The Use of Monte-Carlo Studies for the Evaluation of Thermodynamic Properties of Polymer Solutions from Their Intrinsic Viscosity

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ABSTRACT: The Monte-Carlo calculations of McCrackin, Mazur, and Guttman (*Macromolecules*, 6, 859 (1973)) lead to a verification of the empirical Mark–Houwink–Sakurada relation $[\eta] = KM^a$. The data of McCrackin et al. are used for the development of a new method of analysis of viscometric data. The constant of unperturbed dimensions K_Θ and the reduced contact energy parameter are obtained from the values of the MHS parameters K, a. The method yields extremely plausible results when applied to the measurement of the intrinsic viscosity of polystyrene in *trans*-decalin as a function of temperature.

Since the early thirties when Kuhn[1] recognized the relation between the statistics of random phenomena and observable properties of polymer solutions, the theory of the conformation of a polymer chain in solution followed a long and tortuous development. In the simplest case of completely unrestricted random walk, the original Kuhn's segment model of coil leads to a proportionality between the mean square end-to-end distance of the coil $\bar{R}^2$ and the number of segments N. After Flory[2] discovered that under special circumstances, now known as Θ or pseudoideal conditions, this proportionality is observed experimentally, a general opinion developed that the unrestricted random (Gaussian) walk described the polymer coil very satisfactorily. All the deviations from the proportionality were explained as perturbations of the basic Gaussian model. Numerous studies based on this perturbation model were summarized in the book of Yamakawa.[3]

The perturbation treatment usually leads to the so-called two-parameter theories: the dependence of many experimental properties (intrinsic viscosity, end-to-end distance, virial coefficients, etc.) on molecular weight can be reduced to a single master relation valid for all polymer–solvent systems.

In our previous study[4] we have pointed out the inherent implausibility of the perturbation model: the reference (unperturbed) coil takes into consideration too many nonexisting (i.e., self-intersecting) conformations. The existence of a master relation is also not verified experimentally, at least for viscometric data. Viscometry, being subject to a very small experimental error, is the most suitable method for testing the agreement between theory and experiment. As is well known to most experimentalists and as we have repeatedly shown[5,6] on our own as well as on literature data, the dependence of the intrinsic viscosity $[\eta]$ on the molecular weight M is usually described extremely well and within broad limits by the empirical Mark–Houwink–Sakurada (MHS) relation

$$[\eta] = KM^a \tag{1}$$

The MHS parameters K and a depend on the nature of the polymer and on the polymer–solvent interaction; the exponent a increases as the solvent power of the solvent gets better. The MHS relation is incompatible with the two-parameter theories as it cannot be reduced to a master relation valid for all polymer solutions.

The Monte-Carlo studies[7-9] represent a rather different approach. The polymer solution is simulated in a computer by generating a large number of random walks, calculating the quantities of interest, and averaging them for all the walks. Special attention has been given to self-avoiding walks which exclude from computation all conformations for which two parts of the molecule overlap each other. Such a procedure is inherently more plausible for modeling a polymer coil. However, as far as we know, no serious effort has been made in quantitative application of the Monte-Carlo results to the experimental data on real polymers. The progress along these lines was hampered, no doubt, by the fact that the Monte-Carlo studies did not take into account the polymer–solvent interaction. The self-avoiding walk under these circumstances represents a polymer in an athermal (regular) solvent; such solvents are considered thermodynamically extremely good in the polymer world. McCrackin, Mazur, and Guttman[10] recently published extensive Monte-Carlo calculations taking into account the energy of interaction between neighboring nonbonded chain elements. In the present study we use their results for a quantitative interpretation of the MHS relation. The newly developed procedure is then applied to the study of the temperature dependence of the MHS parameters of polystyrene in *trans*-decalin.

Theoretical

The size of a coil, which is formed in a solution by a linear polymer molecule with a given number of monomer units, depends on the energy of interaction between the atoms and groups constituting the polymer molecule as well as on the interactions with the surrounding solvent molecules. It is customary to divide these interactions into two groups. The so-called short-range interactions deal with restrictions and conformational energies which are related to the valence lengths, valence angles, sterical requirements of constituent groups, dihedral angles, and packing efficiency and/or orientation of solvent molecules in the vicinity of the polymer chain. All these phenomena constitute what we will call local conformation. Each local conformation corresponds to some conformational energy. Thus, in the chain statistics, the different conformations are weighted by different Boltzmann factors. The distribution of these local conformations is, consequently, a function of temperature. Of course, it varies from solvent to solvent. The distribution of local conformations is most conspicuously influenced by the distribution of the dihedral angles, e.g., by the trans-gauche isomerism. The problems of the local conformation have been studied extensively by Flory.[11] The so-called long-range interactions, which are the basis of the excluded volume effect, are due to the interaction among nonbonded polymer segments, which are far apart from each other along the polymer backbone. As far as we know, all the studies of the coil conformation are based, implicitly or explicitly, on separation of the long-range interactions from the short-range ones. However, there is one conceptual problem, which has never been satisfactorily addressed: how far along the chain should the two interacting seg-

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ments be in order that their interaction be qualified as a long-range effect? It is the failure to answer this question that is the source of ambiguity in discussions of the so-called unperturbed dimensions of polymer coils. In our analysis, we will use the following working criterion, which, while still slightly ambiguous, represents a convenient approximation.

