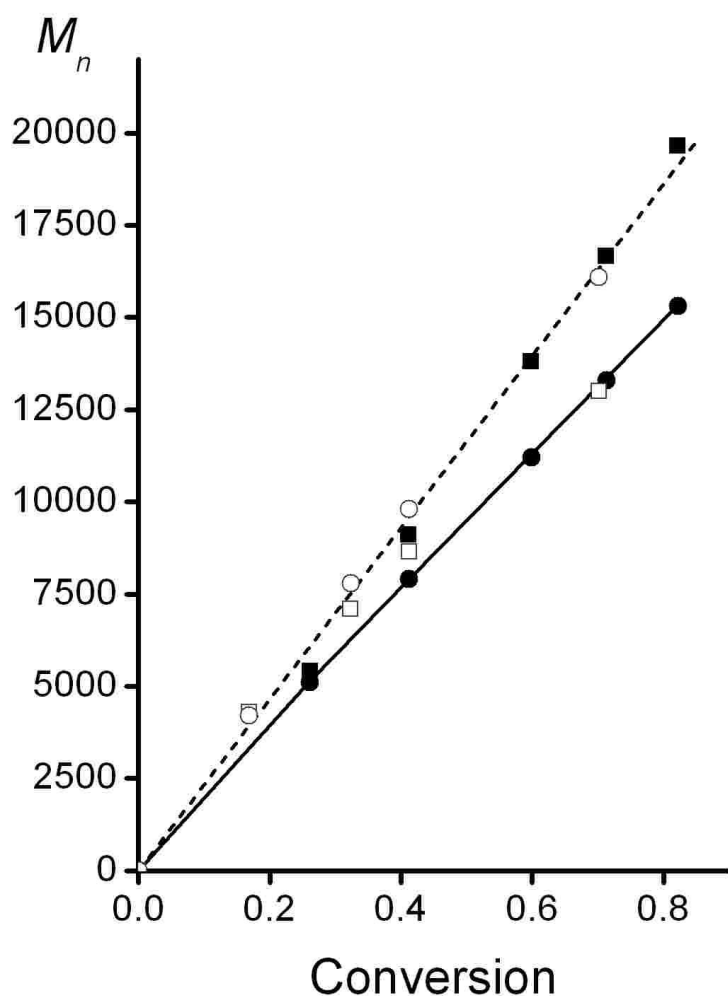


Figure 2: M_n vs Conversion plot; Case a (o) True M_n for simulated controlled polymerization. (\square) Apparent M_n ($K = 30$, $a = 0.5$ for the polymer and $K = 3$, $a = 0.8$ for the standard). (—) Theoretical M_n . (---) Linear correlation of the true M_n (indicative for 80 % initiation efficiency); Case b (\bullet) True M_n for simulated NMP (Table 1 entry 2). (\blacksquare) Apparent M_n obtained from the corresponding apparent MWD ($K = 3$, $a = 0.8$ for the polymer sample and $K = 30$, $a = 0.5$ for the standard). (—) Theoretical M_n . (---) Linear correlation of the apparent M_n (80 % efficiency).

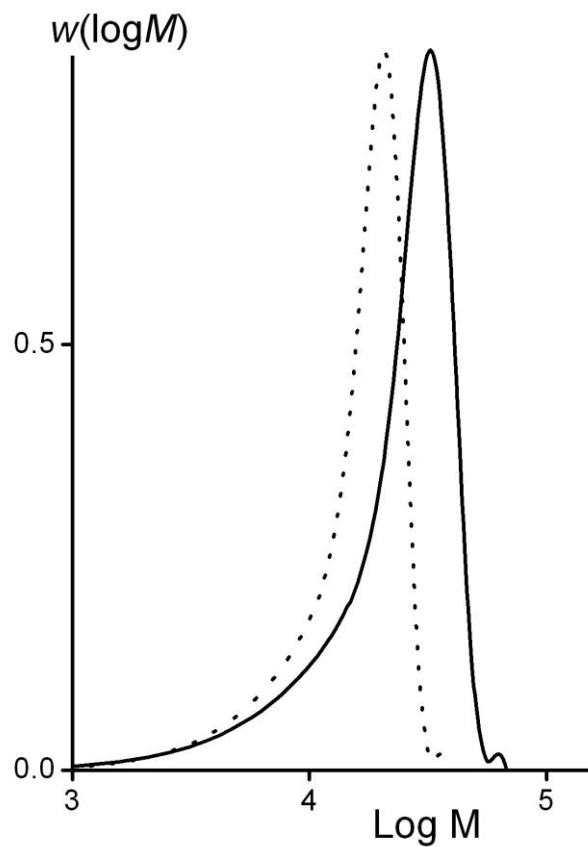


Figure 3: MWD $w(\log M) = f(\log M)$ for simulated poorly-controlled polymerization considered as the true MWD (full line, $M_n = 14,400$, PDI = 1.8, $K = 30$, $a = 0.5$ for the polymer sample) and a corresponding apparent MWD (dotted line, $M_n = 12,900$, PDI = 1.35, $K' = 3$, $a' = 0.8$ for the standard).

