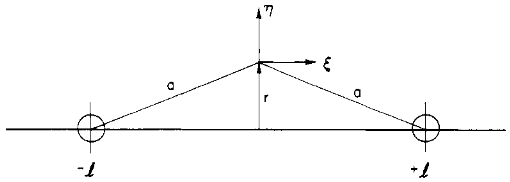

Figure 2. Local (ξ, η) coordinate system used for approximate analysis of the flexible model. Coordinate axes lie in the plane of the three atoms with origin at $r = (a^2 - l^2)^{1/2}$ as shown.

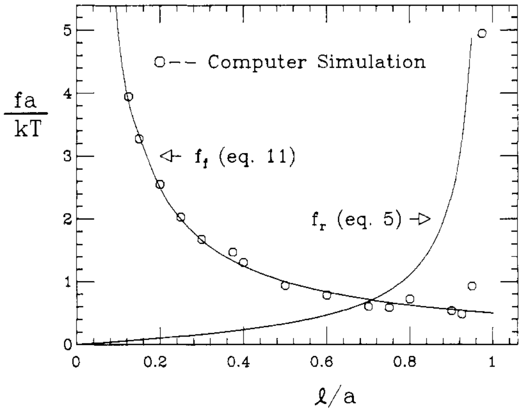

Figure 3. Comparison between end force required for the rigid model, f_r, and for the flexible model, f_f. Also shown are the results of the computer simulation of the flexible model by the method of Brownian dynamics, with spring constant $\kappa a^2/kT = 1.5 \times 10^3$.

as shown in Figure 2. A Taylor series expansion of $V(\mathbf{x})$ up to quadratic terms of ξ and η leads to the result

$$V(\mathbf{x}) \simeq V(\xi,\eta) = \frac{\kappa}{a^2}(l^2\xi^2 + r^2\eta^2) \tag{9}$$

so that for large κ

$$Z_f(l,T) \simeq (2\pi mkT)^{3/2} \int_0^{2\pi} r \, d\theta \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \, e^{(-\beta\kappa/a^2)(l^2\xi^2+r^2\eta^2)}$$

$$= (2\pi mkT)^{3/2} \frac{2\pi^2 kT}{\kappa} \frac{a^2}{l} \tag{10}$$

Therefore, f_f, the force required on the basis of the flexible model, is

$$f_f = -\frac{\partial}{\partial(2l)} kT \log Z_f = kT/2l \tag{11}$$

This result is independent of the spring constant κ, so long as the latter is sufficiently large to justify the approximation made in the evaluation of Z_f.

The results for the two models are compared in Figure 3. We see that their behavior is totally different, and, moreover, the dependence of f_f upon l is not at all like that of an entropic spring.

The behavior of the flexible model may be rationalized as due to the dependence of the curvature of the potential well upon the length l as seen in eq 9. Nevertheless, the resulting force-length relation of eq 11 is sufficiently counterintuitive to warrant a computer simulation of the model described by eq 6 and 7 in order to provide a test of the analysis.[11] This has been performed by the method of Brownian dynamics.[12] The results are shown in Figure 3 and are seen to agree quite well with the theoretical prediction for l/a not too large. When $l/a \to 1$, the approximate evaluation of Z_f is no longer valid. In this region, the computer simulation results show a rapid rise in f_f while the approximate theory indicates a monotonic decline.

This simple model, therefore, provides another example of the possible striking differences in behavior between rigid and flexible macromolecular models. It also suggests that the rigid version, the governor model, is a poor example for the demonstration of the kinetic origin of the force in stretched polymers since its closely related and, in a sense, more realistic flexible counterpart shows such anomalous behavior.

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(11) Computer simulation of the rigid model was not performed since eq 1 or 5 follows directly if the central atom has a mean kinetic energy of $^1/_2 kT$.
(12) The general procedure employed is similar to that described in Appendix B of ref 10. Further details for this computation will be found in the forthcoming doctoral dissertation of D. Perchak.

Method for Gel Permeation Chromatography Calibration and the Evaluation of Mark-Houwink-Sakurada Constants

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The evaluation of the Mark-Houwink-Sakurada constants, K and α, for a particular polymer-solvent system normally requires the preparation of a series of samples having a wide range of molecular weights and their subsequent characterization by light scattering and dilute-solution viscometry. However, gel permeation chroma-

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tography (GPC), i.e., size exclusion chromatography, and the use of two or more samples having different molecular weights can provide[1-5] a convenient alternative route to K and α.

