Viscosity of Polymer Solutions and Molecular Weight Characterization

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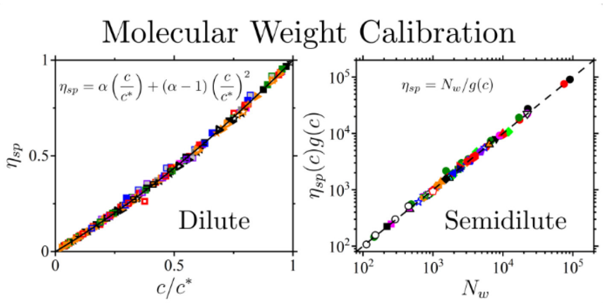
ABSTRACT: Since the pioneering research by Staudinger on dilute solution viscosity and its relation to the polymer molecular weight, viscosity analysis has become a valuable technique for polymer characterization. The conventional approach is based on the Huggins approximation of the solution specific viscosity by a quadratic function of concentration, c. We show how to reformulate this approach in a universal form by representing a solution specific viscosity, η_{sp}, as a generalized universal function $\eta_{sp} = \alpha(c/c^*) + (1-\alpha)(c/c^*)^2$ of chain overlap concentration, c^*, determined at $\eta_{sp} = 1$, with numerical coefficients $\alpha = 0.745 \pm 0.005$ for good and 0.625 ± 0.008 for a θ solvent. This viscosity representation can be viewed as a calibration curve for molecular weight determination from a measurement of the solution viscosity at a given solution concentration. Furthermore, the molecular weight dependence of the overlap concentration provides a means for quantifying the polymer/solvent affinity and the solvent effect on chain flexibility. The extension of the approach to semidilute solutions opens a path for obtaining molecular weight in a broad concentration range without requiring a dilution and monitoring its change during the polymerization reaction from solution viscosity.

TOC Figure



Importance of the solution viscosity for polymer characterization was first recognized by Staudinger in the 1930s;[1] it was essential to proving his conjecture of covalent macromolecules.[2] By adapting Einstein's expression[3] for concentration dependence of the viscosity η to polymer solutions, he postulated that a hydrodynamic volume is related to the polymer molecular weight, M, with proportionality coefficient being a polymer specific constant. Subsequent studies by Huggins,[4] Kraemer,[5] Flory,[6] Fox,[7] Mark[8] and Houwink[9] corrected the Staudinger proposal by accounting for chain flexibility and transformed dilute viscosity measurements into an indispensable technique for characterizing the molecular weight of synthetic and biological macromolecules.[10-12] The current approach is based on the Huggins equation[4, 13, 14] approximating the specific viscosity η_{sp} of a dilute solution with solvent viscosity η_0 by a quadratic function of concentration c

$$\eta_{sp}(c) = (\eta - \eta_0)/\eta_0 = [\eta]c + k_H[\eta]^2c^2 \tag{1}$$

where the Huggins coefficient k_H and the intrinsic viscosity $[\eta]$ are characteristics of dilute polymer solutions. Herein, we take c with units of number density of repeat units, making $[\eta]$ have units of volume. The intrinsic viscosity, $[\eta] = KM^a$, obeys the Mark-Houwink power law of the polymer molecular weight M with coefficient K and exponent a depending on the solvent quality for the polymer.[15] During the last eighty years, these parameters were measured for a variety of polymer solutions and are tabulated in the Polymer Handbook.[15] The popularity of the viscosity technique has grown even further with the introduction of size-exclusion chromatography (SEC),[12, 16] owing to the Benoit's universal calibration for SEC columns[17] and with viscosity detector being commonly implemented for determination of the molecular weight of eluent fractions.[18, 19]