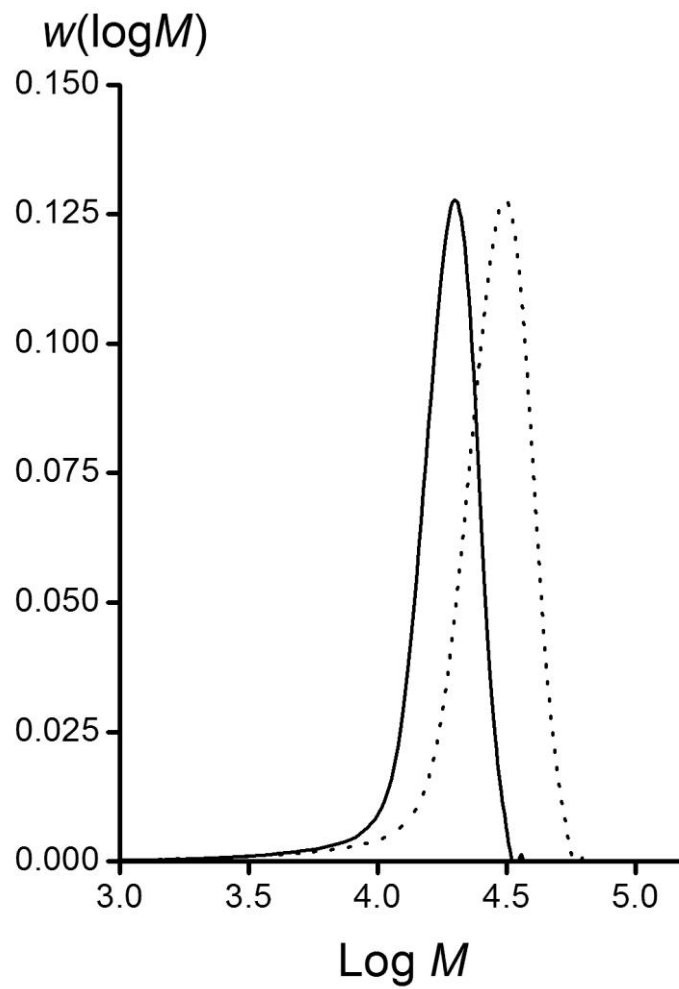


Figure 4: MWD $w(\log M) = f(\log M)$ for simulated controlled polymerization considered as the true MWD (full line, $M_n = 14,900$, $PDI = 1.25$, $K = 3$, $a = 0.8$ for the polymer sample) and converted in apparent MWD (dotted line, $M_n = 16,000$, $PDI = 1.77$, $K = 30$, $a = 0.5$ for the standard).

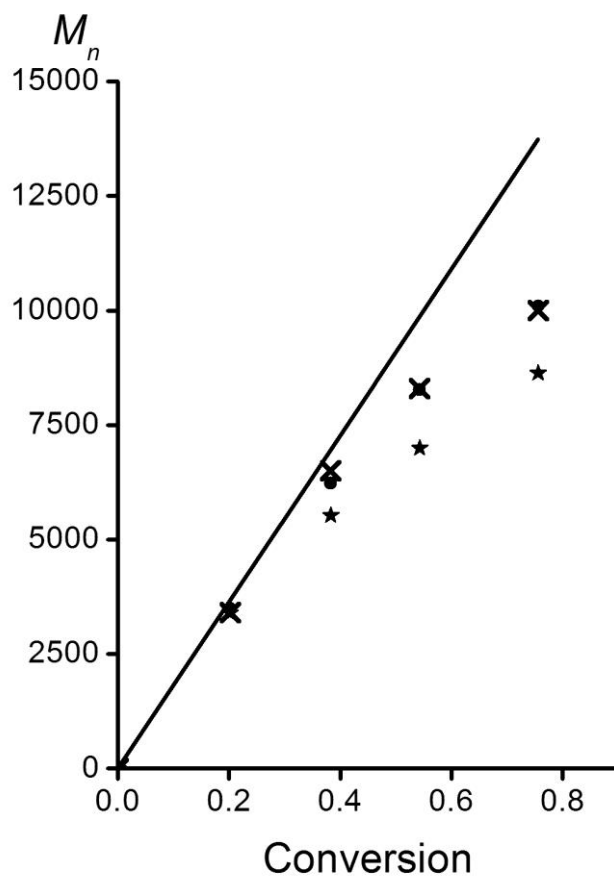


Figure 5: M_n vs Conversion plot. (●) True M_n for simulated controlled polymerization with transfer reaction. (×) M_n obtained with an apparent calibration curve ($K=3, a=0.8$ for the polymer sample and $K=30, a=0.5$ for the standard). (★) M_n obtained with an apparent calibration curve ($K=30, a=0.5$ for the polymer and $K=3, a=0.8$ for the standard) (—) Theoretical M_n .