We present in this paper a method for the evaluation of K and α coupled with a procedure for the calibration of columns used in GPC. The method described uses a combination of gel permeation chromatography and intrinsic viscosity measurements. The samples used should differ in molecular weight by as large a margin as possible and their chromatograms should exhibit Gaussian or near-Gaussian distributions. The method presented is applied to poly(stearyl methacrylate) fractions and near-monodisperse polybutadiene samples, where it is assumed that the log $[\eta]$–log $\bar{M}_w$ relation is linear over the molecular weight range investigated.

Experimental Section

The monomer stearyl methacrylate, $CH_2{=}C(CH_3)(COO(CH_2)_{17}CH_3)$ (Polysciences, Inc.), was purified by distillation under reduced pressure and polymerized at 50 °C via free radical solution (benzene) polymerization under vacuum. Two samples were prepared. The unfractionated samples possessed weight-average molecular weights of 1.68×10^5 and 5.63×10^5 and $\bar{M}_w/\bar{M}_n$ ratios of 3.4 and 3.1, respectively. A series of 12 fractions was prepared[6] by successive fractionations from toluene solutions, with methanol as the nonsolvent. Only samples of low and high molecular weights were used in this work. We will report on the dilute-solution properties, e.g., C_∞, of poly(stearyl methacrylate) (PSM) in a later publication.[7]

The polybutadiene samples (LF series) were prepared by following procedures outlined elsewhere.[8] The initiator was *sec*-butyllithium, with benzene used as the polymerization solvent. The N-285 and N-286 samples were kindly provided by Dr. A. R. Luxton, Revertex, Ltd., Harlow, England. These latter two samples were prepared with *n*-butyllithium as the initiator. The polybutadienes were found, from ^{1}H NMR, to have the anticipated[9-12] microstructure, i.e., ca. 57% trans, 36% cis, and 7% 1,2.

Polymer molecular weights were measured with a Chromatix KMX-6 low-angle photometer and a Hewlett-Packard osmometer. The light scattering measurements were done in cyclohexane at 20 °C, where dn/dc at 633 nm was 0.0539 for poly(stearyl methacrylate) and 0.1059 for polybutadiene. These dn/dc values were obtained with a Chromatix KMX-16 refractometer. The number-average molecular weights were measured in toluene solutions at 37 °C. The Hewlett-Packard 503 osmometer was fitted with S and S-08 membranes. The molecular weights were obtained from a least-squares analysis of the $(\pi/c)^{1/2}$ and concentration data. The correlation coefficients for all runs were greater than 0.99. A semimicro Ubbelohde viscometer having negligible kinetic energy corrections was used. Solvent and solution flow times were measured with a Wescan 221 automatic timing device. The viscometry measurements were done in tetrahydrofuran at 30 °C.

A Waters Ana-Prep GPC instrument was used with a seven-column Styragel arrangement. The length of this column arrangement was 28 ft. The characteristics of this column arrangement have been described.[12,13] The universal calibration[14] was obtained by using eight well-characterized polystyrene standards having near-monodisperse molecular weight distributions.

Solution concentrations of 1/8% (w/v) were used for the GPC analysis. In view of the known dependence of sample retention time of high molecular weight polymers on solute concentration, it is imperative that solutions of relatively low and constant concentration be used. Tetrahydrofuran was the carrier solvent and the GPC instrument temperature was 30 °C.

Results and Discussion

The universal calibration approach of gel permeation chromatography leads to the relation

$$\ln([\eta]M) = A - BV_e \tag{1}$$

where A and B are constants and V_e is the elution volume for species of molecular weight M. The Mark–Houwink–Sakurada relation can be expressed in its usual form

$$[\eta] = KM^\alpha \tag{2}$$

or

$$M = (K^{-1}[\eta])^{1/\alpha} \tag{3}$$

Combination of eq 1 and 3 leads to

$$\ln[\eta] = \frac{\alpha}{\alpha+1}\left[A + \frac{1}{\alpha}\ln K\right] - \frac{\alpha}{\alpha+1}BV_e \tag{4}$$

If the distributions of the GPC chromatograms fit a Gaussian function, we then have

$$W(V_e) = \frac{1}{\sigma(2\pi)^{1/2}}\exp\left[-\frac{1}{2}\left(\frac{V_e - V_{e0}}{\sigma}\right)^2\right] \tag{5}$$

where V_{e0} denotes the peak GPC elution volume of the sample (and thus corresponds to the weight-average molecular weight), W represents the base line width of the chromatogram (Figure 1), $\sigma = W/4$, and σ is the standard deviation of the Gaussian function. Samples with non-Gaussian distributions can lead to values of V_{e0} which do not correspond to the weight-average molecular weight.[15]

