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Registry No. Polyethylene, 8049-65-8.

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Analysis of the Temperature Quotient of the Intrinsic Viscosity of Stiff-Chain Polymers

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ABSTRACT: The temperature quotient of the intrinsic viscosity, d ln $[\eta]/\mathrm{d}T$, of stiff-chain polymers is discussed in terms of the Yamakawa–Fujii wormlike cylinder model. A method of estimating the quotient d ln $(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$ is outlined and applied to the data for some cellulose derivatives (tricarbanilate, tributyrate, nitrate with 12.5% N, ethyl ether). The possibility of assessing the temperature effect on other parameters of the model (chain diameter and shift factor) is analyzed.

The temperature quotient of the intrinsic viscosity, d ln $[\eta]/\mathrm{d}T$, of random-flight chains in the nondraining limit contains contributions from the short-range interactions and the excluded-volume effect. If appropriate corrections are applied for the latter, the temperature quotient, d ln $(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$, of the mean-square unperturbed chain length, $\langle R^2\rangle_0$, in the random-coil limit can be estimated. This quotient is a quantity which provides important information on the energetics of the bond conformation.[1]

With stiff-chain polymers, the excluded-volume effect is usually weak, which seemingly facilitates the estimation of d ln $(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$. Yet hydrodynamic properties of such chains do not comply with the model of nondraining random coils so that the interpretation of the quotient d ln $[\eta]/\mathrm{d}T$ requires a special approach.

This problem is analyzed in the present paper on the basis of the theory of hydrodynamic properties of the continuous wormlike cylinder model.[2] The values of d ln $(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$ for several cellulose derivatives are estimated, and the temperature effect on other parameters characterizing the chain in terms of this model is discussed.

Theoretical Section

The continuous wormlike cylinder model[2] is characterized by its contour length L, diameter d, and the persistence length a or the Kuhn statistical segment length $\lambda^{-1} = 2a$. The latter is connected with $(\langle R^2\rangle_0/M)_\infty$ by

$$\lambda^{-1} = (\langle R^2\rangle_0/M)_\infty M_L \qquad (1)$$

where M_L is the shift factor. In terms of this model, the intrinsic viscosity $[\eta]_0$ of stiff chains unperturbed by the excluded-volume effect is[2]

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$$[\eta]_0 = [\phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2}M^{1/2}]F_1(L_r,d_r) \qquad (2)$$

where

$$F_1 = \phi_0(L_r,d_r)/\phi_{0,\infty} \qquad (3)$$

and L_r and d_r are reduced quantities

$$L_r = L/\lambda^{-1} \qquad (4a)$$

$$d_r = d/\lambda^{-1} \qquad (4b)$$

The viscosity function ϕ_0 depends on L_r and d_r; its limit for $L_r \rightarrow \infty$ is a constant. Since the function F_1 can be given a simple form[3,4]

$$F_1 = (B_0 + A_0/L_r^{1/2})^{-3} \qquad (5)$$

eq 2 can be recast into

$$[\eta]_0 = B_\eta^{-3}M^{1/2}/[1 + (A_\eta/B_\eta)M^{-1/2}]^3 \qquad (6)$$

where

$$A_\eta = A_0 M_L \phi_{0,\infty}^{-1/3} \qquad (7)$$

$$B_\eta = B_0\phi_{0,\infty}^{-1/3}(\langle R^2\rangle_0/M)_\infty^{-1/2} \qquad (8)$$

B_0 is nearly constant, whereas A_0 is a function of d_r.[4]

Differentiation of eq 6 with respect to temperature gives

$$\mathrm{d}\ln[\eta]_0/\mathrm{d}T = S_2 + S_1(A_\eta + B_\eta M^{1/2})^{-1} \qquad (9)$$

where

$$S_1 = 3A_\eta(\mathrm{d}\ln B_\eta/\mathrm{d}T - \mathrm{d}\ln A_\eta/\mathrm{d}T) \qquad (10)$$

and

$$S_2 = -3(\mathrm{d}\ln B_\eta/\mathrm{d}T) \qquad (11)$$

Substitution from eq 6 and rearrangement lead to

$$(M^2/[\eta]_0)^{1/3}(\mathrm{d}\ln[\eta]_0/\mathrm{d}T) = S_1 + S_2(M^2/[\eta]_0)^{1/3} \qquad (12)$$

According to this equation, the plot of $(M^2/[\eta]_0)^{1/3}(\mathrm{d}\ln[\eta]_0/\mathrm{d}T)$ vs. $(M^2/[\eta]_0)^{1/3}$ is expected to be linear, its intercept and slope being S_1 and S_2, respectively.