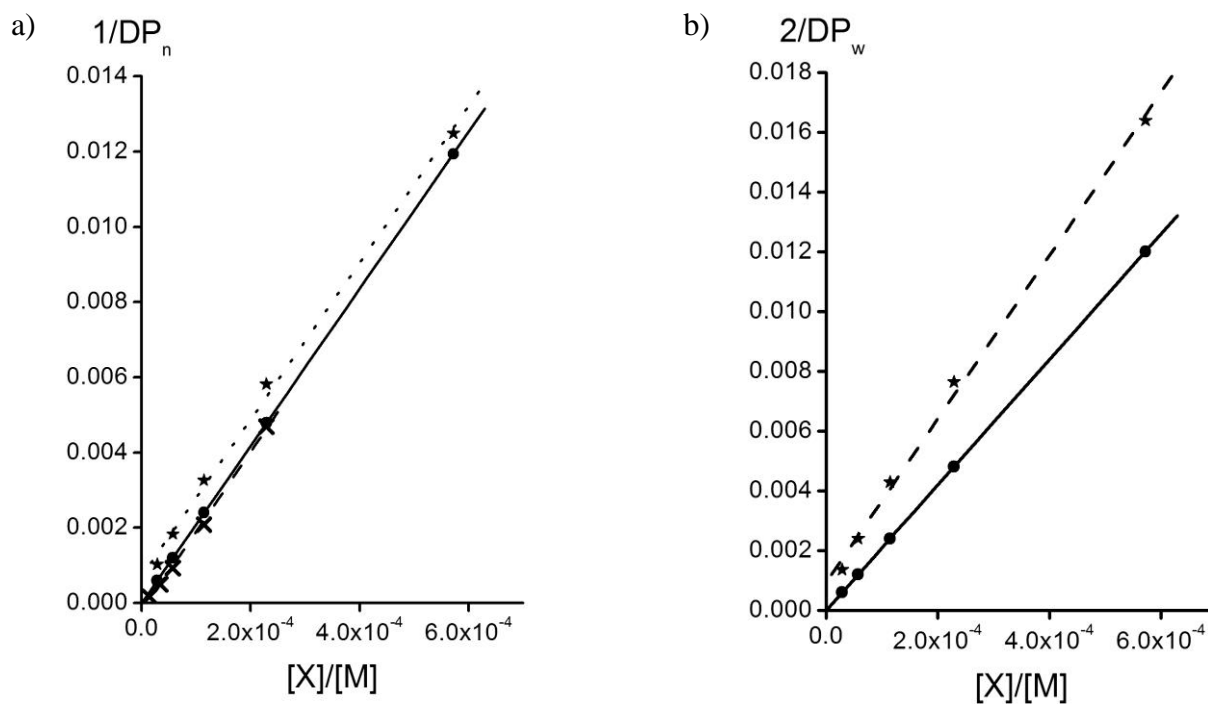


Figure 6: Mayo plots, $1/DP_n$ (a) and $2/DP_w$ (b) against the ratio of the concentration of the transfer agent to the monomer. (●) true MW for Flory-Schulz distributions. (×) MW when the eluent is a better solvent for the polymer sample than the standard ($K=3$, $a=0.8$ for the polymer sample and $K=30$, $a=0.5$ for the standard). (☆) MW when the eluent is a better solvent of the standard than the polymer sample ($K=30$, $a=0.5$ for the polymer sample and $K=3$, $a=0.8$ for the standard).

