points, in contrast to the quadratic dependence for the secant values. Now using Table Ia to redetermine $(\partial y/\partial \tilde{V})_{\tilde{T}}$ and then applying this result to eq 6 gives reasonably good agreement between the values of the new and old derivatives at each point, which is the final test for this procedure. The values of $(\partial y/\partial \tilde{T})_{\tilde{V}}$ also derived from Table Ia were used to evaluate the entropy from eq 7. Using this method, $(\partial y/\partial \tilde{V})_{\tilde{T}}$ and $(\partial y/\partial \tilde{T})_{\tilde{V}}$ are compatible in the sense that they correspond to the same solution.

References and Notes

(1) (a) National Bureau of Standards; (b) Case Western Reserve University.
(2) J. E. McKinney and R. Simha, *Macromolecules*, **7**, 894 (1974).
(3) J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Stand., Sect. A*, **78**, 331 (1974).
(4) (a) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971); (b) A. Quach, P. S. Wilson, and R. Simha, *J. Macromol. Sci., Phys.*, **9** (3), 533 (1974).
(5) O. Olabisi and R. Simha, *Macromolecules*, **8**, 211 (1975).
(6) A. Quach and R. Simha, *J. Phys. Chem.*, **76**, 416 (1972).
(7) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
(8) R. Simha and P. S. Wilson, *Macromolecules*, **6**, 908 (1973).
(9) N. R. Draper and H. Smith, "Applied Regression Analysis", Wiley, New York, N.Y. 1966, p 71.
(10) G. Allen, D. Sims, and G. J. Wilson, *Polymer*, **2**, 375 (1961).
(11) V. Bares and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 861 (1973).
(12) R. F. Boyer, *J. Macromol. Sci., Phys.*, **7** (3), 487 (1973).
(13) M. V. Vol'kenshtein, "Structure of Glass", Vol. 2, Consultants Bureau, New York, N.Y., 1961, p 111 (translation).
(14) C. A. Angell, private communication.
(15) J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962).
(16) M. Goldstein, *J. Phys. Chem.*, **77**, 667 (1973).
(17) R. O. Davies and G. O. Jones, *Adv. Phys.*, **2**, 370 (1953).
(18) E. A. DiMarzio, *J. Appl. Phys.*, **45**, 4143 (1974).
(19) M. Goldstein, *J. Appl. Phys.*, **46**, 4153 (1975).
(20) G. Rehage and W. Borchard, "The Physics of Glassy Polymers", R. N. Haward, Ed., Wiley, New York, N.Y., 1973, p 74.
(21) C. Price, R. C. Williams, and R. C. Ayerst, "Amorphous Materials", R. W. Douglas and B. Ellis, Ed., Wiley-Interscience, New York, N.Y., 1972, p 107.
(22) C. Price, *Polymer*, **16**, 585 (1974).
(23) Submitted to *Rep. Prog. Polym. Phys. Jpn.*

Intrinsic Viscosity of Polymers in Good Solvents

Petr Munk* and Michael E. Halbrook

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.
Received July 7, 1975

ABSTRACT: A semiempirical interpretation of the Mark–Houwink relation $[\eta] = KM^a$ is proposed, which enables one to calculate easily the unperturbed dimensions of the polymer coil from the parameters a and K. It is postulated that there is no thermodynamic interaction among macromolecular segments within a short section of a chain with a characteristic number of segments N_0, estimated as $N_0 \sim 9$. This postulate enables one to calculate the unperturbed parameter K_θ. A test of the method on an extensive range of data for solutions of polystyrene and poly(methyl methacrylate) yields satisfactory results. The method is also applicable to nonvinyl polymers with rather different structures, e.g., polysiloxanes, polycarbonates, and cellulose derivatives.

In most theories of polymer solutions a linear macromolecule is modeled as a string of segments suspended in a solvent. The segments are connected by universal joints. The model is fully described by four parameters: (1) the number of segments, N; (2) the length of a segment, A; (3) the friction coefficient of a segment, ζ; and (4) a thermodynamic parameter expressed as the Flory–Huggins interaction parameter χ or the familiar Flory's expression $\psi(1 - \theta/T)$ or the binary cluster integral (the excluded volume of a segment) β.

All the characteristic quantities of a macromolecular solution (size of the macromolecular coil, relative viscosity, friction coefficient of a coil, virial coefficients, etc.) are then unique functions of these four parameters and of the number of macromolecules in a volume unit, n. Usually, the concentration is expressed in units of mass per volume, c, which is related to n as $c = nM/N_A$, where M is molecular weight and N_A is Avogadro's number. Note that the molecular weight is *not* a basic parameter of the theory of polymer solutions as it enters only as a result of our preference for concentrations expressed as c. Other parameters (molar volume of solvent, V_0; specific volume of macromolecules, $\bar{v}$) enter the theory in a similar way.