The relationship between the elution volume (V_e) and intrinsic viscosity of a polymer fraction can be developed as follows:

$$W(\ln[\eta]) = W(V_e)\left[-\frac{dV_e}{d\ln[\eta]}\right] \tag{6}$$

Substituting into eq 5 for V_e and V_{e0} yields

$$W(\ln[\eta]) = \left(\frac{\alpha+1}{\alpha B\sigma(2\pi)^{1/2}}\right)\exp\left[-\frac{1}{2}\left(\frac{\ln[\eta]_0 - \ln[\eta]}{[\alpha/(\alpha+1)]B\sigma}\right)^2\right] \tag{7}$$

The intrinsic viscosity of a given polymer sample can be expressed as[16]

$$[\eta]_w = [\eta]_0 e^{0.5\sigma'^2} \tag{8}$$

where

$$\sigma' = \left(\frac{\alpha}{\alpha+1}\right)B\sigma$$

Equation 4 can then be recast as

$$[\eta]_0 = \exp\left[\frac{\alpha}{\alpha+1}\left(A + \frac{\ln K}{\alpha}\right) - \frac{\alpha}{\alpha+1}BV_{e0}\right] \tag{9}$$

while eq 9 can be rewritten in terms of $[\eta]_w$ as

$$[\eta]_w = \exp\left[-\frac{\alpha}{\alpha+1}\left(A + \frac{\ln K}{\alpha}\right) - \frac{\alpha}{\alpha+1}BV_{e0}\right] \times \exp\left[\frac{1}{2}\left(\frac{\alpha}{\alpha+1}\right)^2 B^2\left(\frac{W}{4}\right)^2\right] \tag{10}$$

Equation 10 can be cast in terms involving two polymer fractions, w_1 and w_2

$$\frac{[\eta]_{w_1}}{[\eta]_{w_2}} = \exp\left[\left(-\frac{\alpha}{\alpha+1}\right)B(V_{e0_1} - V_{e0_2})\right] \times \exp\left[\frac{1}{2}\left(\frac{\alpha}{\alpha+1}\right)^2 B^2\left(\frac{W_1^2 - W_2^2}{16}\right)\right] \tag{11}$$

For $X = \alpha/(\alpha + 1)$, we have

$$\ln\frac{[\eta]_{w_1}}{[\eta]_{w_2}} = -XB(V_{e0_1} - V_{e0_2}) + \frac{1}{32}X^2B^2(W_1^2 - W_2^2) \tag{11a}$$

Table I
Molecular Parameters of PSM Samples

sample	$[\eta]$, dL g^{-1}	$\bar{M}_w \times 10^{-4}$,^{a} g mol^{-1}	V_{e0}^{b}	W^{b}	$K \times 10^4$, dL g^{-1}	α	$\bar{M}_w/\bar{M}_n$^{c}	$\bar{M}_w/\bar{M}_n$^{d}	A''^{e}	B''^{e}	$\bar{M}_w \times 10^{-4}$,^{f} g mol^{-1}
PSM II-1	0.94_1	93.5	42.7	7.70	0.82	0.68	1.38	1.38	11.05	0.1200	84.3
PSM I-6	0.06_1	1.53	57.2	7.70			1.28				1.53
PSM II-2	0.66_5	51.3	44.2	6.50	1.00	0.66	1.27	1.28	11.13	0.1214	58.1
PSM I-6	0.06_1	1.53	57.2	7.70			1.28				1.53
PSM I-1	0.52_6	46.2	45.5	7.50	0.99	0.66	1.34	1.59	11.13	0.1214	40.4
PSM I-6	0.06_1	1.53	57.2	7.70			1.28				1.53
PSM II-1	0.94_1	93.5	42.7	7.70	0.54	0.71	1.38	1.38	10.96	0.1179	84.3
PSM II-6	0.14_9	6.85	52.2	7.35			1.30	1.35			6.39
PSM II-2	0.66_5	51.3	44.2	6.50	0.76	0.68	1.27	1.28	11.07	0.1200	58.3
PSM II-6	0.14_9	6.85	52.2	7.35			1.30	1.35			6.40
PSM I-1	0.52_6	46.2	45.5	7.50	0.75	0.68	1.34	1.59	11.07	0.1200	40.7
PSM II-6	0.14_9	6.85	52.2	7.35			1.30	1.35			6.40

[a] Via light scattering measurements. [b] The peak elution volume and the base line width are expressed in GPC counts. One count equals 5 mL. [c] Via GPC. [d] Via light scattering and osmometry measurements. [e] GPC calibration constants; $\log M = A'' - B''V_e$. [f] Calculated values.