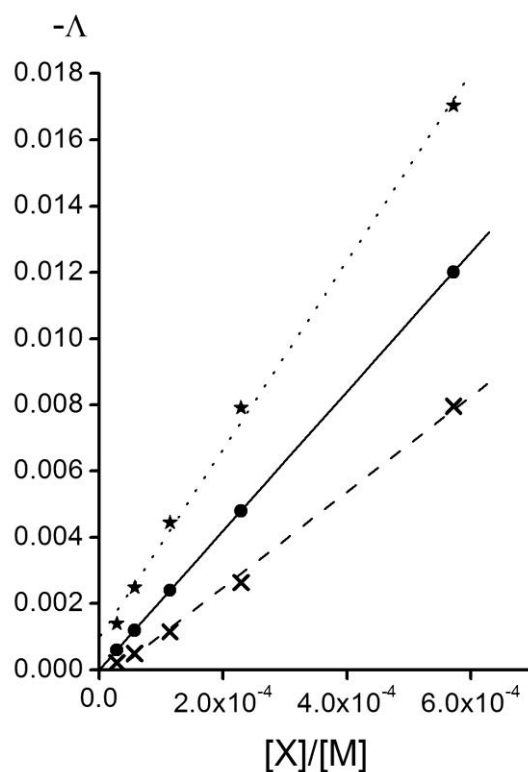


Figure 7: Slope of the $\ln P$ plots, $-\Lambda$, against the ratio of the concentration of the transfer agent to the monomer: (●) slopes from the true $\ln P$, (×) slope of the apparent $\ln P$ when the eluent is a better solvent for the polymer sample than the standard ($K=3$, $a=0.8$ for the polymer sample and $K=30$, $a=0.5$ for the standard) (★) slope of the apparent $\ln P$ when the eluent is a better solvent of the standard than the polymer sample ($K=30$, $a=0.5$ for the polymer sample and $K=3$, $a=0.8$ for the standard).

Table 1: Comparison of the apparent and true transfer constants (theoretical value 21) and correlation number obtained with the graphical Mayo technique (M_n and $M_w/2$) and the CLD method.

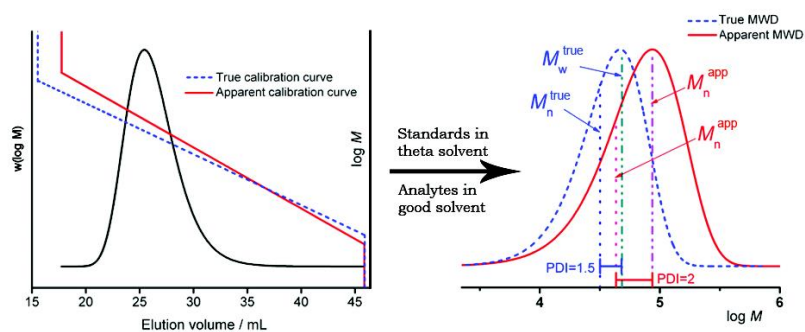
		Mayo with M_n		Mayo with $M_w/2$		Chain Length Distribution	
		C_{tr} (relative difference) ^a	R^2	C_{tr} (relative difference) ^a	R^2	C_{tr} (relative difference) ^a	R^2
True MW		20.94 (-0.29 %)	1	20.99 (-0.05 %)	1	20.99 (-0.05 %)	1
Apparent MW	K= 30, a = 0.5 for the polymer and K= 3, a = 0.8 for the standard	21.13 (0.62 %)	0.9962	27.34 (26,2 %)	0.9971	28.43 (30 %)	0.9972
	K= 3, a = 0.8 for the polymer and K= 30, a = 0.5 for the standard	21.23 (1.1 %)	0.9977	-	-	14.40 (-37,3 %)	0.9966

^a relative difference = $2 \times (\text{experimental } C_{tr} - \text{theoretical } C_{tr}) / (\text{experimental } C_{tr} + \text{theoretical } C_{tr})$

Table 2. Apparent transfer constants (theoretical value 21) obtained with the Mayo equation (M_n and $M_w/2$) and the Chain Length Distribution (CLD) equation with $K=30$, $a = 0.5$ for the polymer and $K= 3$, $a = 0.8$ for the standard.

[1-butanethiol] ₀ (mol·L ⁻¹)	C_{tr} using the Mayo equation (M_n)	C_{tr} using the Mayo equation ($M_w/2$)	C_{tr} using the CLD method
5.0×10^{-3}	21.8	28.7	29.8
2.0×10^{-3}	25.4	33.4	34.6
1.0×10^{-3}	28.6	37.5	38.9
5.0×10^{-4}	32.1	42.1	43.6
2.5×10^{-4}	36.1	47.5	49.0

Graphical Abstract.



Apparent Molecular Weights (MWs) from SEC are still widely used. Calculations corresponding to realistic cases in the field of controlled/living polymerization allow to compare true and apparent MW. Guidelines are proposed based of the quality of the eluent as a solvent for the standard and the polymer sample e.g as an indication of the significance of the apparent polydispersity index. The determination of transfer constants by the traditional Mayo plot can be safely performed using apparent M_n , whereas the use of apparent M_w or apparent ln number distribution, $\ln P$, leads to inaccurate transfer constants.