The Huggins' expression (eq 1) is a virial expansion of the specific viscosity in a power series of polymer volume fraction using $[\eta]c \propto cR^3/N$ in a solution of chains with a degree of polymerization N and a hydrodynamic volume R^3.[4, 14] The unique feature of polymer solutions, separating them from solutions of colloidal particles,[20] is that their viscosity remains finite, $\eta_{sp}(c) \approx 1$, even for chain volume fractions $cR^3/N \approx 1$. The reason for this behavior is the ability of polymer coils to interpenetrate and overlap such that a correction to the linear term in eq 1 is only about 20% of the net value. The concentration $c^* \approx N/R^3$ when this commonly happens is called a chain overlap concentration.[13, 14, 21] At concentrations, $c \geq c^*$ overlapping polymers first form a semidilute solution of unentangled chains wherein the viscosity changes with concentration and weight-average degree of polymerization N_w as[13, 22-25]

$$\eta_{sp}(c) = N_w B^{\frac{3}{1-3\nu}} (cl^3)^{\frac{1}{3\nu-1}} = (c/c^*)^{\frac{1}{3\nu-1}} \tag{2}$$

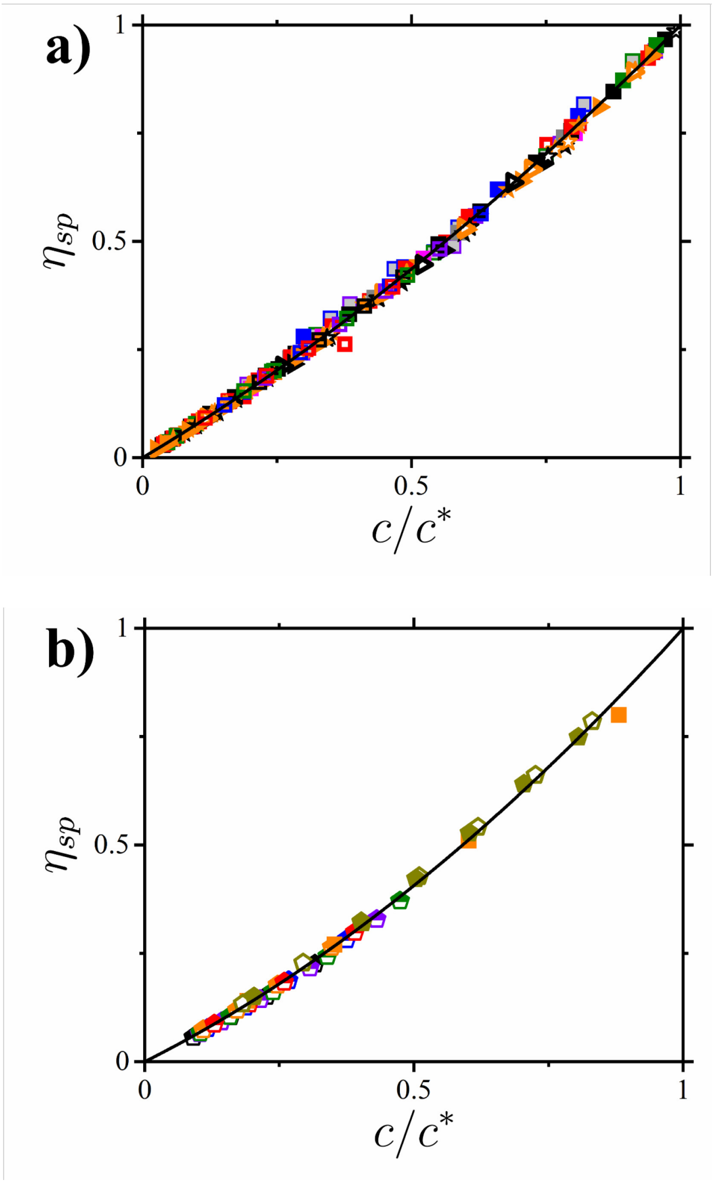


Figure 1: Universal representation of the viscosity data in dilute solutions. Solution specific viscosity as a function of c/c^* in a good **(a)** and θ **(b)** solvents. The solid lines are the best fit to eq 3 with $\alpha = 0.745 \pm 0.005$ and 0.625 ± 0.008 in panels a and b respectively. Panel (a) shows data for polystyrene in toluene (squares), polystyrene in methyl ethyl ketone (stars), and polystyrene in methyl ethyl ketone/isopropyl alcohol mixtures (right facing triangles). Panel (b) shows data for polystyrene (low molecular weight with M_w = 15 kg/mol, smaller than the thermal blob) in toluene (squares), and polystyrene of different molecular weight in the θ solvent cyclohexane (pentagons). See **Table S1** for system details.

