Rheology of Polymeric Solutions I. Zero Shear Conditions

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ABSTRACT: Based on kinetic considerations, the following equation, connecting the zero-shear viscosity of polymeric solutions with temperature and the molecular weight and concentration of the polymer was derived: $RT\ln \eta_R = KB\varphi M^n /(1 + B\varphi M^n)$, where η_R is relative viscosity (i.e., the ratio of the solution viscosity to the solvent viscosity); K represents a change in enthalpy of viscous flow from a pure solvent to a pure polymer at the same temperature or from a polymer of low molecular weight (M) to one of higher molecular weight, and has the dimensions of energy (e.g., J/mol) because the ratio $B\varphi M^n/(1 + B\varphi M^n)$ is dimensionless; φ is the volume or molar fraction of a polymer in solution (concentration units can be used in dilute solutions); B is a constant related to the stiffness of the chains of the polymer in a given solvent; and at $B\varphi M^n >> 1$, $\ln \eta_R = K/RT$. The equation describes published data on the zero-shear viscosity of four polar and nonpolar polymers in nine solvents with $R^2 > 0.98$. This approach allows the use of solutions of moderate concentrations for the characterization of polymers and opens a way for a single-point degree of polymerization (DP) determination of polymers at moderate concentrations if constants K, B, and n of the equation are known. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2064–2073, 2002

Key words: polymers; zero-shear viscosity; one-point characterization

BACKGROUND

Assumptions

In the absence of an established theory of low molecular weight liquid viscosity, much less an established theory of the liquid state, we must remember that theories of transport properties of polymeric solutions are not "built on rock". On the other hand, the difference in size between a polymer molecule and a solvent molecule is so great that the properties of a solvent play a secondary role in the flow phenomena of polymeric solutions.

There are two schools of thought on the viscosity of liquids and solutions. One emphasizes the importance of free volume for the possibility of molecular movement and another stresses the energy necessary to break intermolecular bonds and jump into another position. In the Macedo and Litovitz (ML) theory of viscosity of liquids,[1,2] features of both absolute rate and free-volume theories have been combined to account for the necessity of having an adequate energy and a sufficient local free volume for a molecule to jump from one lattice site to another. Correspondingly, viscosity is expressed as:

$$\eta = A_0 \cdot \exp(\gamma/f + E_f^*/RT) \qquad (1)$$

where f is the fractional free volume, E_f^* is the value of the potential energy barrier at a constant fractional free volume f, and γ is a factor accounting for the overlap of free volume ($0.5 < \gamma < 1.0$).

This work will be limited to the zero-shear viscosity of polymeric solutions far from glass transition temperatures (T_g) and in the absence of

external fields. Molecules or kinetic segments of macromolecules must have a sufficient energy to jump between possible locations. This energy rises steeply for more polar and or larger molecules. For this reason, the viscosity of even non-polar polymers should be rate-controlled rather than free-volume-controlled processes, except for at a small but technologically very important area below $T_g + 50$ °C. Progress of Femtochemistry[3] confirmed many postulates of the Theory of Rate Processes. Following Eyring,[4] we can write

$$\eta = \eta_0 \cdot \exp((\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT)) \qquad (2)$$

Usually, entropy of activation is negative and small (especially, for monomolecular processes); therefore, it is absorbed into Arrhenius pre-exponential factor. In this work we will consider zero-shear viscosity as a function of enthalpy of activation only.

According to Van Ness,[5] "classical thermodynamics furnishes no explicit definitions of these (enthalpy and entropy of activation – V.Y.) properties. Further insight can be gained only through study of statistical mechanics and molecular theory."

Properties of solutions, including their thermodynamic properties, do depend on their composition. For instance, Wei and Rowley[6] were able to express the viscosity of solutions of mixtures of nonaqueous low molecular weight solvents through thermodynamically related factors such as NRTL (nonrandom two-liquid) parameters derived from vapor–liquid equilibria and excess enthalpy of mixing. There is no corresponding treatment for polymeric solutions. As a first approximation, let us suggest that the enthalpy of flow is proportional to the polymer molar or volume fraction and square root of its molecular weight following Einstein and Flory hydrodynamic approach. In essence, we are expanding the Einstein–Flory approach into the region of finite concentrations:

$$\Delta H = RT \ln \eta_R = K\alpha^3 \phi M^{0.5} \qquad (3)$$

where η_R is relative viscosity (i.e., the ratio of the solution viscosity to the solvent viscosity), $K = 2.5k_1 N_A (r_o^2)^{3/2}/M$, N_A is Avogadro's number, M is the molecular weight of a polymer. r_0 is an unperturbed radius of a macromolecular coil, and α is an expansion factor (ratio of the radii of macromolecules in good to very poor or θ solvent).