Let us consider only such conformations of a polymer molecule which correspond to a finite Boltzmann factor (i.e., no atomic overlaps or severe distortions of valence lengths and angles). Now, let us consider two interacting sections of the polymer molecule. If there exist some conformations in which the sections are in contact while in other conformations they are separated by intervening solvent molecule or molecules, then the interaction of these groups contributes to the long-range effect. On the other hand, if these sections are always in contact or never come to contact, their interaction is a part of the short-range effect. In other words, if the sum of the statistical weights of the conformations forming the contact is virtually zero or unity the interaction is a short-range one. For intermediate values of the sum it is a long-range interaction. (Note that under this criterion the contacts within stable helices fall under short-range interactions.)

In the subsequent analysis, we will consider the following *hypothetical* experiment, which is actually frequently implied in the treatment of data in literature. The short-range interactions are kept unchanged and the long-range interactions are adjusted in such a way as to bring the coil into Θ conditions. The coil is then said to be in an unperturbed state. Its dimensions still depend on temperature and solvent due to the short-range effects. The dimensions of the unperturbed coil are considered as one of the most important characteristics of the polymer. We distinguish this hypothetical Θ state from the true Θ state, which may be reached by adjusting the real properties of the solution, e.g., temperature and/or solvent. Of course, during this real adjustment the short-range interactions may have to be changed too.

Experimentally, the dimensions of polymer coils are most conveniently obtained from measurement of intrinsic viscosity. As most polymer coils are hydrodynamically impermeable, the intrinsic viscosity is proportional to the ratio of the effective volume of coil to its molecular weight. Customarily, the volume of the coil is expressed as a quantity proportional to the cube of the square root of the average square end-to-end distance, $(\bar{R}^2)^{3/2}$. Now the familiar relation is written as

$$[\eta] = \Phi(\bar{R}^2)^{3/2}/M \qquad (2)$$

where the value $\Phi = 2.87 \times 10^{23}$ is generally accepted[12] for Flory's constant Φ.

If the short-range interactions are unchanged and the long-range interactions are adjusted to pseudoideal conditions, eq 1 and 2 are changed to eq 3 and 4, respectively, for the resulting Θ state.

$$[\eta]_\Theta = K_\Theta M^{1/2} \qquad (3)$$

$$[\eta]_\Theta = \Phi(\bar{R}_\Theta{}^2)^{3/2}/M \qquad (4)$$

Here the values $[\eta]_\Theta$, K_Θ, and $(\bar{R}_\Theta{}^2)$ correspond to the *hypothetical* Θ state. Comparison of eq 3 and 4 yields

$$K_\Theta \equiv \Phi(\bar{R}_\Theta{}^2/M)^{3/2} \qquad (5)$$

The quantities K_Θ and $\bar{R}_\Theta{}^2/M$ are both used as characteristics of a polymer–solvent system.

A large number of procedures[13-17] has been offered for calculation of K_Θ and also of the characteristic polymer–solvent interaction parameter (defined in a number of ways) from the measurement of intrinsic viscosity in good solvents. All these procedures are based on the two-parameter theories. While under fortuitous circumstances these procedures may lead to plausible values of K_Θ, the inadequacy of the two-parameter theories manifests itself usually by the curvature of dependences which are supposed to be linear. Quite often the curvature is either hidden by the scatter of experimental points or blamed on the experimental error. In the following we will employ the results of Monte-Carlo studies for evaluation of K_Θ and of the interaction parameter.

McCrackin et al.[10] in their Monte-Carlo study were interested in the effect of the energy of intersegmental contacts on the average dimensions of the model coil. For each random self-avoiding walk of N steps on a lattice they recorded, among other quantities, the end-to-end distance R, the number of intersegmental contacts P, and the weighing factor w, which is related to their method of generating the random walks. According to the rules of the statistical thermodynamics, the average value $\bar{v}$ of any calculated property v of the walk is

$$\bar{v} = \sum_{k=1}^{m} v_k w_k \exp(P_K\phi) \Big/ \sum_{k=1}^{m} w_k \exp(P_K\phi) \qquad (6)$$

Here, k is the subscript numbering the walks and m is the total number of walks. The interaction parameter ϕ is defined as

$$\phi \equiv -\epsilon/k_\mathrm{B}T \qquad (7)$$

where ϵ is the excess energy of an intersegmental contact, k_B is the Boltzmann constant, and T is the absolute temperature.