where the B-parameter quantifies the scaling relationship between chain size R and degree of polymerization, $R = \sqrt{\langle R_e^2 \rangle} = l N_w^{\nu}/B$, for a polymer with repeat unit projection length l (the length of repeat unit in trans conformation), repeat unit excluded volume v and Kuhn length *b.* It assumes values $B_{th} = \sqrt{l/b}$ in a θ solvent ($\nu = 0.5$) and $B_g = B_{th}(\mathrm{v}/(lb)^{1.5})^{(1-2\nu)}$ in a good solvent ($\nu = 0.588$) or in the concentration ranges above and below the thermal blob overlap concentration c_{th} respectively.[22, 24, 25] Thus, B_g determines the strength of the polymer solvent affinity and B_{th} defines chain flexibility and Kuhn length. In the case of a θ solvent, substitution of $\nu = 0.5$ recovers a quadratic dependence of the specific viscosity on concentration, $\eta_{sp} \propto c^2$. In a good solvent ($\nu = 0.588$) the viscosity of semidilute solutions follows $\eta_{sp} \propto c^{1.31}$.[13, 22] The change in the scaling exponent describing a chain statistics is a reason behind the nonuniversality of the Huggins' coefficient k_H which could vary between 0.2 and 1.3[10] depending on the solvent quality[10] and polymer degree of polymerization.[26-28]

Herein we present a universal calibration of the solution specific viscosity in terms of the c/c^* ratio which covers the dilute solution regime with c^* determined from $\eta_{sp}(c^*) = 1$. In the semidilute solution regime, $c > c^*$, we implement viscosity representation in terms of the number of correlation blobs per chain. [14, 22, 26-28] This approach allows to obtain a linear polymer's weight-average degree of polymerization N_w from a measurement of the solution viscosity in a broad concentration range, without requiring dilution.

In order to demonstrate the robustness of this approach, we begin with analysis of the dilute solutions of polystyrene in toluene, methyl ethyl ketone, mixtures of methyl ethyl ketone/isopropyl alcohol, and cyclohexane at different temperatures, to make connection with molecular weight determination based on the intrinsic viscosity, $[\eta]$.[29-35] Overlap concentration c^* is obtained from interpolation of $\eta_{sp}(c)$ by a quadratic spline around $\eta_{sp} = 1$ from which the overlap concentration is obtained as a solution of the quadratic equation. The results of this procedure are summarized in **Figure 1a** and **1b** showing universal representation of the solution specific viscosity as a function of c/c^* for good and θ solvents respectively. Each of these data sets have collapsed into universal curves described by a universal function:

$$\eta_{sp}(c) = \alpha(c/c^*)+(1-\alpha)(c/c^*)^2 \tag{3}$$

with values of the parameter $\alpha = [\eta]c^* = 0.745 \pm 0.005$ in a good solvent and $\alpha = [\eta]c^* = 0.625 \pm 0.008$ in a θ solvent (**Table 1**). It is important to point out that in the initial analysis of the data sets we did not constraint the coefficients and power law of the second term, but it turns out that eq 3 describes combined data sets with extremely high accuracy. The functional form of eq 3 immediately follows from the Huggins' expression by extrapolating it to $\eta_{sp} = 1$. Comparing eqs 1 and 3 finds the Huggins coefficient $k_H = (1-\alpha)/\alpha^2 = 0.46$ in a good solvent and $k_H = 0.96$ in a θ solvent. Collapse of the data with different molecular weights indicates that the coefficient $\alpha = [\eta]c^*$ has a weak dependence on the width of the molecular weight distribution, $\alpha \propto \langle N^{3\nu}\rangle N_w^{1-3\nu}/N_n$ (**Supporting Information**). This ratio