By analogy with the well-known Mark–Houwink equation, eq. 3 can be rewritten as:

$$\Delta H = RT \ln \eta_R = K\phi M^n \qquad (4)$$

where $0.5 < n < 1.0$

Equations 3 and 4 suggest that the logarithm of viscosity will linearly increase with the polymer concentration, which is correct only in the limit of low concentrations. The expansion factor α has been experimentally[7,8] shown to decrease with the polymer concentration in a complicated way. (It is entirely possible that the physical contraction of macromolecular coils with the increase in the solute concentration is only one of the causes of the nonlinear dependence of enthalpy on the solute concentration. Formally, at sufficiently high concentrations, we must use activities instead of concentrations.) One can change eq. 4 to take into account the dependence of α on concentration as follows:

$$\Delta H = RT \ln \eta_R = K\phi M^{n-m\phi} \qquad (5)$$

This equation implies that the size of the macromolecular coil does decrease with the polymer concentration. Actually, this idea has been tested before.[9]

Alternatively, it is well known[11–23] (Table I) that the apparent activation energy of viscous flow does increase with a polymer concentration (see also Hammes[24]). Depending on the system studied, the increase can be linear, Langmuirian, or exponential with concentration. However, there is no explanation of this phenomenon. In fact, the effect of a polymer concentration and molecular weight on zero-shear viscosity is one of the primary unsolved problems in modern rheology.

Analysis of Table I suggests that the majority of researchers found that the calculated E_{act} changes with polymer concentration in a linear, or Langmuir adsorption isotherm, fashion. Results of Oyanagi and Matsumoto[18] on E_{act} of viscous flow for aqueous solutions of poly(vinyl alcohol) are shown in Figure 1, and the results shown in Figure 2 indicate that the data can be described by the Langmuir equation ($R^2 > 0.98$ for all three curves). By comparison, the same data are plotted in Figure 3 in the log–log scale to test the fit to a power law. It appears that the fit of the power law is inferior in this case. In essence, the data of

Table I   Effect of the Solution Concentration on the Apparent Activation Energy

Author	System Studied	Limit of Concentration	Synopsis
Bleishmidt, N., et al.[11]	Cellulose in n-methyl-morpholine-oxide (MMO)	9–27%	E_{act} increases with the cellulose concentration
Mikezhova, J.; Quadrat, O.[12]	Several vinyl polymers in different solutions	Dilute solutions	E_{act} increases with the polymers concentration, shape depends on solution quality
Miroshnichenko, N., et al.[13]	Water-soluble cellulose acetates in several solvents	8–16%	E_{act} increases with the cellulose concentration in a Langmuirian fashion
Navard, P.; Houdin, J.[14]	Cellulose in (MMO)	5–30%	E_{act} increases with the cellulose concentration in a linear fashion
Tager, A.; Dreval, V.[15]	Polystyrene and polyisobutylene in several solvents	0–0.7 volume fraction	E_{act} increases with the polymers concentration, shape depends on solution quality
Tager, A.; Botvinnik, G.[16]	Polyisobutylene in isooctane	0–1.0 volume fraction	E_{act} increases with the polymers concentration as an S-shaped curve
Tager, A.; Dreval, V.; Khasina, F.[17]	Polyisobutylene in isooctane	0–1.0 volume fraction	E_{act} increases with the polymers concentration as an S-shaped curve
Oyanagi, Y.; Matsumoto, M.[18]	Poly(vinyl alcohol) in water	0–20%	E_{act} increases with the cellulose concentration in a Langmuirian fashion
Johnson, M., et al.[19]	Polystyrene in decalin	10–40%	E_{act} increases with the polymers concentration in a linear fashion
Landel, R.; Berge, J.; Ferry, J.[20]	Cellulose tributyrate in trichloropropane	0–50%	E_{act} increases with the cellulose concentration in a Langmuirian fashion
Ferry, J.; Crandine, L.; Udy, D.[21]	Polyisobutylene in decalin	10–20%	E_{act} increases with the polymers concentration in a linear fashion
Pezzin, G.; Gligo, N.[22]	Poly(vinyl chloride) in cyclohexanone	9–20%	E_{act} increases with the polymers concentration in an almost linear fashion
Yano, T.[23]	Polymethyl methacrylate in diethylphthalate	10–40%	E_{act} increases with the polymers concentration in an exponential or power law fashion