McCrackin et al.[10] performed the calculations for two lattices: simple cubic and face-centered cubic. They computed the values of $\bar{R}^2$ for a number of values of ϕ and N. When the values of ϕ were not much larger than ϕ_Θ (the definition of ϕ_Θ is given later), the bilogarithmic plot of $\bar{R}^2$ vs. N was linear over an appreciable range of values of N. Using the method of least squares, McCrackin et al.[10] fitted the data to the relation

$$\bar{R}^2 = AN^\gamma \qquad (8)$$

and tabulated the parameters A and γ as a function of the interaction parameter ϕ for both lattices. In eq 8 the values of R are measured in units equal to the distance b between two neighboring lattice points. For the sake of future convenience, we rewrite eq 8 as

$$\bar{R}^2 = b^2 AN^\gamma \qquad (9)$$

For the athermal case ($\epsilon = \phi = 0$) the exponent γ had a value quite close to 1.2 in agreement with a large number of older Monte-Carlo studies.[7-9] With increasing value of ϕ the exponent γ decreased and reached the value of unity for some characteristic value ϕ_Θ; for this value eq 9 transforms into

$$\bar{R}_\Theta{}^2 = b^2 A_\Theta N \qquad (10)$$

The values ϕ_Θ and A_Θ depend on the lattice; for the simple cubic lattice we have estimated from the data of McCrackin et al.[10] $\phi_\Theta = 0.275$ and $A_\Theta = 1.69$; the values for the face-centered cubic lattice were estimated as $\phi_\Theta = 0.1245$ and $A_\Theta = 1.438$.

Let us define a reduced energy parameter Q as

$$Q \equiv \phi/\phi_\Theta \qquad (11)$$

In Figure 1 the exponent γ is plotted as a function of Q for both lattices; within an experimental error both sets of data fall on the same line. We surmise that the de-

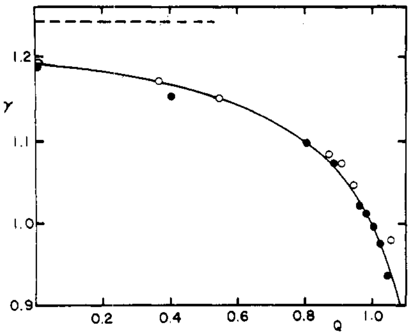

Figure 1. The dependence of the exponent γ on the reduced excess energy Q. Open points: simple cubic lattice. Solid points: face-centered cubic lattice. Full line represents eq 12; broken line is the limit at $Q = -\infty$.

pendence of γ on Q is universal, independent of the lattice (this postulate should be tested by extending the calculations to other lattices). By a nonlinear least-squares method we have fitted the dependence to an empirical relation

$$\gamma = 1.2530 - 0.05922/(1 - 0.7660Q) \qquad (12)$$

For computation of the relation 12, the value given by McCrackin et al.[10] for simple cubic lattice and for $\phi = -\infty$ (double excluded volume) was modified. The original value $\gamma = 1.18$ was lower than the value for athermal solvent ($\gamma = 1.20$) and exhibited a coefficient of variation much larger than the rest of the data. We have estimated that the appropriate value is $\gamma = 1.25$, i.e., the same value as the corresponding exponent for the radius of gyration. The corresponding value of A was changed from 1.52 to 1.445; the latter value was obtained by drawing a line with a slope 1.25 through the midpoint of the experimental values of N in the log $\bar{R}^2$ vs. log N plot. We have also included into the data the value $\gamma = 1.255$ given for tetrahedral lattice and double excluded volume by Mark and Windwer.[18]

The exponent γ as a function of Q seems to be independent of the type of lattice. We will now show that this is also true for the overall size of the coil. Let us assume that the real polymer system and its corresponding hypothetical Θ system, which are described by eq 1–4, are also described by Monte-Carlo eq 9 and 10. In the Monte-Carlo equations the constancy of the short-range interactions manifests itself in the constancy of the lattice parameter b. Let us define a contour length of the coil L as the end-to-end distance of the coil in a conformation which is acceptable (i.e., has a finite Boltzmann factor) and which exhibits the largest value of the end-to-end distance. For many vinyl polymers, it is the all-trans (zig-zag) conformation. The length L for a real coil may be written as relation 13 and for a Monte-Carlo coil as relation 14

$$L = lM \qquad (13)$$

$$L = bN \qquad (14)$$

The structural parameter l is given by relation 15, where M_0 is the molecular weight of a monomer unit and L_0 is the contribution of a monomer unit to the contour length

$$l \equiv L_0/M_0 \qquad (15)$$

Eliminating now the quantities $[\eta]$, $[\eta]_\Theta$, $\bar{R}^2$, $\bar{R}_\Theta{}^2$, L, b, and N from the set of eight equations 1–4, 9–10, 13–14 we find

$$K_\Theta = [K(\Phi l^3)^{1-\gamma}]^{1/(2-\gamma)}[A_\Theta A^{1/(\gamma-2)}]^{3/2}M^{(3\gamma-2-2a)/2(\gamma-2)} \qquad (16)$$

The left-hand side of eq 16 is independent of molecular weight, so the right-hand side must also be independent of molecular weight. The exponent of M must be equal to zero and γ is given by eq 17

$$\gamma = 2(a + 1)/3 \qquad (17)$$

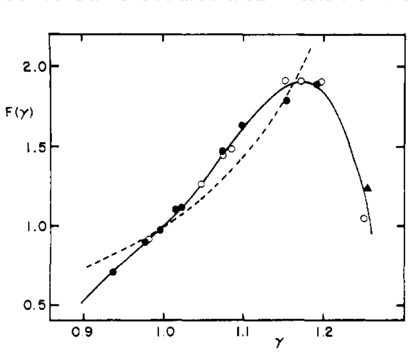

Figure 2. The volume factor $F(\gamma)$ as a function of exponent γ. Open points: simple cubic lattice. Solid points: face-centered cubic lattice. Triangle: tetrahedral lattice. Full line represents eq 20; broken line represents eq 21.