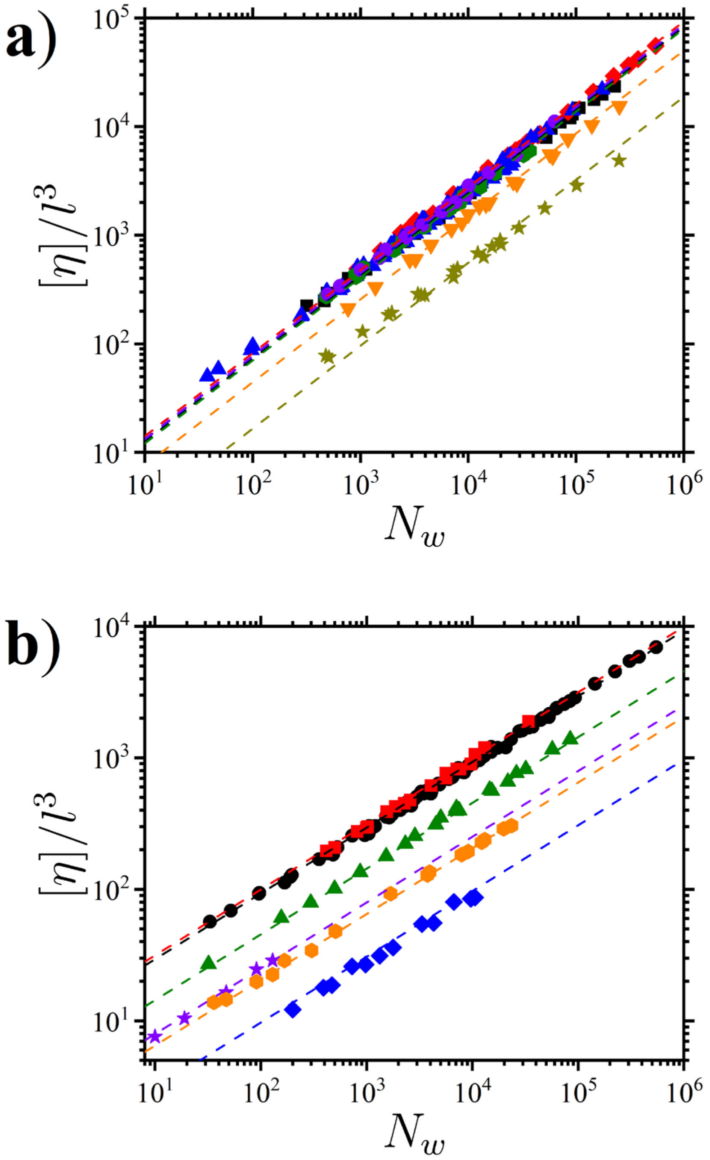


Figure 2: Intrinsic viscosity in dilute solutions. Dependence of normalized intrinsic viscosity $[\eta]/l^3$ on the weight average degree of polymerization N_w in a good **(a)** and θ **(b)** solvents for polymers with a repeat unit projection length l. The lines are the best fit to $[\eta]/l^3 = AN_w^{3\nu-1}$ with coefficient A as a fitting parameter. Panel (a) shows data for polystyrene in toluene (black squares), polystyrene in benzene (red rhombi), polystyrene in tetrahydrofuran (blue triangles), polystyrene in ethylbenzene (green hexagons), poly(α-methylstyrene) in toluene (purple circles), poly(isobutylene) in cyclohexane (orange downward triangles), and poly(ethylene oxide) in water (dark yellow stars). Panel (b) shows data for polystyrene in cyclohexane (black circles), poly(α-methylstyrene) in cyclohexane (red squares), poly(isobutylene) in isoamyl isovalerate (green triangles), polybutadiene in 1,4-dioxane (blue rhombs), poly(ethylene oxide) in water (purple stars), and poly(ethylene oxide) in 0.45M potassium sulfate (orange hexagons).

changes between 1 and 0.95 when the system dispersity $Đ \equiv N_w/N_n$ varies from unity for monodisperse to two for linear condensation polymers with a most-probable distribution[36, 37] of the molecular weights as shown in the **Supporting Information**. Thus, it can be considered as a universal constant for systems in good and θ solvents. Furthermore, by analyzing together different data sets, we minimize statistical uncertainty of the individual data associated with a finite concentration range and errors in measurements of the solution viscosity and concentration.