Supporting Information

for

Using apparent Molecular Weight from SEC in controlled/living polymerization and kinetics of polymerization

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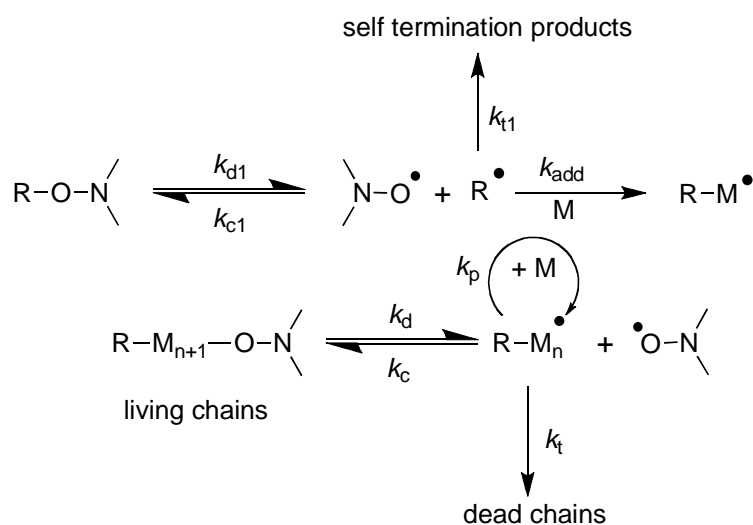
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1 Simulation of nitroxide-mediated polymerization

Realistic MWDs ($w(\log M)$ against $\log M$) for controlled radical polymerization were generated by using the PREDICI[®] software.¹ This software has been proved to be efficient to describe all the controlled radical techniques such as nitroxide mediated polymerization (NMP)^{2,3}, atom transfer radical polymerization (ATRP)⁴ and reversible addition fragmentation chain transfer (RAFT)⁵ experiments. For the sake of simplicity, we used only one CRP technique to simulate different MWDs, the others should give very similar results. Nitroxide-mediated polymerization (NMP) is widely used in the literature, its kinetics mechanism is well known and is based on the reversible dissociation of a (macro)alkoxyamine (scheme 1), which forms a (macro)radical and a nitroxide.⁶



Scheme 1. Mechanism of the NMP

This mechanism was simulated accurately using PREDICI^{®2,3} and the key parameter lies in a pseudo equilibrium constant $K^{\text{eq}} = k_d/k_c$ (the ratio between respectively the dissociation and recombination rate constant). The range of possible k_d and k_c values being well known,⁷ it is possible to model special cases such as

polymerization with a poor initiation efficiency, polymerization with transfer either to the monomer or to solvent, etc. For the sake of simplicity, the penultimate effect⁸ was disregarded and it was assumed that the rate constants were chain length independent although this introduces some inaccuracies in the dissociation rate coefficient k_d ,⁹ the propagation rate coefficient k_p ,¹⁰ the termination rate coefficient k_t ¹¹ and k_c . The rate coefficients used for the different modeling studies are listed in Table 1.

- **Poorly-controlled polymerization:** A poorly-controlled polymerization was simulated using the kinetic parameters given in Table 1 (entry 1). An inadequate (too high) equilibrium constant $K^{eq} = k_d/k_c = 10^{-7} \text{ L}\cdot\text{mol}^{-1}$, a high termination rate constant ($5.0 \times 10^8 \text{ L}\cdot\text{mol}^{-1}$) and a dissociation rate constant for the initiating alkoxyamine lower than that of the macroalkoxyamine were used.
- **Perfectly controlled polymerization:** A perfectly controlled and living system was simulated using equilibrium constant $K^{eq} = k_d/k_c = 10^{-9} \text{ L}\cdot\text{mol}^{-1}$ close to $K^{perfect} = 1.1 \times 10^{-9} \text{ L}\cdot\text{mol}^{-1}$, see Table 1- entry 2)¹².
- **Polymerization with a low efficiency:** A polymerization suffering from poor initiation efficiency was simulated using the kinetic parameters given in the Table 1, entry 3 in the main text. The poor efficiency was obtained by decreasing the k_c value of the initiating alkoxyamine and by increasing the k_d value. This leads to a higher concentration of radicals during the initiation. Decreasing the value of the kinetics constant related to the first addition increases the probability of the irreversible termination of the primary radical against propagation. This results in true M_n values above the theoretical curve (Figure 3, empty circles). Since the apparent M_n lie below the true value with these SEC conditions, the plot of the apparent M_n against conversion can completely hide the initiation problem (Figure 3, empty squares). While the true initiation efficiency is close to 80 %; the apparent

one can be increased up to 100 %.

- **Controlled Polymerization:** A quite living (67 % of living fraction for 82.5 % of conversion) and controlled (PDI = 1.25) polymerization was simulated and the kinetic parameters are given in Table 1 entry 4.
- **Perfectly controlled polymerization with transfer:** Transfer to solvent with the same kinetic constants as in Table 1, entry 3 but adding a transfer reaction to the solvent ($[S]_0 = 5.0 \text{ mol}\cdot\text{L}^{-1}$; $C_{tr} = 2.5 \times 10^{-3}$).

Table 1. Kinetic parameters used for the PREDICI[®] simulation.