It follows from eq 7 that

$$\mathrm{d}\ln A_\eta/\mathrm{d}T = \mathrm{d}\ln A_0/\mathrm{d}T + \mathrm{d}\ln M_L/\mathrm{d}T \qquad (13)$$

From an approximate formula[4] valid for $d_r \lesssim 0.1$

$$A_0 = 0.46 - 0.23\ln d_r \qquad (14)$$

we obtain

$$\mathrm{d}\ln A_0/\mathrm{d}T = (\mathrm{d}\ln d_r/\mathrm{d}T)/(\ln d_r - 2) \qquad (15)$$

Combining eq 13, 15, 4b, 1, 10, and 11, we have the equation

$$Q_1 \equiv -\tfrac{1}{3}[(4 - \ln d_r)S_2 + (2 - \ln d_r)(S_1/A_\eta)] = (3 - \ln d_r)(\mathrm{d}\ln M_L/\mathrm{d}T) - (\mathrm{d}\ln d/\mathrm{d}T) \qquad (16)$$

The Q_1 parameter can be evaluated from experimental data. Thus, in principle eq 16 offers a means to analyze the variation with temperature of the shift factor M_L and diameter d.

Strictly speaking, eq 12 holds for systems where the excluded-volume effect and its dependence on temperature are negligible. In practice, this may be a serious limitation which should be considered before applying eq 12 to experimental data.

No workable theory has been advanced for the intrinsic viscosity, $[\eta]$, of the wormlike cylinder taking into account excluded volume. We assume that, for the purpose of the present paper, this effect can be introduced in the way usual with nondraining random coils, i.e., by means of the viscosity expansion factor α_η^3,

$$[\eta] = [\eta]_0\alpha_\eta^3 \qquad (17)$$

connected with the excluded-volume parameter z

$$z = (3/2\pi)^{3/2}(\langle R^2\rangle_0/M)_\infty^{-3/2}BM^{1/2} \qquad (18)$$

where B is the polymer–solvent interaction parameter.[5]

For low z, we can write[5]

$$\alpha_\eta^3 = 1 + C_\eta z + \ldots \qquad (19)$$

The coefficient C_η has been calculated[5] for the nondraining random coil only ($L_r \rightarrow \infty$), but its chain-length dependence is unknown. It will probably be similar to that of the coefficient C_R in the equation

$$\alpha_R^2 = 1 + C_R z + \ldots$$

where $\alpha_R^2 = \langle R^2\rangle/\langle R^2\rangle_0$. Yamakawa and Stockmayer[6] found theoretically that $C_R = 0$ at $L_r \leq 1$ and $C_R^\infty = 4/3$ (where $C_R^\infty = \lim C_R$ for $L_r \rightarrow \infty$) at $L_r \gtrsim 10^3$.

After an analysis of the radii of gyration for several stiff-chain polymers, Norisuye and Fujita[7] concluded that the excluded volume effect is observable at $L_r > L_{r,c} \simeq 50 \pm 30$. We assume that a similar "critical" value, $L'_{r,c}$, also exists for the intrinsic viscosity.

Differentiation of eq 17 with respect to temperature gives

$$\mathrm{d}\ln[\eta]/\mathrm{d}T = \mathrm{d}\ln[\eta]_0/\mathrm{d}T + \mathrm{d}\ln\alpha_\eta^3/\mathrm{d}T \qquad (20)$$

The first term is given by eq 12. The second term (for low z) follows from eq 19

$$\mathrm{d}\ln\alpha_\eta^3/\mathrm{d}T = (C_\eta/\alpha_\eta^3)(\mathrm{d}z/\mathrm{d}T) + \ldots \qquad (21)$$

where

$$\mathrm{d}z/\mathrm{d}T = (3/2\pi)^{3/2}(\langle R^2\rangle_0/M)_\infty^{-3/2}\left\{(\mathrm{d}B/\mathrm{d}T) - \frac{2}{3}B[\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T]\right\} \qquad (22)$$

Combination of eq 12, 21, and 22 would yield an equation of general validity but of little practical use. It reduces to eq 12 if either $\mathrm{d}z/\mathrm{d}T$ or C_η is zero. The former case would result from accidental compensation of the terms in brackets of eq 22; the latter occurs at low chain lengths ($L_r < L'_{r,c}$) even in good solvents ($B \neq 0$).