Having established the relationship between intrinsic viscosity $[\eta]$ and overlap concentration c^*, we need to know B_g and B_{th} to determine a chain degree of polymerization from the viscosity measurements. These parameters are obtained by plotting normalized intrinsic viscosity $[\eta]/l^3$ as a function of the weight-average degree of polymerization N_w and fitting the data by a power law function:

$$[\eta]/l^3 = AN_w^{3\nu-1} \tag{4}$$

with exponent $\nu = 0.588$ and 1/2 in a good and θ solvent and considering coefficient A as a fitting parameter. Note that eq 4 is a dimensionless form of the Mark-Houwink expression with a single adjustable parameter A and exponent being fixed by the solvent quality for the polymer. This is illustrated in **Figure 2a** and **2b** for polymer solutions in a good and θ solvents respectively. [29, 30, 33-35, 38-75] The values of the B_g and B_{th} parameters are directly calculated from the obtained A values as, $B_{[\eta]} = (\alpha/A)^{1/3}$. Results of these calculations for different polymer/solvent pairs are listed in **Table 1** with additional plots shown in the **Supporting Information**.

Combining rheology data with scattering data for the radius of gyration, we establish a relationship between B-parameters determined by these two techniques. The collection of the $\sqrt{\langle R_e^2 \rangle}$ vs N_w plots is given in the **Supporting Information** for 12 polymer/solvent systems. [29-31, 33-35, 38-77] Since chain radius of gyration also has a numerical coefficient which depends on the exponent ν, in calculation of the B-parameters, we converted radius of gyration to the square-root of mean-square end-to-end distance.

$$R \equiv \sqrt{\langle R_e^2 \rangle} = \sqrt{(2 + 6\nu + 4\nu^2)\langle R_g^2 \rangle} = lN_w^{\nu}/B_R \tag{5}$$

The results are summarized in **Table 1**. While the actual values of the B-parameters depend on the polymer/solvent pair, their ratio splits into two groups corresponding to good and θ solvents. For polymer solutions in good solvent, the ratio of B_g parameters calculated from radius of gyration and the intrinsic viscosity is equal to 0.698 ± 0.013. In a θ solvent this ratio is larger, equal to 0.871 ± 0.005. This points out that the hydrodynamic volume is proportional to R^3 with proportionality coefficient being different in good and θ solvents and determined by the chain statistics. **Figure 3** confirms this assessment by showing