One of the five basic parameters, the friction coefficient ζ, influences only the hydrodynamic properties. Moreover, experimental evidence shows that for macromolecules with a sufficient degree of coiling (i.e., for a high enough number of segments, typically M larger than 10^4) the value of ζ is such that the coil is hydrodynamically in the limiting nondraining state. In this state, the hydrodynamic properties no longer depend on ζ and the number of basic parameters is reduced to four.

Most theories (see Yamakawa[1]), even when one is studying the dependence of various phenomena on the molecular weight of the macromolecule, assume that the number of segments N is always so large as to be effectively infinite when compared to small integers. Using this implicit assumption, one finds that the basic parameters are always combined into two parameters and that the properties of macromolecular solutions are fully described by the two-parameter theories. (Actually M and c are also used, but are not counted as parameters.) The two parameters are the unperturbed dimensions of a coil $\bar{r}_0^2/M$ and a parameter z, defined as:

$$z = BM^{1/2} \tag{1}$$

$$B = 2(3/2\pi)^{3/2}(\bar{v}^2/N_A V_0)(\bar{r}_0^2/M)^{-3/2}\psi(1 - \theta/T) \tag{2}$$

where $\bar{r}_0^2$ is the mean end-to-end distance of an unperturbed coil, i.e., the distance which exists if the parameter $\psi(1 - \theta/T)$ is zero and all other parameters are the same.

In the following we will restrict our attention to intrinsic viscosity $[\eta]$. The two-parameter theory predicts for $[\eta]$

$$[\eta] = K_\theta M^{1/2}\alpha_\eta^3 \tag{3}$$

$$K_\theta = \phi_0(\bar{r}_0^2/M)^{3/2} \tag{4}$$

$$\alpha_\eta^3 = 1 + bz + \ldots \tag{5}$$

The expansion factor for viscosity α_η^3 may be expanded by a McLaurin series, eq 5; the perturbation theory[2] yields $b =$

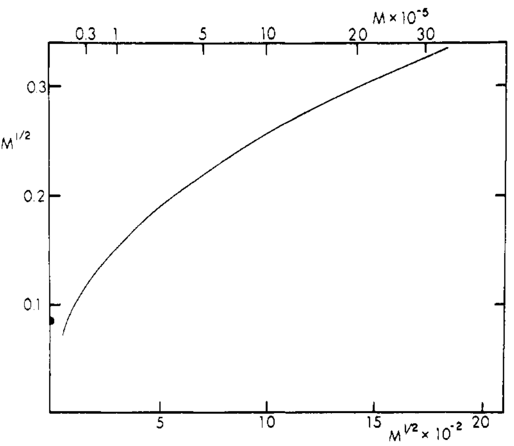

Figure 1. The Mark–Houwink relation for polystyrene in benzene (eq 14) plotted according to Stockmayer and Fixman.[4] The point on the axis represents $K_\theta = 8.5 \times 10^{-2}$.

1.06. However, the series converges very slowly and the coefficients of higher terms cannot be computed easily. K_θ is the characteristic viscometric constant for the unperturbed coil (θ solvent); $\phi_0 = 2.87 \times 10^{23}$ is a universal viscometric constant.[3]

The unperturbed dimensions of the polymer coil ($\bar{r}_0^2/M$) and the thermodynamic interaction parameter $\psi(1 - \theta/T)$ are of considerable experimental interest. The former provides information about the local conformation of the polymer chain as influenced by the steric and/or thermodynamic interaction with the solvent. The latter parameter describes the basic thermodynamic interaction of the solvent–polymer pair and governs all excluded volume type long range interactions. Thus, considerable effort has been devoted to the calculation of these parameters from the experimental data, mainly from the intrinsic viscosity and the second virial coefficient.

For small values of z, eq 1, 3, and 5 may be combined to yield

$$[\eta]M^{-1/2} = K_\theta + bK_\theta BM^{1/2} + \ldots \tag{6}$$

Thus Stockmayer and Fixman[4] propose to graphically extrapolate the quantity $[\eta]M^{-1/2}$ to zero molecular weight. The intercept would yield K_θ and the limiting slope would yield the thermodynamic parameter B defined by eq 2. This procedure works reasonably well for rather poor solvents; the dependences for good solvents are curved and the extrapolation is ambiguous. The curvature of the plot is blamed on the higher terms in eq 5. Several other analytical forms of the function α_η^3 (z) have been offered[5–7] to improve the linearity of the plot and the usefulness of the extrapolation procedure. None of these trials was very successful.[8]

All of these procedures[4–7] are based on the extrapolation of experimental data to vanishing molecular weight. However, as was pointed out by Flory,[9] many assumptions of the perturbation theory are violated in the region of low molecular weight. Any extrapolation into that region may, therefore, yield grossly distorted results. In the next section we will develop an alternative semiempirical approach which will be based on the following two experimental observations.