Oyanagi and Matsumoto[18] (Figures 1–3) are expressed as:

$$E_{act} = KB\phi M^n/(1 + B\phi M^n) \qquad (6)$$

The enthalpy equals activation energy less the value of $2RT$ for condensed phases,[24] so eq. 5 can be rewritten as follows:

$$\Delta H = RT \ln \eta_R = KB\phi M^n/(1 + B\phi M^n) \qquad (7)$$

where η_R is relative viscosity (i.e., the ratio of the solution viscosity to the solvent viscosity); K represents a change in the enthalpy of viscous flow from a pure solvent to a pure polymer (eq. 7 can describe the effect of molecular weight on the viscosity of polymer melts provided the temperature of the melt is $>T_g + 50$ °C of a polymer) at the same temperature (or from a polymer of low to higher molecular weight) and has the dimension of energy (e.g., J/mol) because the ratio $B\phi M^n/(1$
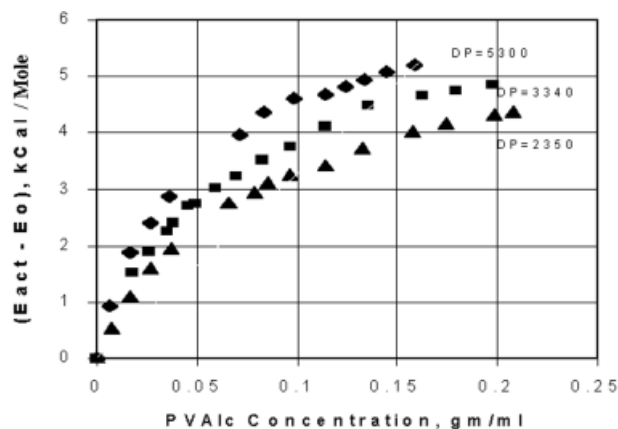
Figure 1 Effect of concentration on apparent E_{act} (Oyanagi and Matsumoto[18] data).

Figure 3 Test of power law for E_{act} versus PVAlc concentration (Oyanagi and Matsumoto[18] data).

$+ B\varphi M^n$) is dimensionless; φ is the volume fraction of a polymer in solution (concentration units can be used in dilute solutions); B is a scaling constant (later on we will show that it is related to the stiffness of polymer coil); and , at $B\varphi M^n \gg 1$, $\ln \eta_R = K/RT$.

Equation 7 has remarkable properties. Let us tabulate the following exponential function at different ratios of A/B and plot the Y (viscosity) values versus X (concentration and molecular weight) values on a log–log scale:

$$Y = \exp[Ax/(1 + BX)] \qquad (8)$$

where X represents $\varphi M^{0.5}$, A represents KB/RT, and B is arbitrarily set at 0.1. The tabulated and calculated values are given in Tables II and III, respectively, and Figures 4 and 5 depict a familiar picture of two intersecting straight lines. The
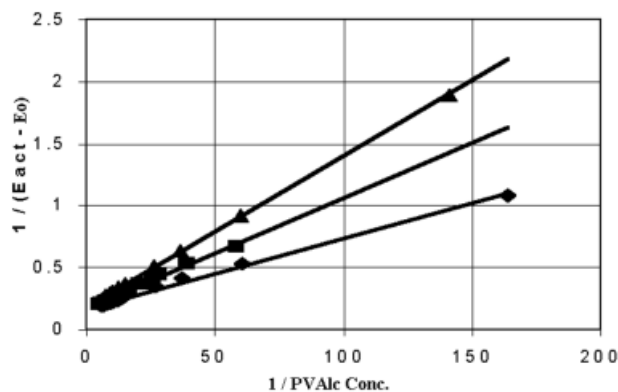
slope of the upper line can vary between one and five and depends on the A/B ratio; it is equal to ~ 3.4 at the A/B ratio of 30. The slope of the lower line can vary between zero and one. The R^2 of the upper line is 0.998 and that of the lower line is ~ 0.92. It is well known that an exponential function $Y = e^X$ will increase faster than the power function $Y = X^n$ at any value of n. It turns out that, when $\log_{10} Y = \log_{10} [\exp(Ax/(1 + Bx))] = 2.303 \cdot AX / (1 + BX)$, the function is nearly linear on a log–log scale if BX is not significantly greater than unity. The transition point between two lines comes at X values approaching 1.