	Entry 1 ^{a,b}	Entry 2 ^{a,c}	Entry 3 ^a	Entry 4 ^{a,d}
k_{d1} (s^{-1})	$5.0 \cdot 10^{-2}$	$8.0 \cdot 10^{-2}$	0.3	$5.0 \cdot 10^{-2}$
k_{c1} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	$5.0 \cdot 10^6$	$5.0 \cdot 10^6$	$1.0 \cdot 10^6$	$5.0 \cdot 10^6$
k_{add} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	$8.0 \cdot 10^2$	$8.0 \cdot 10^3$	$8.0 \cdot 10^2$	$8.0 \cdot 10^3$
k_{t1} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	$2.0 \cdot 10^9$	$2.0 \cdot 10^9$	$2.0 \cdot 10^9$	$2.0 \cdot 10^9$
k_p ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	2000	2000	2000	2000
k_d (s^{-1})	$1.0 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$
k_c ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	$1.0 \cdot 10^5$	$5.0 \cdot 10^6$	$5.0 \cdot 10^6$	$5.0 \cdot 10^5$

$$k_t^e \quad \left| \quad 5.0 \cdot 10^8 \quad \right| \quad \left| \quad 2.0 \cdot 10^8 \quad \right| \quad \left| \quad 2.0 \cdot 10^8 \quad \right| \quad \left| \quad 2.0 \cdot 10^8 \quad \right|$$

(L·mol⁻¹·s⁻¹)

^a Bulk Polymerization (i.e. $[M]_0 = 8.74 \text{ mol.L}^{-1}$) at 120 °C. ^b Duration of the experiment = 14 000 s. 79.6 % conversion obtained. ^cA polymerization in solvent (1/1 : v/v) has been carried out and the concentration of the solvent has been taken to 5.0 mol.L⁻¹. ^d Duration of the experiment = 14 000 s. 82.5 % conversion obtained. ^e For the sake of simplicity, the termination mode in the styrene polymerization is assume to be only combination.

2 Transfer-dominated polymerization (Schulz-Flory Distribution).

In a chain polymerization, when transfer is the main chain-stopping event, a probability factor α of propagation is defined as the probability of chain growth over chain-stoppage and corresponds to the ratio of the rate of propagation over the sum of the rates of all possible stoppage reactions the macroradical can undergo:¹³

$$\alpha = \frac{R_p}{R_p + R_{tr}} = \frac{k_p[M]}{k_p[M] + k_{tr}[X]} \quad (1)$$

with R_p is the rate of propagation and R_{tr} is the rate of transfer to a species X.

The probability of obtaining a macromolecule of chain length i and therefore the number distribution P_i is given by the following equation, counting $i-1$ propagation steps and one chain-stoppage step.

$$P_i = \alpha^{i-1}(1 - \alpha) \quad (2)$$

The average MW or degree of polymerization (DP) can be evaluated by calculating the moments of this distribution function and the PDI can be determined from the ratio of the weight and number averages DP_w and DP_n :

$$DP_n = \frac{1}{1-\alpha} \text{ and } DP_w = \frac{1+\alpha}{1-\alpha}, \text{ thus PDI} = 1+\alpha \quad (3)$$

When α tends towards 1, we can assume that $\alpha \approx \exp(\alpha-1)$ which from eq 2 leads to the following equation for the number molecular distribution:

$$P_i = \frac{1}{DP_n} \alpha^{i-1}, \text{ thus } \lim_{\alpha \rightarrow 1} P_i = \frac{1}{DP_n} \exp(i(\alpha-1)) \text{ and } \lim_{\alpha \rightarrow 1} (\ln P_i) = -\ln DP_n + i(\alpha-1) \quad (4)$$

The limiting values for high α and high DP gives an exponential function for P and a PDI close to 2:

$$\lim_{\alpha \rightarrow 1} (\ln P_i) = -\ln \left(\frac{k_p [M]}{k_r [X]} \right) - i \left(\frac{k_r [X]}{k_p [M]} \right) \quad (5)$$

In this limit, one has a continuum of DP s, for which we use N as the continuous variable replacing i as an integer, or equivalently the continuous variable $M = N \times M_0$, where M_0 is the molecular weight of the monomer unit. The chain transfer rate constant can be determined by plotting the inverse of the slope of number chain length distribution $\lambda = d \ln P(M) / dM$ versus the ratio $[X]/[M]$.¹³⁻¹⁵

Instead of arbitrarily choosing values, the rate coefficients in the present work correspond to a bulk styrene polymerization at 60 °C ($[M]_0 = 8.74 \text{ mol}\cdot\text{L}^{-1}$; $k_p = 341 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) with 1-butanethiol as transfer agent ($C_{tr} = k_{tr}/k_p = 21$).¹⁶

3 Importance of the polynomial order of the calibration curve

All the results presented in the main text were obtained assuming that the calibration curve is linear. SEC calibration curves are generally fitted with a third order polynomial function, especially if one takes into account a broad range of MW, which is necessary to determine accurate average MWs.¹⁷ The shape of the calibration curve affect the shape of $w(\log M)$ as described by the equation:¹⁸

$$S_{\text{DRI}}(V_e) \equiv \frac{d \log M}{dV_e} \times w(\log M) \quad (6)$$

where V_e is the elution volume and $S_{\text{DRI}}(V_e)$ the signal from the refractometer (or any mass-sensitive detector).