We may now rewrite eq 16 in the final form as

$$K_\Theta = [K(\Phi l^3)^{1-\gamma}]^{1/(2-\gamma)}F(\gamma) \qquad (18)$$

$$F(\gamma) \equiv (A_\Theta A^{1/(\gamma-2)})^{3/2} \qquad (19)$$

The volume factor $F(\gamma)$ has been calculated from McCrackin et al.[10] data for both lattices and plotted as a function of γ in Figure 2. We have included in the plot the data ($A = 4.15$; $\gamma = 1.255$) of Mark and Windwer[18] for the random walk with double excluded volume on tetrahedral lattice. The corresponding A_Θ value (7.69) was estimated assuming that the volume factor $F(\gamma)$ for their regular solution (single excluded volume) was equal to the value obtained from McCrackin's data on cubic lattices. Within a small experimental error, all the data fall on a single line. By a nonlinear least-squares method the data were fitted to an empirical dependence

$$F(\gamma) = 1 + 5.12(\gamma - 1) + 13.3(\gamma - 1)^2 + 38.0(\gamma - 1)^3 - 640.5(\gamma - 1)^4 \qquad (20)$$

The solid line in Figure 2 represents eq 20. The reliability of eq 20 is probably diminished in the regions below $\gamma = 0.97$ and above $\gamma = 1.20$ due to the scarcity of experimental points and to their somewhat tenuous nature in the latter region.

It is interesting to note that the method for calculating K_Θ which we have offered previously[5] can be formulated also in a form of eq 18 with $F(\gamma)$ given by eq 21

$$F(\gamma) = N_0{}^{3(\gamma-1)/2(2-\gamma)} \qquad (21)$$

The value of $N_0 = 9$ has been recommended.[5] With this value, eq 21 predicts the values of $F(\gamma)$, which differ from eq 20 by less than 10% in the region $\gamma \in (0.95, 1.18)$. Equation 21 is represented in Figure 2 by a broken line.

When evaluating the experimental data, γ is obtained first from the MHS exponent a according to eq 17. Then $F(\gamma)$ is calculated from eq 20 and K_Θ from eq 18. The value of the structural parameter l is usually obtained easily from the knowledge of the chemical structure of the polymer. The reduced energy parameter Q is obtained from eq 22, which is an inversion of eq 12

$$Q = 1.3055 - 0.07731/(1.2530 - \gamma) \qquad (22)$$

Experimental Section

Polystyrene samples were purchased from Pressure Chemical Co., Pittsburgh, Pa. The same samples were used in our previous studies.[6,19–21] The manufacturer's codes of these samples together with the molecular weights measured previously are given in the headings of Tables I and II.

Table I
Intrinsic Viscosities of Polystyrene Samples in Benzene and in *trans*-Decalin

	temp, °C	sample no. 7b	4b	1c	3b	13a
mol wt		35000	113000	177000	379000	619000
benzene	20	23.25	52.4	73.2	126.7	179.4
trans-decalin	16	14.88	24.9	30.5	42.5	52.0
	21	15.27	26.5	33.1	48.1	60.8
	25	15.48	27.6	34.9	51.5	66.0
	30	15.72	28.8	36.8	55.2	72.0
	40	16.06	30.8	39.6	61.5	81.8
	50	16.35	32.4	42.0	66.0	88.8
	65	16.72	34.0	44.8	71.2	96.8
	80	17.03	35.1	47.0	75.0	101.6

Table II
Huggins' Constants, k_H, of Five Polystyrene Samples in Benzene and in *trans*-Decalin at Several Temperatures

	temp, °C	sample no. 7b	4b	1c	3b	13a
mol wt		35000	113000	177000	379000	619000
benzene	20	0.420	0.377	0.381	0.345	0.338
trans-decalin	16	0.780	0.817	0.805	0.742	0.656
	21	0.745	0.714	0.644	0.634	0.572
	25	0.700	0.653	0.582	0.562	0.531
	30	0.652	0.580	0.530	0.524	0.521
	40	0.609	0.553	0.498	0.481	0.513
	50	0.577	0.510	0.477	0.444	0.503
	65	0.532	0.483	0.450	0.432	0.472
	80	0.519	0.476	0.446	0.409	0.462

The *trans*-decalin was purified from a commercial mixture of *cis*- and *trans*-decalin using a Nester/Faust spinning band column. The purity of the *trans*-decalin was determined as 99.6% by gas chromatography. Because of the limited amount available, the *trans*-decalin was recovered from the used solutions by distillation at reduced pressures.