The lines in Figure 5, representing the upper part of the lines ($R^2 = 0.998$), are slightly S-shaped; a scatter in experimental data will tend to obscure this slight curvature. Note that these lines represent a change of 2.5 orders of magnitude in the X values ($C \cdot M$ product) and up to 10 orders of magnitude in the Y values (viscosity).

With regard to suspensions, there are several equations[25–27] wherein the viscosity of concentrated suspensions was described as follows:

$$\eta = \eta s \cdot \exp[A \cdot (\phi/\phi_{max})/(1 - \phi/\phi_{max})] \text{ or}$$
$$\ln \eta_R = A(\phi/\phi_{max})/(1 - \phi/\phi_{max}) \quad (9)$$

and

$$\eta_R = A \cdot (\phi/\phi_{max})^{1/3}/(1 - (\phi/\phi_{max})^{1/3}) \qquad (10)$$

suggesting that, indeed, the viscosity (or ΔH) of concentrated suspensions rises much faster than the viscosity (or ΔH) of solutions. The viscosity of

Figure 2 Test of Langmuir equation for E_{act} versus PVAlc concentration (Oyanagi and Matsumoto[18] data).

Table II   Log–Log Data Generated from Equation 7 for 10 < A/B < 35

		Log Y (Log[EXP(AX/(1 + BX)]) at					
X	Log X	A/B = 10	A/B = 15	A/B = 20	A/B = 25	A/B = 30	A/B = 35
0.0001	−4.000	0.004339	0.006508	0.008677	0.010847	0.013016	0.015185
0.0002	−3.699	0.006133	0.0092	0.012266	0.015333	0.0184	0.021466
0.0005	−3.301	0.009689	0.014534	0.019379	0.024224	0.029068	0.033913
0.001	−3.000	0.01369	0.020535	0.027381	0.034226	0.041071	0.047916
0.002	−2.699	0.019336	0.029004	0.038672	0.048339	0.058007	0.067675
0.005	−2.301	0.030494	0.04574	0.060987	0.076234	0.091481	0.106728
0.01	−2.000	0.042999	0.064499	0.085999	0.107499	0.128998	0.150498
0.02	−1.699	0.060562	0.090843	0.121124	0.151405	0.181686	0.211967
0.05	−1.301	0.094987	0.142481	0.189974	0.237468	0.284962	0.332455
0.1	−1.000	0.133126	0.199689	0.266252	0.332815	0.399378	0.465942
0.2	−0.699	0.185908	0.278862	0.371817	0.464771	0.557725	0.650679
0.5	−0.301	0.286812	0.430218	0.573624	0.71703	0.860436	1.003842
1	0.000	0.394813	0.59222	0.789626	0.987033	1.184439	1.381846
2	0.301	0.538088	0.807132	1.076176	1.34522	1.614264	1.883308
5	0.699	0.793647	1.190471	1.587294	1.984118	2.380941	2.777765
7.5	0.875	0.933669	1.400503	1.867337	2.334172	2.801006	3.26784
10	1.000	1.043406	1.565109	2.086812	2.608515	3.130218	3.65192
12.5	1.097	1.134394	1.701591	2.268788	2.835985	3.403182	3.970379
15	1.176	1.212439	1.818659	2.424879	3.031099	3.637318	4.243538
17.5	1.243	1.280932	1.921398	2.561864	3.20233	3.842796	4.483262
20	1.301	1.342044	2.013066	2.684088	3.355109	4.026131	4.697153
35	1.544	1.614292	2.421439	3.228585	4.035731	4.842877	5.650024
50	1.699	1.798907	2.69836	3.597813	4.497267	5.39672	6.296173
65	1.813	1.938514	2.907771	3.877028	4.846285	5.815542	6.784799
85	1.929	2.083295	3.124942	4.166589	5.208236	6.249884	7.291531
100	2.000	2.171472	3.257209	4.342945	5.428681	6.514417	7.600153
250	2.398	2.660376	3.990563	5.320751	6.650939	7.981127	9.311315
500	2.699	3.000901	4.501352	6.001802	7.502253	9.002703	10.50315
750	2.875	3.181299	4.771948	6.362598	7.953247	9.543896	11.13455
1000	3.000	3.299539	4.949308	6.599078	8.248847	9.898617	11.54839

suspensions goes to infinity or to the solid body viscosity at a certain volume fraction of particles when they are touching each other. Even though Vand[26] arrived at eq. 9 from purely hydrodynamic viewpoint, the equation is very similar to the suggested eq. 7. In effect, eqs. 9 and 10 suggest that