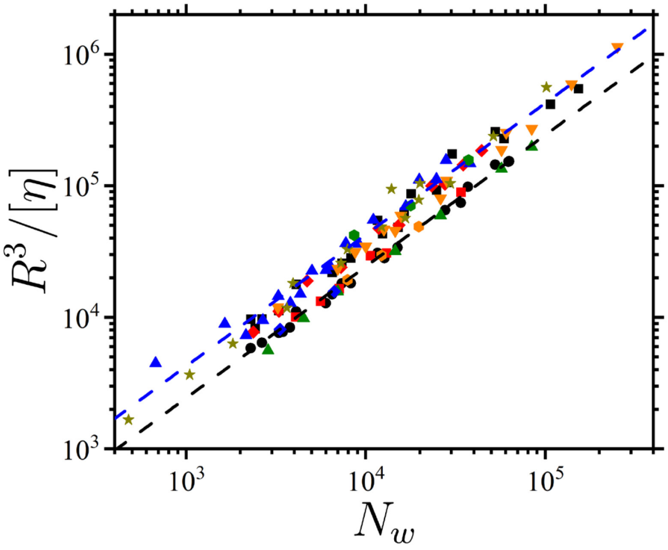


Figure 3: Chain pervaded volume normalized by intrinsic viscosity. Dependence of the ratio of the chain volume and intrinsic viscosity $R^3/[\eta]$ on the weight average degree of polymerization N_w. Dashed lines represent fits to $R^3/[\eta] = \Phi^{-1} N_w$ with Φ being dimensionless Flory-Fox parameter equal to 0.235 ± 0.006 in good (blue dashed line) and 0.410 ± 0.004 in θ (black dashed line) solvents. Symbol notations are the same as in **Figure 2**.

$R^3/[\eta]$ as a function of weight-average degree of polymerization N_w for different polymer/solvent systems. Indeed, this normalization of the chain volume by intrinsic viscosity eliminates specifics of polymer/solvent pair keeping intact a numerical coefficient. This coefficient is inversely proportional to the dimensionless Flory-Fox parameter[7, 13]

$$\Phi = \frac{[\eta]N_w}{R^3} = \alpha\left(\frac{B_R}{B_{[\eta]}}\right)^3 = \begin{cases} 0.235 \pm 0.006\,, & good\ solvent \\ 0.410 \pm 0.004, & \theta - solvent \end{cases} \tag{6}$$

The obtained value of the Flory-Fox parameter for polymers in a θ-solvent is within the range of reported theoretical values $0.38 \div 0.48$ calculated by using different approximations for the Zimm model of dilute chain dynamics.[78-80] The smaller value of the parameter in a good solvent is consistent with an expected trend for Flory-Fox parameter value to decrease with improving solvent quality for the polymer backbone.[7, 78, 81] The universal representation of the viscosity and scattering data (**Figure 3**) allow us to use scattering data in calculations of $B_{[\eta]}$- parameters required for determination of the chain N_w from universal calibration curves in **Figure 1**, if no viscosity data are available and vice versa. Note that since the solvent quality for a polymer could be *a priori* unknown, we can define a Flory-Fox parameter for the radius of gyration

$$\Phi_{R_g} = [\eta] N_w / \langle R_g^2 \rangle^{3/2} = \begin{cases} 4.27 \pm 0.07, & good\ solvent \\ 6.03 \pm 0.06, & \theta - solvent \end{cases} \tag{7}$$

and use it to establish a solvent quality for the polymer.

Table 1. Summary of Parameters for Analyzed Systems

Polymer	Solvent	ν	$\alpha^{a)}$	$A^{b)}$	$B_{[\eta]}$	B_R	$\frac{B_R}{B_{[\eta]}}$
Polystyrene	Cyclohexane	0.5	0.625	9.300	0.407	0.354	0.871
	Toluene	0.588	0.745	2.165	0.701	0.480	0.685
	Toluene	0.5[c)]	0.625	9.714	0.401	N/A	N/A
	Benzene	0.588	0.745	2.433	0.674	0.466	0.692
	Tetrahydrofuran	0.588	0.745	2.257	0.691	0.481	0.696
	Ethylbenzene	0.588	0.745	2.083	0.710	0.501	0.706
Poly(α-methyl styrene)	Cyclohexane	0.5	0.625	9.947	0.398	0.347	0.873
	Toluene	0.588	0.745	2.285	0.688	0.478	0.695
Poly(isobutylene)	Isoamyl isovalerate	0.5	0.625	4.543	0.516	0.449	0.869
	Cyclohexane	0.588	0.745	1.312	0.828	0.589	0.712
Poly(butadiene)	1,4-dioxane	0.5	0.625	0.967	0.865	0.757	0.876
Poly(ethylene oxide)	Water	0.5[c)]	0.625	2.512	0.629	N/A	N/A
	Water	0.588	0.745	0.487	1.152	0.811	0.703
	0.45M Potassium Sulfate	0.5	0.625	2.049	0.673	0.584	0.867