1. The Mark–Houwink relation, eq 7, holds up remarkably well for most polymers in most solvents over a rather broad range of molecular weights

$$[\eta] = KM^a \tag{7}$$

For a given polymer, the better the solvent the higher the value of the exponent a and the lower the value of the constant K.

If eq 7 is considered as a good representation of the experiment and is replotted as $[\eta]M^{-1/2}$ vs. $M^{1/2}$ (Figure 1), a slightly curved dependence is obtained. In a real experiment the scatter of points may obscure the curvature completely. If the line is replaced by a straight line, the values of its intercept and slope depend on the selected range of molecular weights and, consequently, their interpretation in terms of eq 6 is rather meaningless. Similarly, relation 7 replotted in other proposed coordinates gives other slightly curved lines.

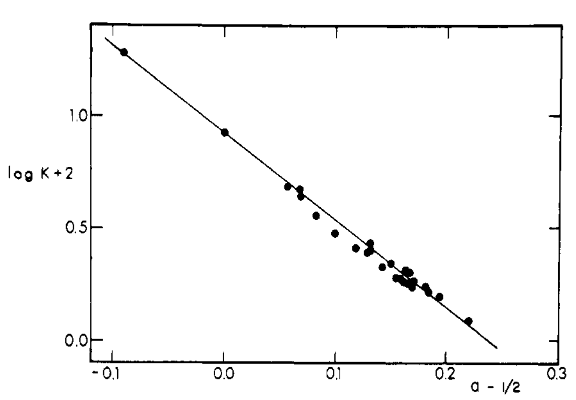

Figure 2. The Mark–Houwink parameters for polystyrene in different solvents plotted as log K vs. ($a - \frac{1}{2}$). The straight line represents $K_\theta = 8.5 \times 10^{-2}$ and $N_0 = 9$.

2. For good solvents in the region of the lowest molecular weights, the parameters K and a gradually change to values close to those of the unperturbed system,[10–12] i.e., K_θ and $\frac{1}{2}$. In the log $[\eta]$ vs. log M plot, the limiting tangent for low molecular weights intersects the limiting tangent for high molecular weights (i.e., the usual Mark–Houwink line) at a molecular weight somewhere between 2 and 30 thousand.

Theoretical

The intersection of both limiting tangents to the log $[\eta]$ vs. log M plot will be used as the starting point of our approach. If the two tangents are described respectively by eq 3 (with the expansion factor α_η^3 equal to unity) and eq 7, then they intersect at a point with molecular weight M_0 given by the relationship

$$K_\theta = KM_0^{a-1/2}. \tag{8}$$

We will now develop a model in which M_0 has a direct physical significance. The quantity M_0 represents a section of a chain containing N_0 statistical segments. In the following we will use the familiar segment model of Kuhn;[13] for this model the parameters A and N are chosen in such a way as to satisfy the relations

$$L = NA \tag{9}$$

$$\bar{r}_0^2 = NA^2 \tag{10}$$

Here, L is the contour length of the macromolecular coil (the length of a completely stretched coil in zig-zag conformation). The interaction between two neighboring segments is essentially spatial and, as such, it is accounted for in the choice of the segment length A (short-range interaction). Consequently, it does not contribute appreciably to the essentially thermodynamic long-range interaction. The latter interaction gradually increases with increasing distance (along the chain) between the segments and reaches its limiting value (the binary cluster integral β) for segments far apart.

We will replace this gradual increase by a step increase: we postulate that there is no interaction among the segments within a section of the chain with molecular weight M_0; among all segments farther apart there is full interaction given by β. The quantity M_0 thus becomes another characteristic of the *short*-range interaction within the coil. The situation is quite analogous to the building of Kuhn's segment model of the

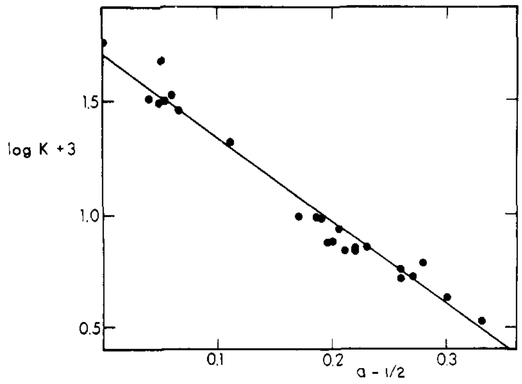

Figure 3. The Mark–Houwink parameters for poly(methyl methacrylate) in different solvents plotted as long K vs. $(a - ½)$. The straight line represents $K_\theta = 5.0 \times 10^{-2}$ and $N_0 = 9$.