Polystyrene–*trans*-decalin solutions were prepared by weighing. The concentrations of the polystyrene at the particular temperature were calculated by employing the density–temperature relation for *trans*-decalin reported by Nakata et al.[22]

$$\rho(\mathrm{g/cm^3}) = 0.88463 - 7.338 \times 10^{-4}t - 0.191 \times 10^{-6}t^2 \quad (23)$$

where t is the temperature in degrees centigrade. The concentrations ranged from 0.006 g/mL for the lowest molecular weight sample to 0.004 g/mL for the highest.

The viscosities of the polymer solutions were measured at eight temperatures by an automatic viscometer Fica Viscomatic marketed by Bausch and Lomb. The dilutions were performed manually; five concentrations were measured for each sample with the following fraction of the original concentration: 1, 2/3, 1/2, 2/5, 1/3. The relative viscosities $[\eta]_{\rm rel}$ for the final dilution of the original concentration ranged between 1.03 and 1.14. The flow times for *trans*-decalin ranged from 98 s at 16 °C to 40 s at 80 °C. The reproducibility was typically within 0.005 s. The kinematic correction and the correction for non-Newtonian flow were not applied. Temperatures were controlled to ±0.02 °C with a Lauda K-2R waterbath. The reproducibility of the flow times at high temperatures demonstrated the adequacy of the temperature control.

Results

For the evaluation of our raw experimental data we employed the same strategy as in our previous study.[6] For each polymer sample $\ln \eta_{\rm rel}/c$ was plotted in a Zimm-type double-correlation plot vs. $(c + kt)$, where c is the concentration in g/mL, t is the temperature in degrees centrigrade, and k is an arbitrary constant. This plotting technique significantly improved the consistency of the data while not introducing any significant bias; for example, in the plot for polystyrene sample 4b, only 8 points out of 45 differed more than 1% from the correlation net. Two examples of these plots are presented in Figures 3 and 4. (The concentrations of polystyrene, for which the viscosity was measured, were different for different temperatures. Consequently, the experimental points do not have the same abscissa as the intersections of the correlating net. The lines for constant concentration in Figures 3 and 4 have been drawn through points which were interpolated on lines for constant temperature.)

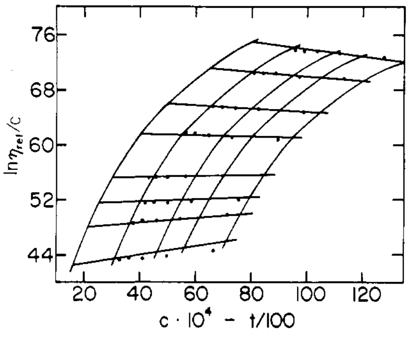

Figure 3. Double correlation of $\ln \eta_{\rm rel}/c$ as a function of concentration and temperature. Polystyrene sample 3b in *trans*-decalin.

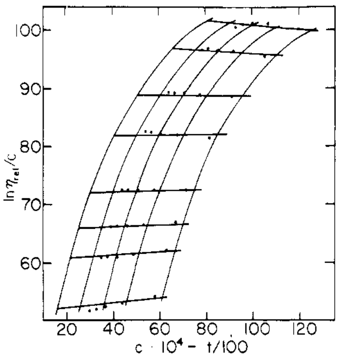

Figure 4. Double correlation of $\ln \eta_{\rm rel}/c$ as a function of concentration and temperature. Polystyrene sample 13a in *trans*-decalin.

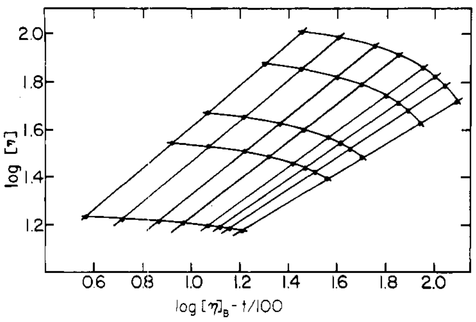

Figure 5. Double correlation of intrinsic viscosity of five polystyrene samples in *trans*-decalin as a function of their intrinsic viscosity in benzene at 20 °C and of temperature.

Table III
MHS Parameters and Some Derived Quantities for Polystyrene in *trans*-Decalin at Several Temperatures

t, °C	a	$K \times 10^2$	$K_\Theta \times 10^2$	Q	ϵ/ϵ_Θ
16	0.441	14.78	8.11	1.041	1.016
21	0.487	9.30	8.16	1.010	1.003
25	0.510	7.40	8.20	0.991	0.998
30	0.536	5.69	8.16	0.968	0.990
40	0.573	3.94	8.08	0.927	0.980
50	0.595	3.23	8.13	0.898	0.980
65	0.615	2.68	8.12	0.868	0.991
80	0.626	2.43	8.16	0.848	1.011

The intrinsic viscosities at different temperatures $[\eta]_t$ of the five polystyrene samples in *trans*-decalin extrapolated from the above plots were correlated further. The log $[\eta]_t$ was plotted against (log $[\eta]_B + kt$), where $[\eta]_B$ was the intrinsic viscosity measured previously[6] for the same samples in benzene at 20 °C (Figure 5). The double correlation yielded excellent straight lines for the dependences of log $[\eta]_t$ on log $[\eta]_B$. None of the points differed more than 1% from the correlation net; in fact, only 9 out of 40 intrinsic viscosities differed from the net more than 0.5%.