Table III   Representation of Log–Log Data Generated from Equation 7 for 10 < A/B < 35

| Curve	A/B	Range of X	Constant	Standard Error of Y (est.)	R²	No. Observations	Degrees of Freedom	Slope	Standard Error of Coefficient
Upper	10	5 < X < 1000	−0.0941	0.0382	0.9980	16	14	1.1333	0.0135
	15	5 < X < 1000	−0.1412	0.0571	0.9980	16	14	1.700	0.0203
	20	5 < X < 1000	−0.1883	0.0763	0.9980	16	14	2.2667	0.0270
	25	5 < X < 1000	−0.2354	0.0952	0.9980	16	14	2.8334	0.0339
	30	5< X < 1000	−0.2824	0.1143	0.9980	16	14	3.4000	0.0406
	35	5< X < 1000	−0.3295	0.1333	0.99805	16	14	3.9667	0.0474
Lower	10	0.01 < X < 1	0.0794	0.0350	0.9386	—	—	0.3421	—
	35	0.01< X < 1	1.1950	0.1409	0.9185	—	—	0.5954	—
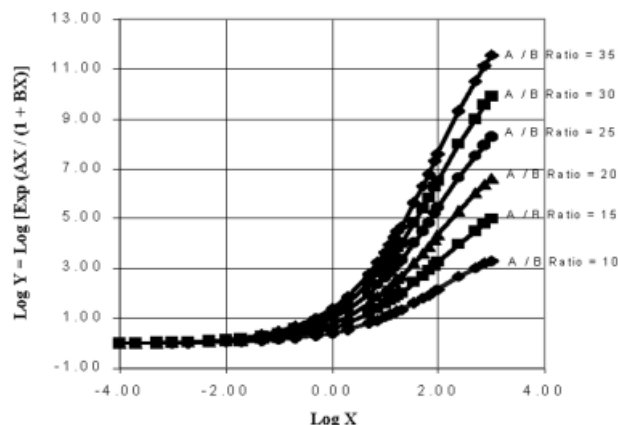
Figure 4 Equation 7 on a log–log scale.

the calculated ΔH of viscous flow for suspensions rises asymptotically to infinity, or to a solid body viscosity, when φ/φ_{max} approaches 1. Interestingly, Lyons and Tobolsky[28] found that an equation, identical to eq. 9, described the viscosity of aqueous solutions of low molecular weight polyoxyethylene in the entire range of concentrations. Unfortunately, there was no follow-up to this work.

Therefore, the kinetic approach enables us to have a unified approach to the problem of zero-shear viscosity of both solutions and suspensions. How well the derived equation describes experimental data is discussed next.

EXPERIMENTAL

No actual experimental work was performed in this study. Instead, data from Ph.D. dissertations of several researchers[29–32] as well as publications[33, 34] were analyzed to prove the hypothesis. Therefore, this work can be considered as a meta-study of the zero viscosity problem. Whenever possible, solution concentrations were recalculated into volume fractions. In several cases, the zero-shear viscosity had to be calculated by extrapolating shear viscosity–shear rate data to the zero shear rate.

A check of derived equations showed that eq. 5 was accurate but somewhat inconvenient to use. Also, both eq. 5 and eq. 7 have three adjustable constants. Therefore the literature data analysis was carried out with eq. 7. To analyze data, eq. 7 has to be rearranged as follows:

$$\phi/RT \ln \eta_R = 1/KBM^n + \phi/K \qquad (11)$$

The slope of a straight line yields a value of $1/K$, from which one can calculate value of K. From K and the intercept, one can get a value of BM^n. The values of n and B can be found by plotting $\ln BM^n$ versus $\ln M$ (value of n cannot be found unless M is known; like the value of a in the Mark–Houwink equation). The calculations can be performed using any spreadsheet software. To improve the accuracy of the estimates and to obtain the R^2 of the overall fit, the data were fitted to eq. 7 using Newton's method (with the preliminary values of K, B, and n as starting values) with the help of SAS nonlinear least square statistics procedure, PROC NLIN [SAS].[35]

RESULTS

Ashare[29] and Harris[30] studied shear-thinning phenomena using identical monodisperse polystyrene solutions in chlorinated (Arochlor) solvents using the same equipment. Because their results are directly compatible, their data were combined and extrapolated to zero shear conditions. Figure 6 shows how well experimental data are described by eq. 7. The results, given in Table IV, show that Arochlor(s) is a poor solvent for polystyrene ($n = 0.54$) and the value of K was ~50 KJ/mol. The overall R^2 was 0.998.