Table II
Molecular Parameters of Polybutadiene Samples

sample	$[\eta]$, dL g^{-1}	$\bar{M}_w \times 10^{-4}$,^{a} g mol^{-1}	V_{e0}	W	$\bar{M}_w/\bar{M}_n$^{b}	$\bar{M}_w/\bar{M}_n$^{c}	$\bar{M}_w \times 10^{-4}$,^{d} g mol^{-1}	$\bar{M}_w \times 10^{-4}$,^{e} g mol^{-1}
LF-1		1.08	55.6		1.03	1.02		1.04
LF-2	0.42_6	2.21	52.9	2.8	1.04	1.04	2.25	2.20
N-285		2.53	52.4		1.04	1.05		2.53
LF-3		5.27	49.8		1.04	1.03		5.24
N-286		7.17	48.8		1.05	1.06		6.93
LF-4		9.60	47.6		1.07	1.06		9.69
LF-7		23.2	44.7		1.08	1.07		21.8
LF-6		52.2	41.6		1.10			51.8
LF-5	4.54_8	57.1	41.4	3.6	1.09		55.3	54.7

[a] Via light scattering measurements. [b] Via GPC. [c] Via light scattering and osmometry measurements. [d] From eq 14. [e] From $\log M = 10.76 - 0.1213V_e$.

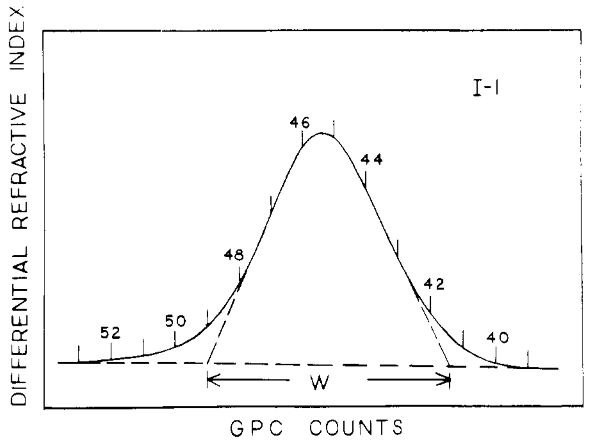

Figure 1. Gel permeation chromatogram of PSM I-1.

When the universal calibration is expressed as $\log([\eta]M) = A' - B'V_e$, we then have

$$\log \frac{[\eta]_{w_1}}{[\eta]_{w_2}} = -XB'(V_{e0_1} - V_{e0_2}) + 0.07197X^2B'^2(W_1^2 - W_2^2) \quad (11b)$$

The use of eq 8 and 9 along with eq 11a or 11b allows the calculation of K and α when the appropriate values of $[\eta]_w$, V_{e0}, and W have been determined. This method of analysis represents a simpler method for the evaluation of K and α than those requiring[1-3,5] the application of computer procedures, e.g., iterative techniques.

The application of the foregoing analysis has been done using a series of poly(stearyl methyacrylate) (PSM) fractions and near-monodisperse polybutadienes. The results for the PSM fractions are shown in Table I. The values of K and α can be compared with those in eq 12, obtained[7] by conventional evaluation involving 12 PSM fractions ranging in molecular weight ($\bar{M}_w$) from 1.53 × 10^4 to 9.35 × 10^5.

$$[\eta]^{30\,°C}_{THF} = 9.0 \times 10^{-5}\bar{M}_w^{0.67} \quad (12)$$

The method we have presented can, of course, be used to establish K and α by involving measurements on more than two samples. Obviously the success of this method is partly dependent upon the resolution obtainable in the GPC measurements.

The universal calibration curve obtained for the seven-column Styragel set used in this work is expressed as follows:

$$\log([\eta]\bar{M}_w) = 14.48 - 0.2016V_e \quad (13)$$

The constants A'' and B'' can be calculated from

$$\log \bar{M}_w = \frac{A' - \log K}{\alpha + 1} - \frac{B'}{\alpha + 1}V_e \quad (13a)$$

where A' and B' are the constants of eq 13. The values of A'' and B'' for the PSM fractions are given in Table I. These may be compared with the values of A'' and B'' (eq

13b) obtained from the GPC evaluation based on the 12 PSM fractions.