The MHS parameters a and K were calculated from the slopes and intercepts of the log $[\eta]_t$ – log $[\eta]_B$ lines using the relation for the intrinsic viscosity of polystyrene in benzene[19,23]

$$[\eta]_B = 1.23 \times 10^{-2} M^{0.72} \tag{24}$$

The correlated values of intrinsic viscosity (in mL/g units) are collected in Table I, the values of Huggins' constant k_H in Table II, and the parameters a and K together with some derived data in Table III. The MHS exponent a is plotted as a function of temperature in Figure 6. The Θ temperature was interpolated to t = 23 °C. This is in good agreement was literature values[22,24-27] reported in the region 20–24 °C.

Discussion

The values of K_Θ, which are reported in the fourth column of Table III, have been calculated from experimental data using eq 17, 18, and 20. For Φ the value 2.87 × 10^{23} was used. The value $l = 2.450 \times 10^{-10}$ cm/dalton is based on the all-trans conformation of the polystyrene chain, on the length of the backbone carbon–carbon bond equal to 1.53 Å, and on the average bond angle 113°; these values are recommended by Yoon et al.[28] The computed values of K_Θ are independent of temperature within an experimental scatter of ±0.6%. The values of K_Θ are in excellent agreement with the directly measured value 8.05 × 10^{-2} of Fukuda et al.[26] and with the value 7.95 × 10^{-2} derived from measurements of Inagaki et al.[25]

For an analysis of the dependence of K_Θ on temperature, values of K_Θ at several temperatures are needed. However, when K_Θ values for several solvents, which exhibit different Θ temperatures, are compared, the specific solvent effect may completely obscure the true temperature dependence (cf. ref 29). Values of K_Θ at (at least) two temperatures *in the same solvent* are needed. Such data are available for systems exhibiting both upper and lower critical solution temperature. For polystyrene in cyclopentane[30] the value of K_Θ at 19.6 °C is 1.5% higher than at 154.2 °C. For polystyrene in *tert*-butyl acetate[31] K_Θ at 23 °C is (for two samples) 0.7 and 3.1% lower than at 84 °C. All these changes are well within the experimental error; K_Θ in these solvents is essentially independent of temperature. Thus the fact that our computational procedure produces values of K_Θ which are sensitively independent of temperature serves as a strong test for our method and, by extension, as a verification of the usefulness of the Monte-Carlo modeling technique.

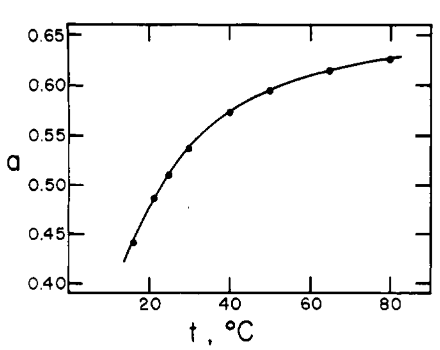

Figure 6. The MHS exponent a as a function of temperature for polystyrene in *trans*-decalin.

To get more insight into the applicability of the proposed method as well as into the short-range interactions of polystyrene, we have applied the method to data compiled in our previous communication.[5] The results are presented in Table IV. The calculated K_Θ values depend primarily on the chemical nature of the solvent. The aromatic solvents exhibit the highest values of K_Θ above 9.0 × 10^{-2}. The value remains high even in mixtures of an aromatic solvent (toluene) with other solvents as long as the content of the other solvent is not too high. The carbonyl solvents, butanone and ethyl acetate, exhibit values similar to values found in *trans*-decalin. In the mixtures of ethyl acetate and cyclohexane, the values of K_Θ are rising with increasing content of cyclohexane toward the value directly measured for cyclohexane. The only value which does not seem to be satisfactory is for cyclohexane at 20 °C, i.e., well below the Θ temperature. This discrepancy is either caused by low reliability of experimental data (only two samples of polystyrene of rather low molecular weight were measured) or by an inadequacy of eq 20 in the region far below the Θ temperature.