It is seen that for good solvent systems, the plot according to eq 12 can be expected to be linear at $L_r < L_{r,c}$. Nonlinearity at high molecular weights would indicate that the corresponding L_r values are higher than $L'_{r,c}$.

Estimation of d ln $(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$. Since $\phi_{0,\infty}$ and B_0 are independent of temperature, the term S_2 is

$$S_2 = (3/2)[\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T] \qquad (23)$$

so that the quotient $\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T$ is easily estimated from the slope S_2.

With some stiff-chain polymers, the quotient $\mathrm{d}\ln[\eta]/\mathrm{d}T$ is found to be independent of molecular weight. This means, according to eq 12, that $S_1 = 0$ and

$$(\mathrm{d}\ln[\eta]/\mathrm{d}T)_{S_1=0} = (3/2)[\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T] \qquad (24)$$

According to eq 10, this situation can arise if either

$$\mathrm{d}\ln A_\eta/\mathrm{d}T = \mathrm{d}\ln B_\eta/\mathrm{d}T \qquad (25)$$

or $A_\eta = 0$. The former case is rather accidental; the second is worth discussion.

Equation 2 with $F_1 = 1$ holds for thick chains[4] ($d_r \cong 0.4$). In this case the intrinsic viscosity, $[\eta]_0$, should be proportional to $L_r^{1/2}$ even at very low L_r. This proportionality is generally found with flexible-chain polymers under

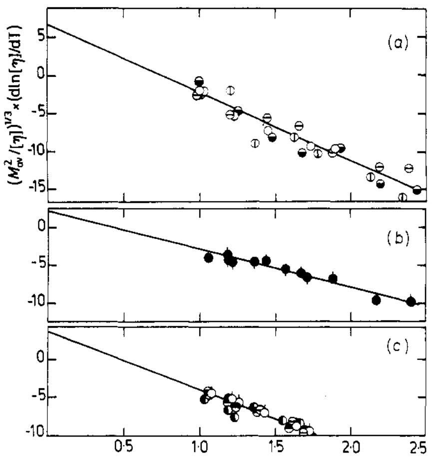

Figure 1. Plot according to eq 12 for ethylcellulose. (a) Data from ref 8: (O) acetone, (◓) butanol, (◐) butyl chloride, (⊖) ethyl acetate ($M_{av} = M_w$). (b) Data for benzene solutions: (● pip upward) $M_{av} = M_w$,[8] (● pip downward) $M_{av} = M_n$.[9] (c) Data from ref 9 ($M_{av} = M_n$): (O pip upward) ethyl methyl ketone, (◓) butyl acetate, (⊖) ethyl acetate, (◐) chloroform.

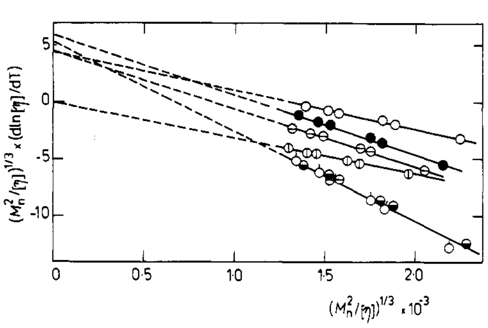

Figure 2. Plot according to eq 12 for cellulose nitrate (12.5% N). Data from ref 10: (O) acetone, (●) methyl acetate, (⊖) butyl acetate, (O) nitrobenzene, (O pip upward) amyl methyl ketone, (◓) cyclohexanone.