[a)] The Huggins coefficient $k_H = (1-\alpha)/\alpha^2$ for these values of α is equal to $k_H = 0.46$ in a good solvent and $k_H = 0.96$ in a θ solvent. [b)]Fitting coefficient A for each system is calculated using the data given in the **Supporting Information** and is used in calculations of $B_{[\eta]} = (\alpha/A)^{1/3}$. [c)] For chains shorter than the number of repeat units in a thermal blob which is estimated as $g_{th} = \left(B_{[\eta],g}/B_{[\eta],th}\right)^{2/(2\nu-1)}$(where $B_{[\eta],g}$ is the B-parameter obtained using $\nu = 0.588$ and $B_{[\eta],th}$ is the B-parameter obtained using $\nu = 0.5$). These calculations result in $g_{th} = 569$ for polystyrene in toluene and g_{th} = 969 for polyethylene oxide in water.

Determined $B_R/B_{[\eta]} \approx 0.871$ ratio (**Table 1**) can be used to calculate the Kuhn length of polystyrene in toluene using $B_{th,[\eta]}$=0.401 determined from the intrinsic viscosity $b_K = l/B_{th,R}^2 \approx 2.09nm$ which is close to the Kuhn length of polystyrene in cyclohexane, $b_K = 2.03nm$. Thus, solvent type has a weak effect on the polystyrene flexibility.[82] Universality of the $B_R/B_{[\eta]}$ ratios for good and θ solvents allows calculations of the corresponding B_R values for all polymer/solvent systems analyzed in refs [22-25].

Constructing the universal calibration curve in semidilute solution, we take advantage of the linear relationship between specific viscosity $\eta_{sp}(c)$ and the number of correlation blobs per chain with the weight-average degree of polymerization, N_w,