The energy parameter Q was calculated using eq 17 and 22; it is presented in Tables III and IV. For the understanding of the significance of the parameter Q we need to recall the relation between the hypothetic Θ state as defined earlier and the true Θ state. The former is defined as a state which would be achieved if the short-range interactions were preserved and the energy parameter ϕ (eq 7) were adjusted to value ϕ_Θ, which brings the system to the Θ state. Within the Monte-Carlo model, it is irrelevant whether we adjust the temperature or the excess contact energy ϵ or both quantities simultaneously. The true Θ state may be achieved only by adjusting the temperature to the experimental value Θ; the excess energy will acquire the value ϵ_Θ, which depends on the properties of the system at the true Θ temperature. The change of temperature may be accompanied by the change of

Table IV
MHS Parameters and Some Derived Quantities for Polystyrene in Different Solvents

solvent	t, °C	a	$K \times 10^2$	$K_\Theta \times 10^2$	Q
chloroform	25	0.719	1.22	8.81	0.585
benzene	20,25	0.720	1.23	9.02	0.578
ethylbenzene	25	0.667	2.02	9.80	0.761
toluene (T)	25	0.694	1.56	9.46	0.679
10% Hp,[a] 90% T	25	0.684	1.65	9.20	0.713
20% Hp, 80% T	25	0.670	1.85	9.24	0.751
30% Hp, 70% T	25	0.650	2.21	9.31	0.799
40% Hp, 60% T	25	0.631	2.52	8.92	0.839
55% Hp, 45% T	25	0.557	4.82	8.44	0.946
5% MeOH,[b] 95% T	25	0.681	1.76	9.64	0.720
10% MeOH, 90% T	25	0.663	2.06	9.70	0.770
15% MeOH, 85% T	25	0.632	2.70	9.71	0.837
20% MeOH, 80% T	25	0.567	4.72	9.20	0.934
butanone	25	0.599	3.01	7.87	0.892
ethyl acetate (EA)	20	0.582	3.62	8.06	0.916
90% EA, 10% CH	20	0.618	2.60	8.12	0.862
80% EA, 20% CH	20	0.642	2.12	8.15	0.818
70% EA, 30% CH	20	0.655	1.91	8.26	0.789
60% EA, 40% CH	20	0.663	1.82	8.42	0.771
50% EA, 50% CH	20	0.666	1.78	8.47	0.763
40% EA, 60% CH	20	0.669	1.71	8.35	0.754
30% EA, 70% CH	20	0.658	1.89	8.38	0.782
20% EA, 80% CH	20	0.629	2.49	8.57	0.843
10% EA, 90% CH	20	0.568	4.38	8.57	0.933
cyclohexane (CH)	20	0.410	19.18	7.58	1.059
cyclohexane	34	0.500	8.50	8.50	1.000

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

short-range interactions and consequently by change of K_Θ. At the level of the Monte-Carlo model, the change of short-range interactions is analogous to the change of lattice type; it may be accompanied by a change of ϕ_Θ. It is now obvious that *in general* we cannot use the properties of the true Θ state for the analysis of the parameter Q.

Fortunately, as we have seen above, the K_Θ value for polystyrene in a given solvent is essentially independent of temperature. The variation of unperturbed dimensions with temperature is very small for other polymers too.[32] If we interpret the constancy of K_Θ as a preservation of the short-range interactions, then we may consider the true Θ state as an acceptable hypothetical Θ state and write

$$\phi_\Theta = -\epsilon_\Theta / k_B \Theta \qquad (25)$$

where ϵ_Θ is the true excess energy of contact at the true Θ temperature Θ. Combination of eq 7, 11, and 25 now yields

$$\epsilon / \epsilon_\Theta = QT/\Theta \qquad (26)$$

The values of ϵ/ϵ_Θ were calculated for polystyrene in *trans*-decalin using eq 26 and are reported in the last column of Table III. Over our range of temperatures ϵ/ϵ_Θ is independent of temperature within ±2%. For most of the solvents and solvent mixtures reported in Table IV, the experimental value of Θ is not known and their ϵ/ϵ_Θ cannot be computed. However, Θ temperature for polystyrene in ethyl acetate is approximately −39 °C; that value leads to $\epsilon_{20\,°\mathrm{C}}/\epsilon_\Theta = 1.146$ (the excess contact energy seems to increase with increasing temperature). For polystyrene in cyclohexane $\epsilon_{20\,°\mathrm{C}}/\epsilon_\Theta$ is calculated as 1.010; however, we do not consider this number to be reliable for reasons stated earlier.

For real polymer solutions, the excess contact energy depends on the specific interaction between polymer and solvent as well as on the difference of characteristic temperature reduction parameters T^* for the polymer and the solvent in the equation of state.[33] The parameter T^* generally increases with increasing boiling point of the solvent. It is, therefore, not surprising that ϵ is a different function of temperature for a low-boiling solvent (ethyl acetate) than for a high-boiling solvent (*trans*-decalin). It will be interesting to study the relation between ϵ and the equation of state parameters in more detail.

Conclusions

In this study, we have proposed a method for the interpretation of the Mark–Houwink–Sakurada relation, i.e., of the experimentally obtained dependence of intrinsic viscosity of polymers in good solvents on their molecular weight. The method is based on the assumption that some fundamental features of polymer coils are reproduced well by the Monte-Carlo technique of modeling polymer coils by a random nonintersecting walk on a lattice. The method yields the characteristic constant of the pseudo-ideal solutions K_Θ and the reduced energy parameter Q. We have applied the method to critically evaluated older data for polystyrene in a number of solvents as well as to the newly measured values for polystyrene in *trans*-decalin at eight temperatures.

