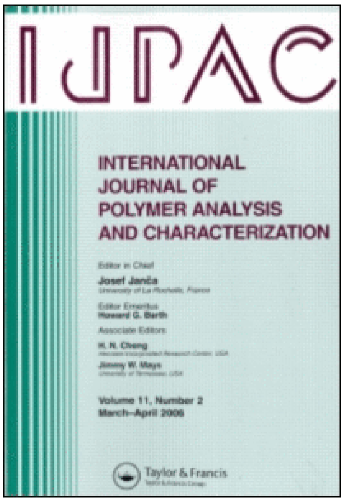

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An Approximation for the Intrinsic Viscosity of Brush-Shaped Polymers

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Abstract: The dependence of the intrinsic viscosity $[\eta]$ on molecular weight and side-chain length for brush-shaped polymers is analyzed using a simplified expression for $[\eta]$, in which a brush-shaped polymer is modeled as a linear chain with a contour length equal to that of the backbone of the brush-shaped chain and a repeat unit molar mass that includes the molar mass of the side chain. The treatment is used to estimate the ratio $\hat{a}/\hat{a}_{\mathrm{ref}}$ of the persistence length $\hat{a}$ of the brush-shaped chain relative to a reference chain as a function of side-chain molecular weight. Values of $\hat{a}/\hat{a}_{\mathrm{ref}}$ deduced for data on a series of brush-shaped polymers are found to be in good accord with values derived in a more complete treatment of the dependence of $[\eta]$ on M based on the wormlike chain model. Estimates of $\hat{a}/\hat{a}_{\mathrm{ref}}$ are also given for a series of poly(alkyl methacrylate) chains as a function of the alkyl chain length, and the approximate expression is applied to the evaluation of the true molecular weight from the apparent molecular weight determined in a size exclusion chromatography analysis based on the calibration of the columns in terms of the molecular weight of a standard polymer.

Keywords: Brush-shaped; Intrinsic viscosity; Persistence length

INTRODUCTION

The development of controlled radical polymerizations (CRP) has augmented the role of anionic polymerizations in the ability to synthesize

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polymers with well-controlled structure and narrow molecular weight and shape distributions.[1] One example of this is the polymerization of brush-shaped polymers, in which every repeat unit bears a side chain that is short compared to the length of the backbone, i.e., a densely branched comb-shaped chain. Among other applications, structures of this type have been devised as components in polymers characterized by an unusually low equilibrium modulus.[2] The purpose here is to note an expression for the dependence of the intrinsic viscosity $[\eta]$ on the molecular weights M_{bb} and M_{sc} of the backbone and the side chains, respectively, that can provide a useful approximation over a range of these parameters, provided these components are fully miscible, and $M_{sc} \ll M_{bb}$. In essence, this expression is a special case of the application of the wormlike chain model that has been applied to correlate $[\eta]$ with chain structure for brush-like chains without the $M_{sc} \ll M_{bb}$ constraint.[3,4] The expression to be developed is in the form of the Mark-Houwink-Sakarada (M-H-S) relation with $[\eta] = kM^{\mu}$, with emphasis on the dependence of the M-H-S constant k on effects related to M_{sc}.

THE APPROXIMATION TO THE M-H-S CONSTANT K

As a general form, it is useful to represent the dependence of $[\eta]$ on the molecular weight M, the mean-square radius of gyration R_G, the hydrodynamic radius R_H, and a function K by the expression[5]