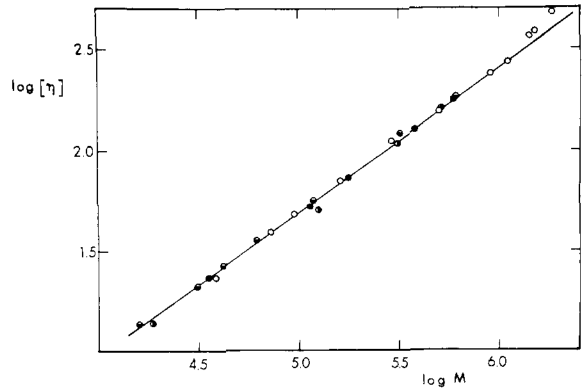

Figure 4. Dependence of intrinsic viscosity of benzene solutions of polystyrene on its molecular weight: (●) 20 °C, ref 20; (○) 25 °C, ref 14; (◒) 25 °C, ref 17; (◑) ref 18. The straight line represents eq 14.

coil[13] where the gradual change in the direction of the chain is replaced by a step change at the end of every statistical segment.

Let us now return to eq 8. First, we test the assumption that the unperturbed dimensions (i.e., K_θ) and the parameter M_0 for a given polymer are the same for all solvents. Then, according to eq 8, the plot of log K vs. $(a - ½)$ should be linear for a given polymer in all solvents. Figures 2 and 3 represent such plots for polystyrene and poly(methyl methacrylate). (For details see the Experimental Section.) The relationship is generally linear and the slope suggests for both polymers a value of M_0 around 5000. However, the deviations from the interpolated line are far too large to be blamed on experimental error. Consequently, we reject the above assumption and replace it by a more realistic one: the unperturbed dimensions of a given polymer vary with the solvent and the temperature. The variation with the temperature is caused by the Boltzmann factor describing the relative concentrations of trans and gauche conformations in the chain backbone as well as the rotational barriers in the side chains. The solvent may influence the unperturbed dimensions through specific interactions between groups on the polymer and solvent.

In order to be able to handle the variable unperturbed dimensions, we postulate that a characteristic section of the chain always contains the same number of statistical segments N_0. Our postulate leads to a model in which N_0 is a constant characteristic for a polymer or possibly for a group of polymers or even a universal constant. We can now eliminate A and $\bar{r}_0^2$

Table I
Parameters of Mark–Houwink Relation and K_θ for Polystyrene in Different Solvents

				$K_\theta \times 10^2$			
Solvent	T, °C	a	$K \times 10^2$	$N_0 = 6$	$N_0 = 9$	$N_0 = 12$	Ref
Chloroform	25	0.719	1.22	7.55	8.38	9.02	14
Benzene	20, 25	0.720	1.23	7.75	8.60	9.26	14, 18, 20
Ethylbenzene	25	0.667	2.02	8.17	8.81	9.30	14
Toluene (T)	25	0.694	1.56	7.93	8.68	9.26	14
10% Hp,[a] 90% T	25	0.684	1.65	7.67	8.36	8.88	15
20% Hp, 80% T	25	0.670	1.85	7.69	8.32	8.79	15
30% Hp, 70% T	25	0.650	2.21	7.78	8.33	8.74	15
40% Hp, 60% T	25	0.631	2.52	7.53	7.98	8.32	15
55% Hp, 45% T	25	0.557	4.82	7.74	7.93	8.06	15
5% MeOH,[b] 95% T	25	0.681	1.76	8.05	8.75	9.28	15
10% MeOH, 90% T	25	0.663	2.06	8.09	8.71	9.18	15
15% MeOH, 85% T	25	0.632	2.70	8.19	8.69	9.06	15
20% MeOH, 80% T	25	0.567	4.72	8.31	8.55	8.73	15
Butanone	25	0.599	3.01	6.84	7.14	7.37	14
Ethyl acetate (EA)	20	0.582	3.62	7.15	7.40	7.59	20
90% EA, 10% CH	20	0.618	2.60	6.92	7.29	7.57	20
80% EA, 20% CH	20	0.642	2.12	6.84	7.29	7.62	20
70% EA, 30% CH	20	0.655	1.91	6.90	7.40	7.77	20
60% EA, 40% CH	20	0.663	1.82	7.02	7.56	7.96	20
50% EA, 50% CH	20	0.666	1.78	7.06	7.62	8.03	20
40% EA, 60% CH	20	0.669	1.71	6.96	7.52	7.94	20
30% EA, 70% CH	20	0.658	1.89	6.99	7.51	7.90	20
20% EA, 80% CH	20	0.629	2.49	7.25	7.68	8.00	20
10% EA, 90% CH	20	0.568	4.38	7.73	7.96	8.13	20
Cyclohexane (CH)	20	0.410	19.18	8.97	8.66	8.45	20
Cyclohexane	34	0.500	8.50	8.50	8.50	8.50	27

[a] Hp, *n*-heptane. [b] MeOH, methanol.