The calculated values of K_Θ were clustered in a rather narrow region; the variations within this region clearly reflected the effect of solvent on the short-range interactions. For polystyrene in *trans*-decalin, K_Θ was independent of temperature within rather small experimental error. Such behavior is fully compatible with the known behavior of polystyrene solutions.

When K_Θ is independent of temperature and when the experimental Θ temperature is known, the dependence of the reduced energy parameter Q on temperature may be interpreted in terms of the dependence of the excess contact energy ϵ on temperature. The calculated values of ϵ are within our experimental error independent of temperature for polystyrene in *trans*-decalin but increase with temperature for polystyrene in ethyl acetate. Such behavior seems to be reasonable from the viewpoint of the equation of state theories; our method may provide valuable experimental data for these theories. We plan future research in that direction.

In summary, the proposed method when applied to polystyrene solutions yields data which are very plausible and are compatible with all the known properties of such systems. Thus, the usefulness of the Monte-Carlo calculations for the analysis of measurements on polymer solutions seems to be well established.

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Solid State Extrusion of Poly(vinylidene fluoride). 1. Ram and Hydrostatic Extrusion

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ABSTRACT: Oriented films and fibers of poly(vinylidene fluoride) have been prepared by solid state extrusion and hydrostatic extrusion to an extrusion draw ratio of 8. The properties of the fibers and films have been assessed by several techniques including infrared spectroscopy, thermal analysis, and X-ray. A maximum birefringence of 0.039, a modulus of 3.5 GPa, a melting point increase of 5 °C, and a crystallinity of 50% were obtained for the extrudates. Shrinkage of fibers observed along the chain orientation axis is possibly due to retractive forces of the deformed noncrystalline phase. Infrared bands of the α- and β-polymorphic phases showed that extrusion produced a conversion from the α to the β phase.

The solid state extrusion of polyethylene[1] and the higher Nylons[2] has produced ultraoriented morphologies. Enhanced tensile moduli up to 70 GPa have been obtained for polyethylene which is approximately one-forth of the theoretical crystal modulus for its orthorhombic unit cell.[3-7] The theoretical crystal modulus for poly(vinylidene fluoride), PVF$_2$, in the chain direction has been shown to be 235 GPa, a value comparable with those for the higher Nylons[8] and polyethylene. Solid state extrusion of PVF$_2$ might also be expected to produce an ultraoriented fiber with high modulus. Further interest for extrusion of PVF$_2$, apart from the potential of producing a high modulus morphology, however, is due to its pronounced potential piezo- and pyroelectric activity.

PVF$_2$ can exist in three crystalline conformations:[9,10] phase I (or β form) has a planar zig-zag structure; phase II (or α form) has a sequence of approximately alternating gauche and trans bonds. The existence of a third phase was first suggested by Natta, et al.[11] Cortili and Zerbi[12,13] and Gal'Perrin et al.[14] have described the preparation and characteristics of this third polymorph, phase III (γ form). Lando and Doll[10] and others[15] speculate on the conformation of phase III as planar zig-zag, based on the similarity of infrared spectra between forms I and III.

The crystallites of the β form exhibit a permanent polarization. The relative amounts of α and β forms reportedly depend on the draw temperature and draw ratio. Lando and Doll[10] showed that PVF$_2$ films conventionally drawn at 50 °C produced only the β form, whereas drawing above 100 °C increased the α form content. The solid state extrusion temperature should therefore be at least 50 °C below the PVF$_2$ ambient melting point (~170 °C) with the limitation of ever decreasing extrusion rates at lower temperatures.[5] Solid state extrusion has produced polyethylene extrudates with near perfect crystal orientation and with a birefringence greater than the intrinsic birefringence of the single crystal.[6] It is thus anticipated that the method may provide a possible route for obtaining increased pyroelectricity and/or piezoelectric activity for ultraoriented PVF$_2$, since Glass et al.[16] have reported a correlation between birefringence and pyroelectricity of PVF$_2$.

Kolbeck and Uhlmann,[17] using the method of extrusion reported by Southern and Porter,[18] have independently shown that solid state extrusion of PVF$_2$ is possible.

In the present paper, preliminary experiments on ram and hydrostatic extrusion of PVF$_2$ are presented, and the resulting filament and film properties are analyzed using the techniques discussed elsewhere.[5-7]

Experimental Section

Materials. The Pennwalt Corp. Kynar series 301, 450, and 820 were used having cited melting points of 156, 155, and 166 °C, respectively. A further sample, a copolymer of vinylidene fluoride and tetrafluoroethylene (73% CH$_2$CF$_2$, 27% C$_2$F$_4$), Kynar 7201 (not available commercially), was supplied kindly by Dr. G. T. Davis and Dr. M. Broadhurst of the U.S. National Bureau of Standards.

Extrusion. Poly(vinylidene fluoride) was oriented by solid state extrusion procedures described elsewhere.[19] Briefly the PVF$_2$ was isothermally crystallized under high pressure (0.23 GPa). The

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