It was thus important to examine whether the shape of the calibration curve can induce a difference between the true and apparent $w(\log M)$. The relation between the two calibration curves is given by:

$$\text{Log } M^{\text{app}} = \frac{1}{a' + 1} \log \frac{K}{K'} + \frac{a + 1}{a' + 1} \log M, \quad (7)$$

where M^{app} is the apparent MW, K' and a' are the MHKS parameters of the standards, K and a are the MHKS parameters of the studied polymer,

Any difference would arise from differences between the derivatives of the calibration curves: $d \log M / dV_e$ and $d \log M^{\text{app}} / dV_e$. The relation between these two quantities is:

$$\frac{d \log M^{\text{app}}}{dV_e} = \left(\frac{a + 1}{a' + 1} \right) \frac{d \log M}{dV_e} \quad (8)$$

The two quantities being directly proportional, the shape of the calibration curve cannot induce any difference between the apparent and true average MW or even the MWD after normalization. The results and conclusions presented in this work are thus independent of the order of the calibration curve. In consequence, it will be considered for the following of this work that $w(\log M^{\text{app}})$ and $w(\log M)$ are the same.

4 Example of calculation for the determination of true and apparent MWD when using PREDICI (results presented in Figure 1)

SEC MWDs ($w(\log M)$ against M) for controlled radical polymerization were

simulated using the PREDICI[®] software.¹ The rate coefficients used for this simulation are given in table 1, entry 1 in the supporting information.

The calculation sheet is the following (only the very first few lines are displayed):

input PREDICI		True MW			Apparent MW				
M (g.mol ⁻¹)	w(log M)	log M	W(M)	P(M)	w(log M _{app})	M _{app}	W(M _{app})	P(M _{app})	log M _{app}
1.04E+02	5.73E-06	2.02E+00	5.51E-08	5.30E-10	5.73E-06	1.72E+02	3.33E-08	1.93E-10	2.24E+00
5.20E+02	1.30E-04	2.72E+00	2.49E-07	4.80E-10	1.30E-04	6.59E+02	1.97E-07	2.99E-10	2.82E+00
1.04E+03	4.60E-04	3.02E+00	4.42E-07	4.25E-10	4.60E-04	1.17E+03	3.92E-07	3.34E-10	3.07E+00
1.56E+03	9.23E-04	3.19E+00	5.92E-07	3.79E-10	9.23E-04	1.65E+03	5.61E-07	3.41E-10	3.22E+00
2.08E+03	1.47E-03	3.32E+00	7.08E-07	3.41E-10	1.47E-03	2.09E+03	7.04E-07	3.37E-10	3.32E+00
2.60E+03	2.08E-03	3.41E+00	8.00E-07	3.08E-10	2.08E-03	2.52E+03	8.25E-07	3.27E-10	3.40E+00

We first determined the $W(M)$ and $P(M)$ by $W(M)=w(\log M)/M$ and $P(M)= W(M)/M$.

The true M_n , M_w and PDI are determined using $M_n = \sum(W(M))/ \sum(P(M))$; $M_w = \sum(w(\log M))/ \sum(W(M))$ and $PDI = M_w/M_n$.

$$M_n = 14,400 \text{ g.mol}^{-1}; M_w = 25,700 \text{ g.mol}^{-1}; PDI = 1.80$$

To convert the true MW into the apparent MW we used:

$$w(\log M^{\text{app}}) = w(\log M)$$

$$\log M^{\text{app}} = \frac{1}{a' + 1} \log \frac{K}{K'} + \frac{a + 1}{a' + 1} \log M$$

with $K= 30$, $a = 0.5$ for the polymer and $K' = 3$, $a' = 0.8$ for the standard.

The $W(M^{\text{app}})$ and the $P(M^{\text{app}})$ are calculated using: $W(M^{\text{app}})=w(\log M^{\text{app}})/M^{\text{app}}$ and $P(M^{\text{app}})= W(M^{\text{app}})/M^{\text{app}}$.