Table II
Parameters of Mark–Houwink Relation and K_θ for Poly(methyl methacrylate) in Different Solvents

Solvent	T, °C	a	$K \times 10^2$	$K_\theta \times 10^2$			Ref
				$N_0 = 6$	$N_0 = 9$	$N_0 = 12$	
Chloroform	25	0.83	0.34	4.69	5.56	6.29	21
	25	0.779	0.615	5.89	6.77	7.47	24
	30	0.80	0.43	4.67	5.43	6.05	22
Dichloroethane	30	0.77	0.53	4.50	5.15	5.65	22
Benzene	25	0.76	0.57	4.47	5.07	5.56	24
	30	0.76	0.52	4.00	4.54	4.97	22
Toluene	25	0.73	0.71	4.37	4.88	5.28	21
	25	0.706	0.873	4.46	4.91	5.26	24
	30	0.71	0.70	3.58	3.95	4.24	22
Acetone	25	0.69	0.96	4.30	4.70	5.00	21
	25	0.695	0.75	3.39	3.71	3.96	24
	30	0.70	0.77	3.65	4.01	4.29	22
Butanone (MEK)	25	0.72	0.71	3.99	4.43	4.76	21
	25	0.686	0.98	4.25	4.63	4.92	24
	30	0.72	0.683	3.81	4.23	4.56	22
Acetonitrile	30	0.50	3.93	3.93	3.93	3.93	22
Methyl isobutyrate	30	0.67	0.99	3.73	4.03	4.26	22
Methyl methacrylate	30	0.72	0.675	3.76	4.17	4.49	22
Butyl acetate	25	0.554	3.14	4.83	4.94	5.02	23
Heptanone-4	42	0.540	3.18	4.36	4.43	4.48	23
	45	0.547	3.10	4.50	4.58	4.65	23
	50	0.566	2.85	4.82	4.96	5.06	23
55% MEK, 45% 2P[a]	23	0.55	4.70	7.09	7.24	7.35	21
50% MEK, 50% 2P	25	0.500	5.81	5.81	5.81	5.81	23
	35	0.560	3.34	5.41	5.56	5.66	23
	45	0.611	2.10	5.11	5.37	5.55	23

[a] 2P, 2-propanol.

from eq 4, 9, and 10 and obtain a relationship between M and N. This relationship for the pair of values M_0 and N_0 is

$$N_0 = M_0 K_\theta^{-2/3}\phi_0^{2/3}(M/L)^{-2} \tag{11}$$

where the molecular weight per unit length of the chain (M/L) may be obtained from the known lengths of bonds and the valence angles. Finally, the elimination of M_0 from eq 8 and 11 yields for K_θ

$$K_\theta = [K N_0^{a-1/2}\phi_0^{(1-2a)/3}(M/L)^{2a-1}]^{3/(4-2a)} \tag{12}$$

According to the present model, the expansion factor α_η^3 is given by the expression

$$\alpha_\eta^3 = (M/M_0)^{a-1/2} \tag{13}$$

This expression is not easily related either to eq 5 or to other theoretical expressions for α_η^3. Thus, the thermodynamic factor cannot be evaluated easily. However, further study in this direction is in progress.

Experimental Section

The Mark–Houwink parameters a and K were compiled partly from our data and partly from the literature. In the literature, there is considerable scatter in the values of these parameters for the same polymer in the same solvent. This is caused by a relatively large uncertainty in the values of molecular weights due to different techniques of measurement and to the relatively large (5–10%) error in measured values. On the other hand, the measurement of intrinsic viscosity is usually quite reproducible even in different laboratories.

For polystyrene we were able to design a scheme of data evaluation aimed at increasing the consistency of the parameters for different solvents. Only the data of Bawn et al.[14,15] and our own[16] were utilized. Benzene at 20 °C was chosen as the reference solvent. The experimental data of several authors[14,16–18] were compiled in a plot of log $[\eta]$ vs. log M (Figure 4). In our opinion, the composite data are described best by the relation of Meyerhoff:[18]

$$[\eta] = 1.23 \times 10^{-2}\, M^{0.72} \tag{14}$$

For all other solvents, the intrinsic viscosity was plotted against the intrinsic viscosity of the same sample either in benzene (our own data) or in toluene (data of Bawn et al.[14,15]) with a double logarithmic plot. In all cases, the plots were strictly linear; this further strengthened our belief in the basic validity of the Mark–Houwink relation. The calculation of the parameters, first for toluene and then for other solvents, from these plots was straightforward. In the case of mixed solvents, we improved the correlation of experimental points still further by using the double correlation of the Zimm-type plot.[19] The details will be given elsewhere.[20] Due to this reevaluation of the experimental data, the values of the parameters a and K in Table I differ slightly from the values in the original papers.