$$[\eta] = \pi N_A K R_G^2 R_H / M \qquad (1)$$

For example, with the wormlike chain model that might be expected to apply for brush-shaped polymers in a dilute solution, R_G can be expected to depend on the chain structure (e.g., linear, branched, etc.), the persistence length â, and the ratios L/â and d_T/â, with L and d_T the contour length and a thermodynamic length, respectively, specified in more detail below. For the same model, R_H may be expected to depend on these same parameters, as well as the ratio d_H/â, where d_H is the diameter of the relevant hydrodynamic repeat unit, and K may exhibit a relatively weak dependence on these same parameters, being in the range 1 for a low molecular weight chain to a limiting value $K \approx 10/3$ for a fully linear flexible chain polymer.[5] For the Flory theta condition, d_T is zero, but d_T tends to the geometric diameter d_G of the chain repeat unit for solutions of nonioinic polymers in so-called "good solvents," for which, for example, the second virial coefficient A_2 tends to proportionality with R_G^3/M^2 independent of M for a homologous polymer series of flexible chain polymers.[6] In this expression, the factor $N_A M^{-1}$ is present simply because the concentration units used in the determination of $[\eta]$ are in wt/vol rather than the number density of the solute. For a linear chain, M may be replaced by L/M_L where L is the chain contour length and $M_L = m_0/l_0$, where m_0 is the molar mass of the chain repeat with length l_0, leading to the trivial, but very useful, transformation of Equation (1) to read

$$M_L[\eta] = \pi N_A K R_G^2 R_H / L \tag{2}$$

Furthermore, for linear chains with persistence $\hat{a} \ll L$, one has $R_H \propto R_G$ and $K \approx 10/3$, and for monodispersed linear chains, application of the wormlike chain model for "good solvent" conditions with the same constraints imposed above gives[6]

$$R_G = (La/3)^{1/2}\alpha \tag{3a}$$

$$\alpha \propto z^{2b} \tag{3b}$$

$$z \propto (d_T/\hat{a})(L/\hat{a})^{1/2} \tag{3c}$$

With these approximations, $[\eta]$ for the wormlike chain model may be reduced to the form

$$M_L[\eta] \propto K(L\hat{a})^{3/2}\{(d_T/\hat{a})^2(L/\hat{a})\}^{3b}/L \tag{4}$$

with K and b constants, but M_L, d_T, and $\hat{a}$ all potentially dependent on m_0 in the behavior for a series of homologous polymers differing in m_0 due to the presence of side chains of different molecular weights. Under Flory theta conditions, $\alpha = 1$, $b = 0$, and the factor in curly brackets in Equation (4) should be set equal to unity. These expressions may not apply for solutions in so-called "mediocre solvents," for which A_2M^2/R_G^3 is neither zero nor near its limiting value.

Equation (4), which may be recognized as an adaptation of the well-known Flory-Fox expression,[7,8] will be applied here in the form of the M-H-S expression, with an expression for k adapted to our purpose:

$$[\eta] = kM^{\mu} \tag{5a}$$

$$k \propto \hat{a}^{3(1-\mu)} d_T^{2\mu-1} / M_L^{1+\mu} \tag{5b}$$

with M the molecular weight of the polymer, and $\mu = 1/2 + 3b$ the usual M-H-S exponent defined as $\partial \ln[\eta]/\partial \ln M$; Equation (5b) is written for a good solvent condition, and under Flory theta conditions the factor $d_T^{2\mu-1}$ should be replaced by unity. The prediction of μ and $\hat{a}$ are beyond the simple treatment presented here, requiring a more complete model, such as the wormlike chain or more complex representations;[9] it may be noted that under Flory theta conditions, $\mu = 1/2$, and the dependence on d_T is suppressed. In the limit of a very good solvent, $\mu \approx 4/5$ for a nonionic flexible chain. Furthermore, although prediction of d_T is in general beyond current theory, $d_T = 0$ under Flory theta conditions, and as noted above, in the good solvent conditions assumed here, for nonionic components, $d_T \approx d_G$.