The apparent M_n , M_w and PDI are determined using $M_n^{\text{app}} = \sum(W(M^{\text{app}}))/ \sum(P(M^{\text{app}}))$;

$$M_w^{\text{app}} = \sum(w(\log M^{\text{app}})) / \sum(W(M^{\text{app}})) \text{ and } \text{PDI} = M_w^{\text{app}} / M_n^{\text{app}}.$$

$$M_n^{\text{app}} = 12,900 \text{ g.mol}^{-1}; M_w = 17,400 \text{ g.mol}^{-1}; \text{PDI} = 1.35$$

5 Example of calculation for the determination of true and apparent MWD in the case of a transfer-controlled polymerization

MWDs ($\log P(M)$ against M) for transfer dominated polymerizations were obtained using the equation 3.¹³ The rate coefficients used for this simulation are given in the main text, section 2.2. (and correspond to realistic values, i.e. bulk styrene polymerization at 60 °C ($[M]_0 = 8.74 \text{ mol.L}^{-1}$; $k_p = 341 \text{ L.mol}^{-1} \text{ s}^{-1}$) with 1-butanethiol as transfer agent ($C_{\text{tr}} = k_{\text{tr}}/k_p = 21$).¹⁶

The calculation sheet is the following (only very first few lines displayed):

input		True MW				Apparent MW				
M (g.mol-1)	log P(M)	P(M)	W(M)	w(log M)	log M	w(log Mapp)	Mapp	W(Mapp)	N(Mapp)	log Mapp
104	-2.40E-03	9.98E-01	1.04E+02	1.08E+04	2.02E+00	1.08E+04	172.4	6.26E+01	3.63E-01	2.24E+00
208	-4.81E-03	9.95E-01	2.07E+02	4.31E+04	2.32E+00	4.31E+04	307.1	1.40E+02	4.57E-01	2.49E+00
312	-7.21E-03	9.93E-01	3.10E+02	9.66E+04	2.49E+00	9.66E+04	430.5	2.24E+02	5.21E-01	2.63E+00
416	-9.61E-03	9.90E-01	4.12E+02	1.71E+05	2.62E+00	1.71E+05	547.2	3.13E+02	5.72E-01	2.74E+00
520	-1.20E-02	9.88E-01	5.14E+02	2.67E+05	2.72E+00	2.67E+05	659.0	4.05E+02	6.15E-01	2.82E+00
624	-1.44E-02	9.86E-01	6.15E+02	3.84E+05	2.80E+00	3.84E+05	767.1	5.00E+02	6.52E-01	2.88E+00
728	-1.68E-02	9.83E-01	7.16E+02	5.21E+05	2.86E+00	5.21E+05	872.3	5.97E+02	6.85E-01	2.94E+00
832	-1.92E-02	9.81E-01	8.16E+02	6.79E+05	2.92E+00	6.79E+05	975.0	6.96E+02	7.14E-01	2.99E+00
936	-2.16E-02	9.79E-01	9.16E+02	8.57E+05	2.97E+00	8.57E+05	1075.5	7.97E+02	7.41E-01	3.03E+00
1040	-2.40E-02	9.76E-01	1.02E+03	1.06E+06	3.02E+00	1.06E+06	1174.2	8.99E+02	7.66E-01	3.07E+00

We first determined the $W(M)$ and $w(\log M)$ by $W(M) = P(M) \times M$ and $w(\log M) = W(M) \times M$.

The true M_n , M_w and PDI are determined using $M_n = \sum(W(M)) / \sum(P(M))$; $M_w =$

$\Sigma(w(\log M))/\Sigma(W(M))$ and $PDI = M_w/M_n$.

$M_n = 43,400 \text{ g.mol}^{-1}$; $M_w = 86,600 \text{ g.mol}^{-1}$; $PDI = 2.0$

To convert the true MW into the apparent MW, we used:

$$w(\log M^{\text{app}}) = w(\log M)$$

$$\log M^{\text{app}} = \frac{1}{a' + 1} \log \frac{K}{K'} + \frac{a + 1}{a' + 1} \log M$$

with $K = 30$, $a = 0.5$ for the polymer and $K' = 3$, $a' = 0.8$ for the standard.

The $W(M^{\text{app}})$ and the $P(M^{\text{app}})$ are calculated using: $W(M^{\text{app}}) = w(\log M^{\text{app}})/M^{\text{app}}$ and

$$P(M^{\text{app}}) = W(M^{\text{app}})/M^{\text{app}}.$$

The apparent M_n , M_w and PDI are determined using $M_n^{\text{app}} = \Sigma(W(M^{\text{app}}))/\Sigma(P(M^{\text{app}}))$;

$$M_w^{\text{app}} = \Sigma(w(\log M^{\text{app}}))/\Sigma(W(M^{\text{app}})) \text{ and } PDI = M_w^{\text{app}}/M_n^{\text{app}}.$$

$M_n^{\text{app}} = 31,800 \text{ g.mol}^{-1}$; $M_w = 48,500 \text{ g.mol}^{-1}$; $PDI = 1.50$.

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