$$\log \bar{M}_w = 11.13 - 0.1214 V_e \qquad (13b)$$

An analysis similar to that involving the PSM fractions was done using the near-monodisperse polybutadienes. The intrinsic viscosity relation was developed from measurements done on samples LF-2 and LF-5 (Table II). The equation obtained follows:

$$[\eta]^{30\,°C}_{THF} = 2.56 \times 10^{-4} \bar{M}_w^{0.74} \qquad (14)$$

This equation is in excellent agreement with the one developed by Rochefort and co-workers[17] using the procedure of Kraus and Stacy.[2] The values of A'' and B'' (eq 13b) for polybutadiene were found to be 10.76 and 0.1213, respectively.[18] These may be compared with the values of 10.77 and 0.1214 obtained in the conventional manner utilizing the nine samples of Table II.

In conclusion, we do not wish to imply or claim that the evaluations outlined herein should be used to replace either the usual methods of determining K and α or the calibration techniques for columns used in gel permeation chromatography. However, these methods can serve where a Mark–Houwink–Sakurada relation does not exist for a particular polymer–solvent system and/or in situations where a series of characterized standards are unavailable for GPC calibration.

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(18) The universal calibration expression used for the calculation of these values of A'' and B'' is $\log([\eta]\bar{M}_w) = 15.14 - 0.2016V_e$. The change in the constants from the values in eq 13 was occasioned by a shift in the calibration during the 5-month interval between the measurements involving the PSM fractions and the polybutadienes.

Influence of Aqueous Salt on Triphase Catalytic Activity[1]

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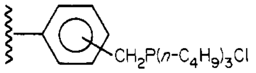
In this note we provide evidence that (1) salt present in the aqueous layer plays a major role in defining the hydration state of polymeric triphase catalysts and (2) imbibed water substantially influences resin activity.

We have previously described the kinetic features of the triphase displacement by chloride ion on *n*-decyl methanesulfonate using polymers **1a** and **1b** (reaction 1).[2-9] In the present investigation we have examined this reaction further under comparable biphase stoichiometric, triphase stoichiometric, and triphase catalytic conditions.[10]

$$n\text{-}C_{10}H_{21}OSO_2CH_3 + Cl^- \xrightarrow{\textbf{1a or 1b}} n\text{-}C_{10}H_{21}Cl + CH_3SO_3^- \qquad (1)$$



functionalized microporous polystyrene–1% divinylbenzene (200–400 mesh)

1a, 52% ring substitution: 2.23 mequiv g^{-1}
b, 17% ring substitution; 1.23 mequiv g^{-1}

All reactions reported herein were carried out under pseudo-first-order conditions with a 20-fold excess of resin. Biphase stoichiometric reactions were performed in the following manner. A 50-mL culture tube (Corning no. 9826, 25 × 150 mm) containing a $^1/_2 \times {}^5/_{16}$ in. octagonal Teflon-coated stirring bar with pivot ring was charged with 0.45 mequiv of dry polymer. A limited volume of distilled water was then injected directly into the resin, followed by addition of 4.0 mL of toluene containing *n*-hexadecane (30 μL) as an internal standard. The tube was then sealed with a Teflon-lined screw cap and placed in an oil bath maintained at 70 °C, and the mixture was stirred (ca. 1000 rpm)[11] for 0.25 h. *n*-Decyl methanesulfonate (4.9 μL, 0.02 mmol) was then injected into the toluene layer and its disappearance was followed as a function of time by GLC.[12] Observed pseudo-first-order rate constants, k_{obsd}, are reported in Table I. Incremental addition of water to **1a** resulted in a reduction in resin activity. When the polymer was fully hydrated, the activity was approximately 0.6% of that found in the absence of water. Results obtained for **1b** were similar but less dramatic; i.e., a maximum water uptake led to a 92% loss in activity. These data clearly show that resin activity is highly dependent on the imbibed water content.

Triphase stoichiometric reactions were carried out by equilibrating 0.45 mequiv of polymer with 4.0 mL of toluene plus 4.0 mL of water at 70 °C for 0.5 h and then injecting 0.02 mmol of *n*-decyl methanesulfonate into the organic layer. For **1b**, the triphase stoichiometric rate was, within experimental error (±10%), identical with that of a biphase reaction using the fully hydrated polymer. In contrast, the activity of **1a** was reduced by 67% when an external aqueous layer was present. These results indicate that under triphase stoichiometric conditions **1b** maintains contact with the organic phase but that **1a** does not.[13]

The activity of **1a** and **1b** was next examined under catalytic conditions, with procedures similar to those of the triphase stoichiometric reactions except that a satu-

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