Hager[31] studied the viscosity of monodisperse polystyrene solutions in four different solvents ranging from good (benzene) to very poor (cyclopentane) at two temperatures. The results (Table IV) also show a very good correlation ($R^2 > 0.97$ for benzene, 2-butanone, and cyclohexane). Cyclopentane, being a very poor solvent with both up-
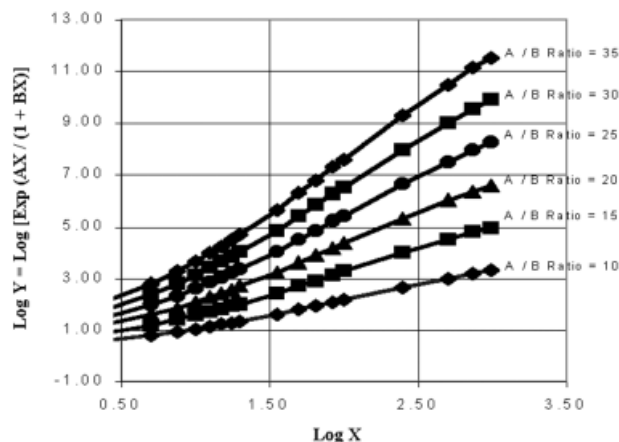

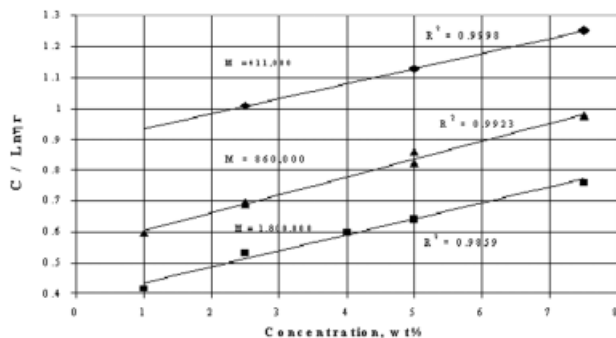**Figure 5** Equation 7 on a log–log scale (upper curve).

Figure 6 Viscosity of polystyrene in Arochlor 48 at 25°C (adapted from Hager[31]).

per and low critical temperatures, had an R^2 of only 0.927.

Graessley et al.[33] also studied the viscosity of monodisperse polystyrene solutions in ethylbenzene. The fit of his data to eq. 7 was very good with the exception of points at high polymer concentration; after removal of the points with $\varphi > 0.41$, the overall R^2 was 0.99. It is possible that his solutions were close to a glass transition temperature at high concentrations and could not be adequately described by this equation.

Liu[32] looked into the entanglement effects on the viscosities and phase separation behavior of polyisobutylene in dilute solutions in benzene. His zero viscosity data include three polydimethyl siloxane fractions at three temperatures. The overall fit of eq. 7 was 0.992 and the value of K was ~50 KJ/mol.

Oyanagi and Matsumoto[18] reported on viscosities of aqueous solutions of poly(vinyl alcohol); the most interesting part of their work was the calculation of apparent E_{act} of viscous flow for their solutions (Figure 1). The overall R^2 was 0.998. Especially stunning is Figure 7 whereby the values of $1/\ln(\eta_R)$ are plotted against $1/C \cdot M^{0.9518}$, and all 41 experimental points fell on a single line with $R^2 = 0.998$ (i.e., eq. 7 allows one to "reduce" the experimental data).