In the simplification of interest here, the brush-shaped chains with $M_{bb} \gg M_{sc}$ and $L/\hat{a} \gg 1$ are treated as linear chains with relatively high molecular weight side chains on (nearly) every repeat unit, so that the contour length to be used in the preceding expressions is given by $L/l_0 = M_{bb}/m_{0,bb} = M/m_0$, where $m_0 = m_{0,bb} + M_{sc}$, with $m_{0,bb}$ the molar mass of the backbone chain devoid of its side chains, i.e., in Equation (5b), $M_L = (m_{0,bb} + M_{sc})/l_0$. The expression for k will be applied in the following to evaluate the dependence of $\hat{a}$ on M_{sc}, relative to $\hat{a}_{ref}$ for a reference chain comprising the backbone devoid of its side chains. In this approximation, one can expect that d_T will also depend on M_L, as discussed in the following. The ratio $\hat{a}/\hat{a}_{ref}$ will be determined from data on $[\eta]$ as a function of M over a range of M_{sc} for a brush-shaped polystyrene, along with a similar analysis for data on poly(alkyl methacrylates) for chains with increasing alkyl chain length. Finally, the interpretation of data obtained in size exclusion chromatography (SEC) will be considered.

PERSISTENCE LENGTH

The data for $[\eta]$ as a function of M for the brush-shaped polystyrenes alluded to above, for which the twin stipulations M_{bb} and M_{sc} and $L/\hat{a} \gg 1$ are valid, are reproduced in Figure 1 for solutions in the good solvent toluene and the theta solvent cyclohexane (T = 34.5°C).[3,4] It may be noted that μ appears to be essentially independent of M_{sc} for the higher molecular weight samples. These same data are shown again in Figure 2 after application of a "vertical shift" log q on the bilogarithmic plot to force a superposition of the data at the higher molecular weights with the correlation for anionically synthesized linear polystyrene.[10] Using the expression for k given above, under good solvent conditions,

$$q^{-1} = k/k_{ref} = (M_{L,ref}/M_L)^{1+\mu}(\hat{a}/\hat{a}_{ref})^{3(1-\mu)}(d_T/d_{T,ref})^{2\mu-1} \qquad (6)$$

with the data for polystyrene providing the reference for the polystyrene brush-like chains; as above, under Flory theta conditions, the factor $(d_T/d_{T,ref})^{2\mu-1}$ is set equal to unity. Since it is anticipated that d_T will increase with increasing M_{sc} under good solvent conditions, in the following the approximation $d_T/d_{T,ref} = (M_L/M_{L,ref})^{\nu}$ is adopted for

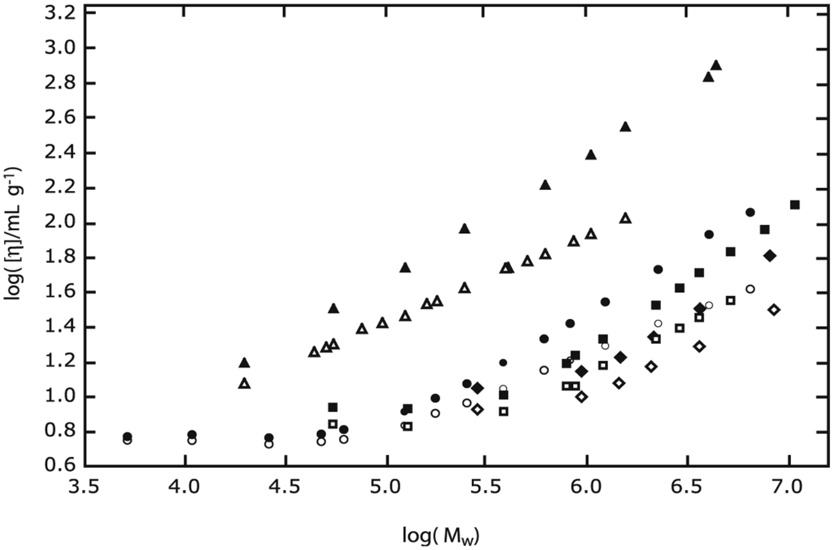

Figure 1. Bilogarithmic plot of $[\eta]$ vs. M_w for solutions in toluene and cyclohexane at the Flory theta condition for linear polystyrenes and brush-shaped polystyrenes for three values of $M_{w.sc}$, equal to 77, 1,755, 3,523, and 6,955 for the triangles, diamonds, circles, and squares, respectively, and for solutions in cyclohexane (white) and toluene (black). Data are from Terao et al.[3] Hokajo et al.[4] and Berry.[10]