Θ-conditions. Nevertheless, the temperature quotient of the intrinsic viscosity at the Θ-temperature, $(d\ln[\eta]/dT)_\Theta$, for such chains depends on the molecular weight, which is at variance with eq 24. This behavior can be explained in the following way. Since the statistical segment length, λ^{-1}, is low for flexible-chain polymers, the $L'_{r,c}$ value is attained already at low molecular weights and most samples of practical importance correspond to $L_r > L'_{r,c}$. Accordingly, the coefficient C_η in eq 19 is finite so that the quotient $d\ln\alpha_\eta^3/dT$ is non-zero (unless $dz/dT = 0$) and depends on the molecular weight. So the molecular weight dependence of $(d\ln[\eta]/dT)_\Theta$ of flexible-chain polymers is due to the $d\ln\alpha_\eta^3/dT$ term.

Results and Discussion

Plots of Data according to Equation 12. The plot based on eq 12 is used to analyze the literature data of $d\ln[\eta]/dT$ for some cellulose derivatives (ethyl ether,[8,9] nitrate with 12.5% N,[10] tributyrate,[11] tricarbanilate[12,13]) (Figures 1–3). With all of them, the dependences of ln $[\eta]$ on T are linear over a broad range of temperatures, so the quotient $d\ln[\eta]/dT$ is independent of temperature. With other stiff-chain polymers (e.g., polypeptides), the dependences of ln $[\eta]$ on T are more complex and will not be discussed here. The $[\eta]$ values in the terms $(M^2/[\eta])^{1/3}$ correspond to the middle of the temperature span.

The temperature dependence of $[\eta]$ for ethylcellulose was studied by Meyerhoff and Sütterlin[9] and Moore and Brown.[8] Although the samples were characterized by the weight-average molecular weight, M_w, in the former paper and by the number-average molecular weight, M_n, in the latter, the values of S_2 for both sets of data (Figure 1) are very close. The plots are almost the same for all solvents, except benzene.

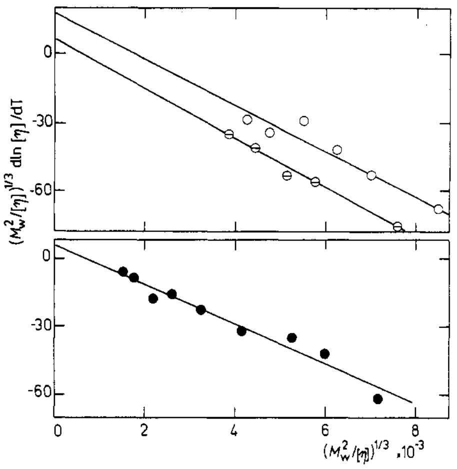

Figure 3. Plot according to eq 12 for cellulose tricarbanilate. Data points: (●) benzophenone;[12] (O) acetone, (⊖) dioxane.[13]

The temperature dependence of $[\eta]$ for incompletely substituted cellulose nitrate was investigated by Moore and Edge.[10] The fractions were characterized by M_n, and the span of molecular weights was narrow. Since the $[\eta]$ values were not tabulated in the original paper, we had to calculate them from the reported Mark–Houwink–Kuhn–Sakurada parameters. These facts may affect the absolute values of the resulting parameters, but differences in slopes for different solvents (Figure 2) seem to be significant.

The quotient $d\ln[\eta]/dT$ for cellulose tributyrate (CTB) in glycerol tributyrate[11] is almost independent of molecular weight so that eq 24 may be used.

The molecular weights of the preceding polymers are such that $L_r < L_{r,c}$ so that the excluded-volume effect is negligible. This is not the case with cellulose tricarbanilate (CTC).[12,13] Consequently, the S_2 values for this polymer should be estimated from the initial slopes in Figure 3. Anyway, the data points at high molecular weights do not deviate significantly from line (probably because of the low values of $d\ln\alpha_\eta^3/dT$) so that eq 12 may be employed even in this case.

Values of $d\ln(\langle R^2\rangle_0/M)_\infty/dT$ for Some Cellulose Derivatives. The quotient $d\ln(\langle R^2\rangle_0/M)_\infty/dT$ is negative and large for all the polymers investigated (Table I). This indicates a strong increase in the rotational freedom of the chain at higher temperatures.