For poly(methyl methacrylate) we were not able to present the data in such a unified way. Thus, the data of Chinai et al.[21] and of Cohn-Ginsberg et al.[22] represent the parameters given by the authors and based on their own light-scattering measurement. In Bohdanecký's papers[23,24] the parameters were not computed. We calculated them using the author's molecular weights which were based on intrinsic viscosities in benzene. Bohdanecký evaluated the molecular weights using the relation $[\eta] = 5.70 \times 10^{-3}\, M^{0.76}$, which he calculated from the data given in the paper of Cantow and Schulz.[25] (Schulz and Meyerhoff[26] claim for the same data the relation $[\eta] = 5.50 \times 10^{-3}\, M^{0.76}$.)

The data for polydimethylsiloxane are taken from Zilliox et al;[27] their data agree quite well with other data in the literature.[28] Viscosity–molecular weight relationships for cellulose tricarbanilate were measured by Shanbhag[29,30] and by Burchard and others.[31,32] Unfortunately, there is rather large discrepancy between the data of both groups as could be seen when plotting them together in a single plot.

Table III
Parameters of Mark–Houwink Relation and K_θ for Polydimethylsiloxane[27]

Solvent	T, °C	a	$K \times 10^2$	$K_\theta \times 10^2$ $N_0 = 9$	$K_\theta \times 10^2$ $N_0 = 20$
Bromocyclohexane	28	0.500	7.95	7.95	7.95
Butanone	20	0.525	6.40	7.81	7.97
Cyclohexane	35	0.735	1.02	6.44	8.05
Toluene	35	0.703	1.25	6.10	7.35

Table IV
Parameters of Mark–Houwink Relation and K_θ for Polycarbonate

Solvent	T, °C	a	$K \times 10^2$	$K_\theta \times 10^2$ ($N_0 = 9$)	Ref
Butyl benzyl ether	170	0.50	21.0	21.0	34
Dioxan/cyclohexane	25	0.50	21.0	21.0	34
Methylene chloride	25	0.80	1.19	12.28	34
Methylene chloride	20 or 25	0.82	1.11	13.70	33
Tetrahydrofuran	20 or 25	0.70	3.99	20.21	33

We have evaluated the Mark–Houwink parameters from measurements in benzophenone;[32] the other data are taken from original papers.[29-31] For poly(4,4′-isopropylidenediphenylene carbonate) the parameters from original papers[33,34] were used. The contour-length parameter (M/L) for the vinyl polymers was calculated from the molecular weight of the monomer, the carbon–carbon bond length 1.54 Å, and the tetrahedral angle. The respective values for polystyrene and poly(methyl methacrylate) were 4.137×10^9 daltons/cm and 3.978×10^9 daltons/cm. The value for polydimethylsiloxane (2.768×10^9) is based on the silicon–oxygen bond length 1.64 Å and the tetrahedral angle. The crystallographic length of 5.15 Å for the glucose unit in cellulose yielded the value 10.08×10^9 for cellulose tricarbanilate. Finally, the value of 2.163×10^9 was calculated for polycarbonate from the length of the phenylene moiety 5.77 Å, length of the C–O bond 1.43 Å, and the tetrahedral angle.[34] The value of 2.87×10^{23} is used for ϕ_0; the intrinsic viscosities are expressed in ml/g units.

Results and Discussion

The data for polystyrene are collected in Table I; it is apparent that the proposed method yields rather similar values of K_θ for both good and poor solvents. The value of K_θ is relatively insensitive to the selection of N_0, as it is proportional to the cube root of N_0 for the best solvents and to even smaller powers of N_0 for poorer solvents. Our choice of N_0 was guided by the desire (1) to have the K_θ values for all solvents confined to a narrow range, and (2) to obtain K_θ values close to the directly determined value in cyclohexane at the theta temperature,[35] $K_\theta = 8.50 \times 10^{-2}$. These criteria led to the selection $N_0 = 9$. The carbonyl solvents, butanone, and ethyl acetate, have K_θ values almost 20% lower than the hydrocarbon solvents; the ethyl acetate–cyclohexane mixtures exhibit a small but clear decrease of K_θ with increasing volume fraction of ethyl acetate. The effect seems to be real and is probably caused by some specific interaction of the carbonyl with the polystyrene.