Morton[34] established a correlation between cellulose viscosities in 0.5% cupriethylenediamine (CED) solution and cellulose degree of polymerization (DP) by converting the same cellulose samples to cellulose tricarbonylates, dissolving them in tetrahydrofuran (THF), and using gel permeation chromatography (GPC)-low angle laser spectroscopy (LALS) technique for the molecular weight determination. CED solutions are widely used in pulp and paper industry for a one-point viscosity determination as a crude

proxy for DP. Morton used 13 cellulose samples with a very wide range of CED viscosity (from 5 to 384 cP). His equation:

$$DP = 118.019 \cdot CED^2$$
$$+ 598.404 \cdot CED - 449.61 \quad (12)$$

describes his data quite well ($R^2 = 0.995$); however, it represents a typical polynomial and has no physical meaning because it predicts negative DP values at CED viscosities < 1.9 cP. Equation 7 describes Morton's data up to CED viscosity of 100 cP (which is a much wider range than is dealt with in the pulp and paper industry), with R^2 of 0.988. The last two points (CED viscosity of 284 and 355.2 cP) represent cotton cellulose with very high DP. It is possible that some degradation was unavoidable during tricarbonylation of these samples or that an undissolved high molecular fraction was filtered out during samples preparation causing a distortion in the data because eq. 7 predicts higher DP values than experimentally found.

Interestingly, values of K for rigid polymers (polystyrene and cellulose) range between 30 and 110 KJ/mol, whereas the value of K for the flexible poly(vinyl alcohol) was 9.23 KJ/mol and only 4.85 KJ/mol for the very flexible chains of polyisobutylene. Comparing values of n and literature values of Mark–Houwink integer a, we can see that, as a rule, $n > a$, which is to be expected because at low concentrations, eq. 7 can be approximated as:

$$\eta_R = 1 + K\phi M^n/RT(1 + B\phi M^n) \text{ or}$$
$$\eta_R - 1 \sim K\phi M^n/(1 + B\phi M^n) \quad (13)$$

Mathematically, the function $K\varphi M^n/(1 + B\varphi M^n)$ should have a higher integer power of M than the Mark–Houwink's function, $K\varphi M^a$ to describe the same data.

A further look at the results, presented in Table IV, suggests that there is an inverse relationship between the estimates of n and B (Figure 8). Furthermore, it appears that B is related to the stiffness of the same polymer chains in different solvents (Figure 9). For instance, in the case of polystyrene solutions in different solvents, $B = 0.0000458 \cdot n^{-7.5}$, with $R^2 = 0.973$. Of course, more data are needed before one can draw definite conclusions.

Table IV contains data of eight researchers who studied rheological properties of four polar

Table IV Constants of Equation 7 for Different Polymer–Solvent Systems

Author	Polymer–Solvent System	Number of Points	MW Range × 10³	Volume Fraction Range	T Range, °C	K, kJ/mol	B × 10³	n	R²	"a", from Mark–Houwink Equation[a]
Ashare[29] and Harris[30]	Polystyrene–Arochlor(s)	18	411–1800	0.033–0.10	25	50.01	3.99	0.539	0.998	—
Hager[31]	Polystyrene–Benzene	60	36.3–2110	0.022–0.172	15 & 40	31.17	0.24	0.807	0.978	0.60–0.78
	2-Butanone	56	36.3–1500	0.015–0.133	15 & 40	31.18	2.46	0.609	0.993	0.58–0.60
	Cyclohexane	36	36.3–1500	0.028–0.167	37 & 60	51.59	1.72	0.601	0.990	0.48–0.50
	Cyclopentane	154	862 & 2110	0.004–0.126	20–155	48.81	1.02	0.649	0.927	—
Graessley[33]	Polystyrene–Ethylbenzene	21	411 & 860	0.164–0.41	30	110.99	0.705	0.524	0.990	0.68
Liu[32]	Polydimethylsiloxane–Benzene	64	1140–6800	0.02–0.2	25, 35, 45	48.48	0.016	0.776	0.992	0.5–0.56
Oyanagi and Matsumoto[18]	Poly(vinyl alcohol)–Water	41	103–235	0–0.2	30–80	9.23	8.66	0.952	0.998	0.56–0.76
Morton[34]	Cellulose-Cu–$C_2H_4(NH_2)_2$	11	9.7–810	0.005	25	31.73	0.02	0.790	0.988	0.905