such systems. The values of $\hat{a}/\hat{a}_{ref}$ determined from the vertical shifts by the application of Equation (5), with $M_L \propto m_0$ and $\nu = 0.5$, are shown in Figure 3 (since only proportionalities are important here, it is not necessary to specify a value for l_0). The results for $\nu = 0$ are also shown for comparison with the data in toluene solution, revealing the substantial effect of the factor $(d_T/d_{T,ref})^{2\mu-1}$ in the good solvent; as noted above, this term is set to unity under Flory theta conditions. The agreement between the values of $\hat{a}$ determined here (with $\nu = 0.5$) and those reported in Hokajo et al.[4] using a full application of the wormlike chain model for data on both $[\eta]$ and R_G is reasonable. A similar result is obtained with data on brush-shaped polystyrenes published earlier,[11] but those are not included here as only a few of those samples meet the twin constraints $M_{bb} \gg M_{sc}$ and $L/\hat{a} \gg 1$. It may be noted for use below that in Figure 3 it can be seen that to a reasonable approximation, $\hat{a} = m_0^{\varepsilon}$, with $\varepsilon \approx 0.85$ for the data in the good solvent toluene. The weaker dependence of $\hat{a}$ on m_0 for the data in the Flory theta solvent than observed in the good solvent may be unexpected in consideration of the higher monomer density under Flory theta conditions, but it may be

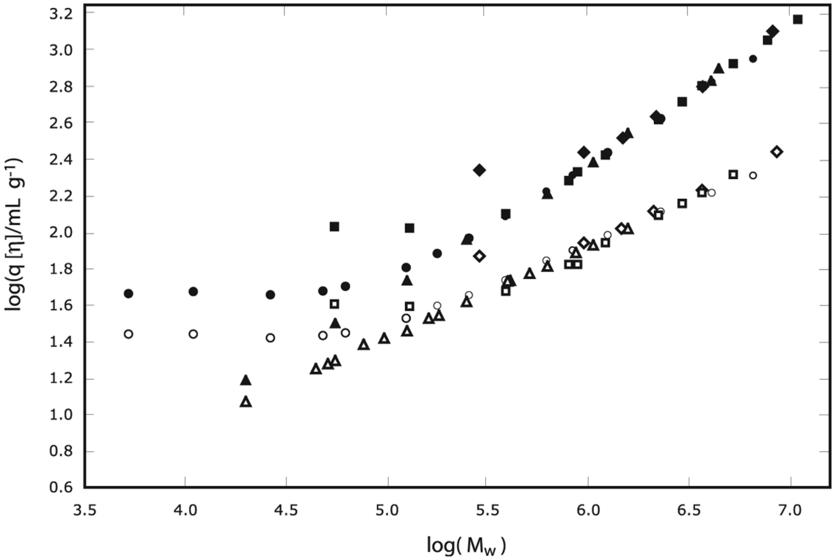

Figure 2. Bilogarithmic plot of q[η] vs. M_w for the data in Figure 1, with q an empirical factor chosen to superpose the data with emphasis on the behavior at high M_w. The symbols are as in Figure 1.

noted that the same trend was obtained using the full analysis based on the wormlike chain model.[4]