For poly(methyl methacrylate), the K_θ values cover a much broader range (Table II). Part of the scatter is, no doubt, due to the poorer quality of the experimetnal data as may be seen from grossly different values for the same solvent obtained by different authors. For example, the value of Chinai[21] for butanone–2-propanol mixture is highly suspect since the solvent is claimed to be a theta solvent, yet the exponent a equals 0.55. On the other hand, part of the variation may be real; the ester function of poly(methyl methacrylate) may participate in various types of specific interaction with the solvent. The choice of $N_0 = 9$ is much less obvious in this case; nevertheless, it confines most of the K_θ values between the two values directly measured at the theta temperature: 3.93×10^{-2} for acetonitrile[22] and 5.81×10^{-2} for butanone–2-propanol mixture.[23]

After the usefulness of the proposed analysis has been established for typical vinyl polymers, polystyrene and poly(methyl methacrylate), it was desirable to verify the method for both very flexible and rather rigid polymers. For a meaningful analysis it was necessary to select polymers, for which

Table V
Parameters of Mark–Houwink Relation and K_θ for Cellulose Tricarbanilate

Solvent	T, °C	a	$K \times 10^2$	$K_\theta \times 10^2$ $N_0 = 3$	$K_\theta \times 10^2$ $N_0 = 9$	$K_\theta \times 10^2$ $N_0 = 20$	Ref
Anisole	94	0.500	13.0	13.0	13.0	13.0	30
Acetone	0	0.93	0.110	5.94	11.52	18.64	29
	25	0.91	0.143	6.60	12.27	19.25	29
	35	0.90	0.131	5.16	9.39	14.51	29
Dioxane	25	0.97	0.0910	7.74	16.41	28.34	29
	35	0.96	0.0937	7.04	14.59	24.78	29
	50	0.95	0.0929	6.08	12.32	20.59	29
Cyclohexanone	25	0.86	0.191	5.22	8.79	12.83	29
	35	0.85	0.202	4.98	8.23	11.85	29
Benzophenone	55	0.763	0.944	12.34	17.53	22.63	32
	65	0.748	1.057	11.82	16.38	20.77	32
	80	0.737	1.097	10.84	14.76	18.47	32
	110	0.696	1.486	9.77	12.52	14.98	32
Acetone	20	0.84	0.466	13.05	21.15	30.05	31
Dioxane	20	0.88	0.420	19.20	33.57	50.41	31
Pyridine	20	0.86	0.346	11.42	19.21	28.04	31

measurements were available in both good and poor solvents (including theta solvent). Due to the differences of data coming from different laboratories, it was again important to include data from only a few laboratories.

As an example of a rather flexible polymer we have selected polydimethylsiloxane. The appropriate data[27] are summarized in Table III. It is apparent that the method still yields a reasonable result, when $N_0 = 9$. When a higher value of N_0 is used the constancy is still improved. That may mean that for very flexible polymers higher N_0 is appropriate. However, the K_θ values calculated using $N_0 = 9$ can be well explained by the different polymer–solvent interaction. At any rate, the data are not extensive enough to warrant deeper analysis.

Poly(4,4′-isopropylidenediphenylene carbonate) was chosen as an example of a relatively stiff chain (Table IV). The proposed method yields the same K_θ for all ether-type solvents while K_θ for methylene chloride is some 40% less (the difference would decrease for higher values of N_0, but not significantly). In our opinion, the difference is real.

The data for cellulose tricarbanilate are collected in Table V. The K_θ values deduced from the measurements of Burchard and Husemann[31] are about twice as large as corresponding values from Shangbag's measurements.[29] Since the differences may be tracked back to the grossly different $\bar{M}_w$–$[\eta]$ relationships in the original papers, we do not consider them as disproving the proposed method. If the Burchard–Husemann[31] data are discounted, then again the choice $N_0 = 9$ confines all the K_θ values within ±35% of the directly measured value in anisole. It should be noted that even such extreme values as $N_0 = 3$ or $N_0 = 20$ produce K_θ differing by a factor <2 from the preferred data with $N_0 = 9$. For all solvents a slight decrease of unperturbed dimensions is observed with increasing temperature. We believe that this decrease is real as well as the differences among K_θ values in different solvents (conf.[9]).