$$\eta_{sp}(c) = N_w/g(c) \tag{8}$$

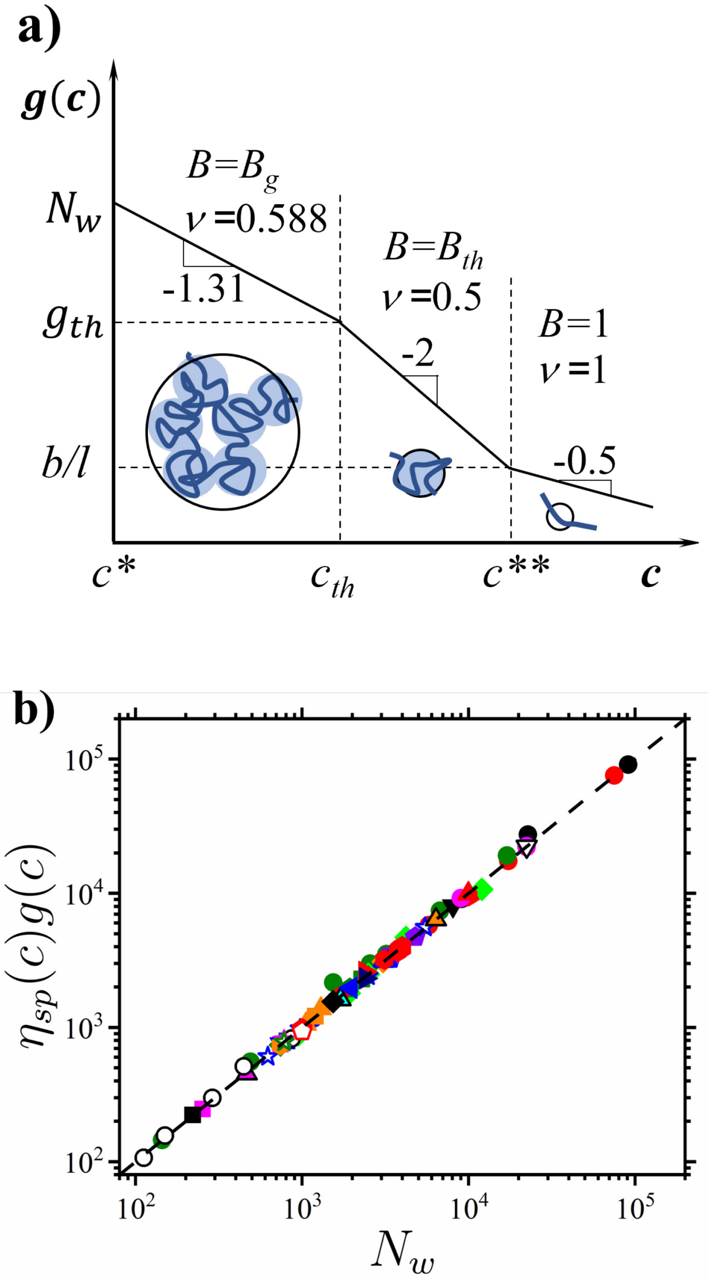


Figure 4: Universal calibration in semidilute solutions. a) Number of repeat units g per correlation blob in different concentration regimes bounded by three characteristic repeat unit concentrations c^* (chain overlap), c_{th} (thermal blob overlap) and c^{**} (concentrated solution regime). Logarithmic scales. Insets show chain conformations at different length scales. **b)** Universal plot of $\eta_{sp}(c)g(\mathrm{c})$ versus N_w for 40 different polymer/solvent systems. List of symbol notations is given in **Table S6**.

in the unentangled (Rouse) semidilute solution regime.[13, 22, 23] The number of repeat units per solution correlation length

$$g(c) = B^{\frac{3}{3\nu-1}}(cl^3)^{\frac{1}{1-3\nu}} \tag{9}$$

is expressed as a function of the B-parameter (**Figure 4a**) which assumes values B_g, B_{th} and 1 for exponent ν =0.588, 0.5 and 1, depending on the different solution regimes bounded by three characteristic repeat unit concentrations c^* (chain overlap), c_{th} (thermal blob overlap) and c^{**} (concentrated solution regime, where solution correlation length is on the order of Kuhn length). The B-parameters can either be obtained from analysis of the viscosity and scattering data in a dilute solution regime (**Table 1**) or directly extracted from the relationship between the specific viscosity as a function of repeat unit concentration in each semidilute solution regime (**Figure 4a**) as illustrated for solutions of cis-poly(1,4 butadiene) in benzene, dioxane and isobutyl acetate[83] (**Supporting Information**) and in our previous publications. [22-25]

Figure 4b shows universal calibration line for 40 different polymer/solvent systems analyzed in refs [22-25]. Note that we opted for this data representation to avoid splitting calibration curves between good and θ-solvent regimes as well as for concentration range $c > c_{th}$. Thus, as in a dilute solution, we can evaluate N_w from a measurement of the specific viscosity for systems with known B-parameter. Note that for a system with unknown B-parameters, we can use a polymer solution with known B-parameters as a reference for a relative molecular weight determination.

In summary, we develop a general framework for universal representation of specific viscosity η_{sp} in dilute (**Figure 1**) and semidilute (**Figure 4b**) solutions. This viscosity representation can be viewed as an analog of Benoit's universal calibration for SEC.[12, 17] There are, however, advantages of our approach, since it does not require dilution and allows determination or verification of the molecular weight from a few measurements of the solution viscosity at different concentrations. The calibration curves in dilute solutions (**Figure 1**) can also be used in a SEC viscosity detector to obtain intrinsic viscosity at any polymer concentration without requiring a dilution, improving accuracy of intrinsic viscosity measurements. Furthermore, we can quantify polymer solvent affinity and chain flexibility by extracting information about chain Kuhn length and interaction parameters as a function of the solvent type (**Table 1** and **Supporting Information**).

The calibration curves in **Figures 1** and **4b** could be used for monitoring polymerization reactions by measuring time evolution of the solution viscosity and for immediate feedback enabling real-time adjustment of synthesis conditions. Our approach can be extended to branched polymers such as combs and bottlebrushes, for which characterization remains a challenge. We hope that this work will inspire such investigations.

ASSOCIATED CONTENT

Supporting Information

Effect of polydispersity, data analysis and tables.

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