It is of interest to apply the preceding procedure to data on a series of vinyl polymers with substituents of variable but still relatively short length. The results obtained for a series of poly(alkyl acrylate)s in solution in tetrahydrofuran (THF)[12] with the data for poly(*n*-butyl acrylate) serving as the reference are given in Figure 4, after application of the vertical shift log q to bring the data as nearly as possible into superposition with the data for poly(*n*-butyl acrylate). Estimates for $\hat{a}/\hat{a}_{\mathrm{ref}}$ based on these data on q and the preceding expressions are included in Figure 5, with $d_T/d_{T,\mathrm{ref}} = (M_L/M_{L,\mathrm{ref}})^{\nu}$, for both $\nu \approx 0.5$ and $\nu = 0$; owing to the reduced range of $M_L/M_{L,\mathrm{ref}}$ for these polymers the choice of the parameter ν has a relatively small effect on the estimate of $\hat{a}/\hat{a}_{\mathrm{ref}}$ The near independence of $\hat{a}$ on m_0 for side chains longer than butyl and the trend in $\hat{a}$ for the isomers of the butyl esters using $\nu = 0.5$ seem reasonable, as does the increase in $\hat{a}$ in proceeding from the normal to iso- to tertiary butyl esters. Additional data are available in Penzel and Goetz[12] for estimates of $R_{G,LS}$ as a function of M_w for determination by light scattering, along with approximate corrections to account for molecular weight polydispersity. Application of the

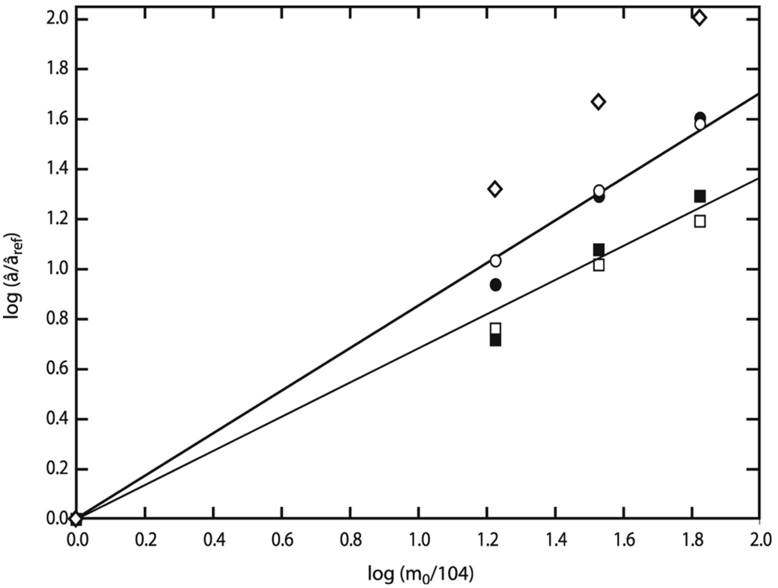

Figure 3. Bilogarithmic plot of $\hat{a}/\hat{a}_{pstyr}$ vs. $m_0/104$ calculated with the q used in Figure 2 as discussed in the text (white points). Data from Terao et al.[3] and Hokajo et al.[4] based on an analysis using the wormlike chain model for the dependence of $[\eta]$ and R_G are included for comparison (black points). The circles and the squares are for data in toluene and cyclohexane, respectively, with $\nu = 0.5$ for the data in toluene solution; the diamonds show the latter with $\nu = 0$ for comparison.

expressions given above gives

$$R_G = k_R M^\gamma \tag{7a}$$

$$k_R \propto M_L^{-\gamma} \hat{a}^{2-3\gamma} d_T^{2\gamma-1} \tag{7b}$$

with $\gamma = 1/2 + b$, where $3b = \mu - 1/2$, or $\gamma = (1+\mu)/3$ for consistency with the expression for $[\eta]$ if neither K nor R_H/R_G depend on M. Similar to the procedure used with $[\eta]$, bilogarithmic plots of $\log(R_{G,w})$ versus $\log(M_w)$ are superposed by "vertical" shifts of q_R, with

$$q_R^{-1} = k_R/k_{R,ref} = (M_{L,ref}/M_L)^\gamma (\hat{a}/\hat{a}_{ref})^{2-3\gamma} (d_T/d_{T,ref})^{2\gamma-1} \tag{8}$$

The data on $R_{G,W}/M_W^\gamma$ given in Penzel and Goetz[12] tend to be somewhat scattered, but are superposed to ±20% through the use of Equations (7)–(8) with the same values for μ, $\hat{a}/\hat{a}_{ref}$, and ν used in the analysis of the data on $[\eta]$.