[a] Values of "a" are taken from Van Krevelen, D.W. Properties of Polymers, 1990, p. 256f.
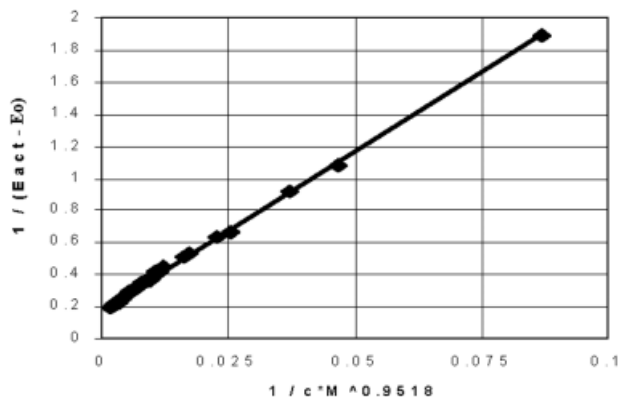
Figure 7 Test of Langmuir equation for reduced Oyanagi and Matsumoto[18] data.

and nonpolar polymers in nine polar and nonpolar solvents. The average fit of eq. 7 for all these data was in excess of 0.98, which, probably coincides with the accuracy of the original data.

Based on a kinetic approach, a modified exponential equation relating polymer solution viscosity to the polymer concentration and molecular weight, was derived. This equation, containing only three adjustable constants, accurately ($R^2 > 0.98$) describes available data on viscosity of polymeric solutions in a wide range of concentrations (compare with equations derived by G. Phillies[36] that contain five adjustable constants). According to this equation, viscosity is a continuous function of polymer concentration and molecular weight. The constants of the eq. 7 do not change within studied limits of the polymer concentration and molecular weight for a given polymer–solvent system. It opens a way for an accurate single-point DP determination of polymers at moderate concen-
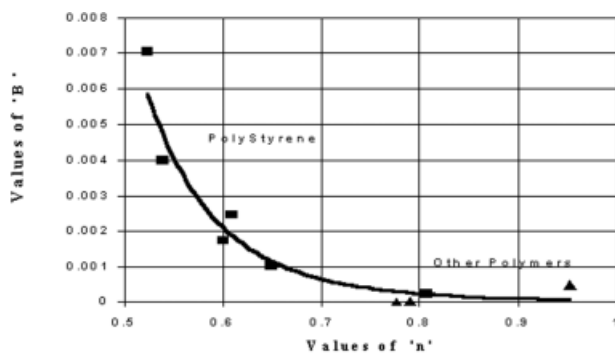

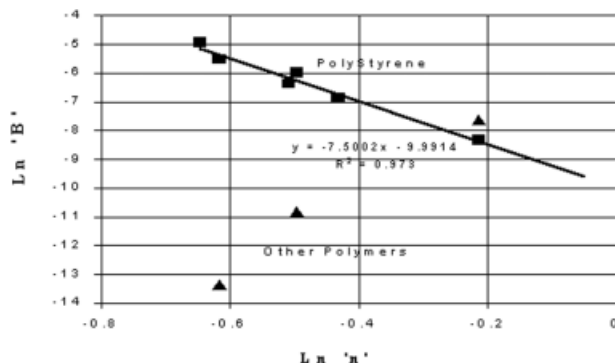**Figure 8** Relationship between values of "n" and "**B**" (from Table IV).

Figure 9 The "n" – "B" relationship (ln–ln) scale.

trations if constants K, B, and n of eq. 7 are known (tabulated).

CONCLUSIONS

1. Based on kinetic considerations, the following equation, connecting viscosity of polymeric solutions with temperature and polymer molecular weight and concentration, was derived:

$$RT \ln \eta_R = KB\phi M^n/(1 + B\phi M^n)$$

where η_R is relative viscosity (i.e., the ratio of the solution viscosity to the solvent viscosity), K represents a change in the enthalpy of viscous flow from a pure solvent to a pure polymer at the same temperature or from a polymer of low to higher molecular weight and has the dimensions of energy, (e.g., J/mol) because the ratio $B\phi M^n / (1 + B\phi M^n)$ is dimensionless. φ is the volume fraction of a polymer in solution (concentration units can be used in dilute solutions), and B is a scaling constant; at $B\phi M^n \gg 1$, $\ln \eta_R = K/RT$. B relates to the stiffness of the polymeric chains in different solvents.

2. The equation describes published data on the zero-shear viscosity of four polar and nonpolar polymers in nine solvents with $R^2 > 0.98$.

3. It is shown that the equation is a general form of the Mark–Houwink equation, and together with the similar in form Vand equation, describes the viscosity of both polymeric solutions and suspensions.

4. The equation allows the use of solutions of

moderate concentration for the characterization of polymers and opens a way for a single-point DP determination of polymers at moderate concentrations if constants K, B, and n of eq. 7 are known.

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