Conclusions

The proposed semiempirical analysis of the viscosity–molecular weight relationship yields quite reasonable and coherent values of K_θ for polystyrene and poly(methyl methacrylate) in a number of good and intermediate solvents. The analysis of the data for polystyrene suggests a value of 9 for the newly proposed characteristic parameter N_0. This value is also supported by the poly(methyl methacrylate) data, albeit with a lesser degree of accuracy. The method yields also satisfactory K_θ values for polymers with such different structures like polysiloxanes, polycarbonates, and cellulose derivatives. In the latter case the performance of the method is quite remarkable as it transforms the Mark–Houwink parameters K, which differ by more than two orders of magnitude from the K_θ values, into K_θ values within 35% of the directly measured value and even this remaining difference is most probably real and is not caused by the method itself. The method is rather insensitive to the choice of N_0 and a value $N_0 = 9$ could be used for all polymers. However, there is a possibility that different classes of polymers require different values of N_0. The present data are not extensive enough to decide this question.

In summary, we believe that the method will satisfactorily serve for two purposes: (1) an estimation of K_θ of those polymers for which the direct measurement is not possible; and (2) studies of slight changes in the unperturbed dimensions with the chemical structure of the solvent.

Acknowledgment. The authors are grateful to the Robert A. Welch Foundation (Grant F-563) for financial support of this work.

References and Notes

(1) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.

(2) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **55,** 3188 (1971).

(3) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16,** 565 (1948); P. L. Auer and C. S. Gardner, *ibid.*, **23,** 1545 (1955).

(4) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C,* **1,** 137 (1963).

(5) P. J. Flory and T. G. Fox, Jr., *J. Am. Chem. Soc.*, **73,** 1904 (1951).

(6) H. Inagaki, H. Suzuki, and M. Kurata, *J. Polym. Sci., Part C,* **15,** 409 (1966).

(7) M. Bohdanecký, *Collect. Czech. Chem. Commun.*, **30,** 1576 (1965).

(8) J. M. G. Cowie, *Polymer,* **7,** 487 (1966).

(9) P. J. Flory, *Makromol. Chem.*, **98,** 128 (1966).

(10) C. Rossi, U. Bianchi, and E. Bianchi, *Makromol. Chem.*, **41,** 31 (1960).

(11) C. Rossi and C. Cuniberti, *J. Polym. Sci., Part B,* **2,** 681 (1964).

(12) U. Bianchi, M. Dalpiaz, and E. Patrone, *Makromol. Chem.*, **80,** 112 (1964).

(13) W. Kuhn, *Kolloid-Z.*, **68,** 2 (1934).

(14) C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46,** 1107 (1950).

(15) C. E. H. Bawn, T. B. Grimley, and M. A. Wajid, *Trans. Faraday Soc.*, **46,** 1112 (1950).

(16) P. Munk and M. E. Halbrook, to be published.

(17) W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11,** 37 (1953).

(18) G. Meyerhoff, *Z. Phys. Chem. (Frankfurt am Main),* **4,** 335 (1955).

(19) P. Kratochvíl and P. Munk, *Collect. Czech. Chem. Commun.*, **25,** 1237 (1960).

(20) M. E. Halbrook and P. Munk, to be published.

(21) S. N. Chinai, J. D. Matlack, A. L. Resnick, and R. J. Samuels, *J. Polym. Sci.*, **17,** 391 (1955).

(22) E. Cohn-Ginsberg, T. G. Fox, and H. F. Mason, *Polymer,* **3,** 97 (1962).

(23) M. Bohdanecký, *Collect. Czech. Chem. Commun.*, **29,** 876 (1964).

(24) M. Bohdanecký, *Collect. Czech. Chem. Commun.*, **30,** 1564 (1965).

(25) H. J. Cantow and G. V. Schultz, *Z. Phys. Chem. (Frankfurt am Main),* **1,** 365 (1954).

(26) G. V. Schulz and G. Meyerhoff, *Z. Elektrochem.*, **56,** 904 (1952).

(27) J. G. Zilliox, J. E. L. Roovers, and S. Bywater, *Macromolecules,* **8,** 573 (1975).

(28) M. Kurata, M. Iwama, and K. Kamada, "Polymer Handbook", J. Brandrup and E. H. Immergut, Ed., Interscience-Wiley, New York, N.Y., 1966.

(29) V. P. Shanbhag, *Ark. Kemi,* **29,** 1 (1968).

(30) V. P. Shanbhag and J. Öhman, *Ark. Kemi,* **29,** 163 (1968).

(31) W. Burchard and E. Husemann, *Makromol. Chem.*, **44–46,** 358 (1961).

(32) H. Janeschitz-Kriegl and W. Burchard, *J. Polym. Sci., Part A-2,* **6,** 1953 (1968).

(33) G. V. Schulz and A. Horbach, *Makromol. Chem.*, **29,** 93 (1959).

(34) G. C. Berry, H. Nomura, and K. G. Mayhan, *J. Polym. Sci., Part A-2,* **5,** 1 (1967).

(35) G. C. Berry, *J. Chem. Phys.*, **46,** 1338 (1967).