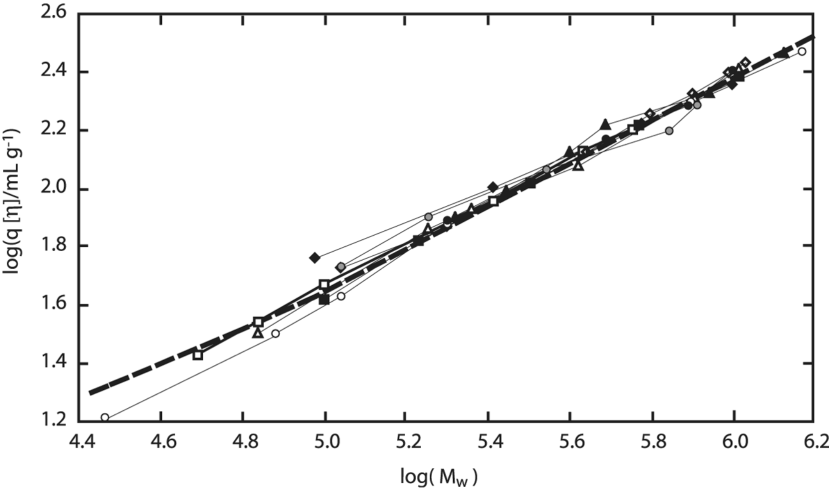

Figure 4. Bilogarithmic plot of q[η] vs. M_w for solutions in THF for a series of poly(alkyl acrylate)s, with a reference of poly(*n*-butyl acrylate). The dashed line represents data for PMMA. The white-filled squares, triangles, and diamonds are for the methyl, ethyl, and butyl esters, respectively, the white-, black-, and grey-filled circles are for the *n*-butyl, *i*-butyl, and *t*-butyl esters, respectively, and the black-filled squares, triangles, and diamonds are for the *n*-hexyl, 2-ethylhexyl, and *n*-lauryl esters, respectively. The lines are merely to guide the eye. Data are from Penzel and Goetz.[12]

SIZE EXCLUSION CHROMATOGRAPHY

One application of the preceding may be in the interpretation of data obtained by size exclusion chromatography (SEC) without the aid of an absolute molecular weight detector, so that it is sometimes the practice to accept an apparent molecular weight M_{app} as a function of the elution volume V_e based on a calibration of M as a function of elution volume V_e for a series of standards. If V_e is a function of M[η] for the column set,[2] independent of the brush side-chain length, it is possible to estimate the true value of M provided the relation between [η] and M is known for the standard polymer solution and can be deduced for the analyte polymer. Accepting that both standard and analyte will obey the Mark-Houwink-Sakarada equation $[\eta] = kM^{\mu}$, then M_{app} corresponds to $M[\eta] = k_{std}M_{app}^{1+\mu_{std}}$, and this may be used to compute the true M for the analyte polymer given reliable estimates for k and μ for that system:

$$M/M_{app} = (k_{std}/k)^{s}\ M_{app}^{s[\mu_{std}-\mu]} \qquad (9)$$

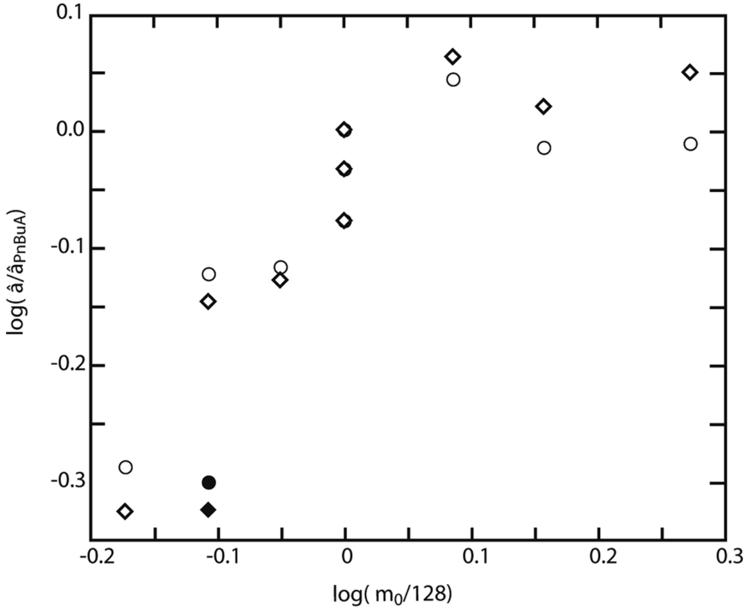

Figure 5. Bilogarithmic plot of $\hat{a}/\hat{a}_{PnBA}$ vs. $m_0/128$ calculated with the q used in Figure 4 as discussed in the text, calculated with $\nu = 0.5$ (circles) or $\nu = 0$ (diamonds); for the poly alkyl esters in Figure 4 (white fill) and PMMA (black fill).

where $s = 1/(1 + \mu)$. If μ is approximately the same for the unknown and the standard polymer, as would be usual in studies on a homologous series of brush-shaped polymers in a good solvent, then this simplifies to

$$M/M_{app} = (k_{std}/k)^s \tag{10}$$

Since here a series of analyte polymers of increasing M_{sc} is of interest, it is convenient to introduce a reference parameter k_{bb} for the backbone polymer to which the side chains are attached, so that Equation (8) may be rewritten in the convenient form

$$M/M_{app} = (k_{std}/k_{bb})^s (k_{bb}/k)^s \tag{11}$$

where the first factor is a constant, and the second will change with M_{sc}. Using the approximate expression for $[\eta]$ with $k \propto q^{-1}$ so that $k \propto \hat{a}^{3(1-\mu)} d_T^{2\mu-1}/M_L^{1+\mu}$ as above, and the proportionality $M_L \propto m_0$ for the homologous series of brush-shaped chains differing only in the side-chain length,

$$(k_{bb}/k)^s = (m_0/m0, bb)(\hat{a}_{bb}/\hat{a})^{3(1-\mu)/(1+\mu)} (d_{T,bb}/d_T)^{(2\mu-1)/(1+\mu)} \tag{12}$$

Further, if $d_{T,bb}/d_T = (m_0/m_{0,bb})^{\nu}$ as assumed in the preceding and if $\hat{a}/\hat{a}_{bb} = (m_0/m_{0,bb})^{\varepsilon}$ and as noted above with the polystyrene brush-shaped chains, then

$$M/M_{app} = (k_{std}/k_{bb})^{s}(m_0/m_{0,bb})^{\beta} \tag{13}$$

with $\beta = 1 - \{3\varepsilon(1-\mu) + \nu(2\mu - 1)\}/(1+\mu)$. An example of the use this expression is afforded by SEC data on a series of poly(*n*-butyl acrylate) (P*n*BA) brush-shaped polymers obtained by the atom transfer polymerization (ATRP) growth of side chains from a preformed linear backbone chain, with samples taken periodically as the monomer conversion via the ATRP process took place, providing a series of brush-shaped polymers with increasing side-chain length.[13] The SEC data reported for the brush-shaped polymer included M_w and M_n determined with a light scattering detector, along with $M_{n,app}$ determined using poly(methyl methacrylate) (PMMA) standards. Data on $M_{n,sc}$ were also given based on the kinetics of the ATRP process. These data are utilized to create Figure 6, which also includes results from a separate experiment[2] in the same laboratory. The poly(2-(2-bromopropionyloxy)ethyl methacrylate) (PBPEM) backbone used as the reference has $m_0 = 265$; the ratio

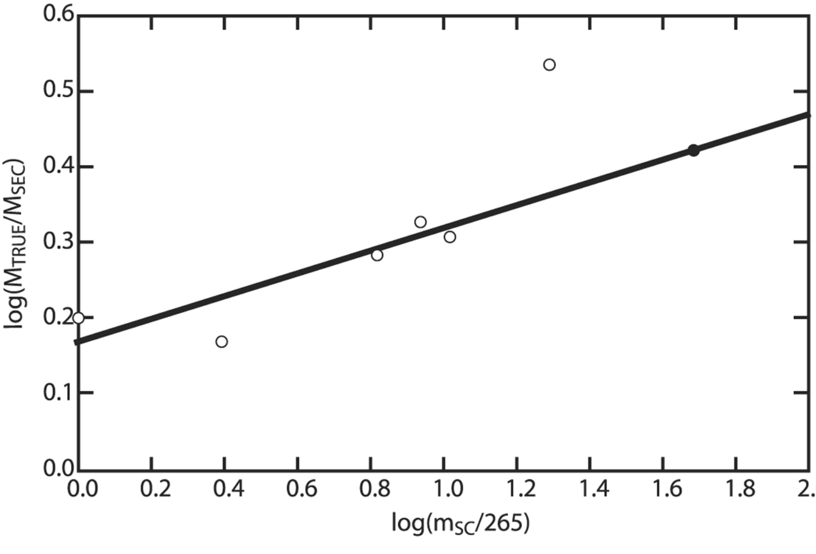

Figure 6. Bilogarithmic plot of M_{TRUE}/M_{SEC} vs. $m_0/266$ calculated with the q used in Figure 4 as discussed in the text. The white and black circles are from data in Sumerlin et al.[13] and Pakula et al.[2] respectively.

M/M_{app} for PBPEM relative to the calibration standard PMMA is similar to that obtained using the â for poly(*n*-hexyl acrylate), which may be reasonable as the side chain in PBPEM has about the same number of atoms as the hexyl ester. The data from Pakula et al.[2] for the series as a function of the conversion are actually complicated by uneven initiation from the initiator sites along the backbone polymer in the early part of the reaction, and an average value based on the conversion is used for m_0 in Figure 6. The substantial deviation of the results in this series with highest m_0 is not understood, but excepting that point, $\beta \approx 0.15$, giving $\varepsilon \approx 1.4$, somewhat larger than the value seen above for the polystyrene brushes, suggesting that the *n*-butyl acrylate moieties are more effective in increasing â than the styrene groups described in the example above; as noted above, this simple treatment does not provide any prediction for such effects.

CONCLUSION

The simple approximations to $[\eta]$ presented in Equation (4) appear to result in a satisfactory representation of the increase of the persistence length â of brush-shaped polystyrenes with increasing side-chain length on a structure with a much longer backbone, for both "good solvent" and Flory theta solvent conditions. For use with solutions in good solvent systems, the approximation includes an exponent ν related to the conformation of the side chains; the empirically determined value $\nu \approx 0.5$ found in the treatment of the polystyrene brushes seems reasonable for the relatively short side chains in the brush-shaped structures.

As shown by the application discussed for SEC data on examples of brush-shaped chains with increasing side-chain length on a fixed backbone length, this approximation for $[\eta]$ may be useful in determining the true molecular weight from SEC data on the apparent molecular weight given by SEC data based on a calibration of M versus elution volume for a standard polymer. This possibility is limited, however, by uncertainty of the dependence of â on the side-chain length, and it appears that this dependence may differ for different chemical structures, an effect beyond the prediction of this simple treatment, or indeed beyond the prediction of any coarse-grained treatment.

The application of Equation (4) to data on a range of poly(alkyl methacrylates) presented above is hampered by the considerable uncertainty in some of the data, but the trend of â given by the results seems reasonable, with â tending to plateau with increasing side-chain length, and is consistent with the available trends in R_G.

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