The behavior of CTB is remarkable. For this polymer, the intrinsic viscosity data are available also for a high-temperature Θ-solvent (decalin–dodecane, Θ = 120 °C).[14] The $[\eta]_\Theta$ values are proportional to $M^{1/2}$ over the whole span of molecular weights. Equation 2 with $F_1 = 1$ can, therefore, be used to estimate $(\langle R^2\rangle_0/M)_\infty$. The obtained value, $(\langle R^2\rangle_0/M)_\infty = 0.5\times10^{-16}$ cm^2, amounts to about 40% of that (1.3×10^{-16} cm^2) calculated from the low-temperature data, $(\langle R^2\rangle_0/M)_\infty = 2.6\times10^{-16}$ cm^2 (at 25 °C), with $d\ln(\langle R^2\rangle_0/M)_\infty/dT$ given in Table I. This fact provides evidence of a pronounced conformational change of the CTB chain at temperatures around 100 °C.

Parameters S_1 and Q_1. The S_1 parameter for most polymer–solvent systems investigated here is positive. It follows from eq 10 that in this case, $d\ln(A_\eta/B_\eta)/dT$ is negative. If the temperature is increased, the denominator in eq 6 becomes close to unity so that the molecules approach the "nondraining behavior". For cellulose nitrate in nitrobenzene and for CTB, the parameter S_1 is close to

Table I
Results of the Treatment of d ln [η]/dT according to Equations 12 and 23

solvent	$-[\mathrm{d}\ln(\langle R^2\rangle_0/M)_\infty/\mathrm{d}T]10^3$, deg^{-1}	S_1
	Ethylcellulose	
acetone[a]	5.6 ± 0.7	5.9 ± 1.6
methyl ethyl ketone[b]	5.2 ± 0.3	4.2 ± 0.7
benzene	3.4 ± 0.3	2.3 ± 0.9
	Cellulose Nitrate[c] (12.5% N)	
acetone	2.3	
methyl n-amyl ketone	5.3	
methyl acetate	3.5	5
n-butyl acetate	3.4	
cyclohexanone	5.3	
nitrobenzene	3.1	
	Cellulose Tributyrate	
glycerol tributyrate	6.0 ± 0.7	
	Cellulose Tricarbanilate	
benzophenone	5.8 ± 0.5	6.0 ± 2.8
acetone	6.2 ± 1.0	14 ± 9.4
dioxane	7.4 ± 0.7	7.1 ± 5.2

[a] Similar value for ethyl acetate, butyl chloride, and butanol (Figure 1). [b] Similar value for ethyl acetate, butyl acetate, and chloroform (Figure 2). [c] Standard deviations are not given because [η] values were calculated from smoothed dependence of [η] vs. M (see text).

zero, which indicates no significant variation with temperature of the denominator in eq 6 and of the F_1 function.

The values of Q_1 calculated according to eq 16 are negative and inaccurate. They cannot be resolved into their components, d ln d/dT and d ln M_L/dT, according to eq 16 unless one of them is estimated independently. No reliable method, however, is known to obtain either of them. So the subsequent discussion is merely an attempt to assess the limits within which these quotients may vary. Cellulose tricarbanilate in benzophenone has been chosen as an example ($Q_1 = 10 \times 10^{-3}$ deg^{-1}, $A_\eta = 300$,[15] $d_r \simeq 0.1$). By substituting these data into eq 16, we obtain

$$Q_1 \equiv 5.303(\mathrm{d}\ln M_L/\mathrm{d}T) - (\mathrm{d}\ln d/\mathrm{d}T) = -10 \times 10^{-3}$$

(i) We assume first that the shift factor M_L is independent of temperature. For $Q_1 < 0$, this necessarily leads to a positive value of d ln d/dT (e.g., 10×10^{-3} for CTC). Accordingly, an increase in temperature by 50 °C would induce a very large increase in d (about 50%). In a study of acetoxypropylcellulose, Laivins and Gray[16] assigned an increase in the diameter with temperature to an extension of the side chains. For CTC, Burchard[17] postulated hydrogen bonds between the side groups to account for the stiffness of the chain. An increase in temperature will disrupt these bonds, thus making the side groups more mobile. Though this explanation seems qualitatively acceptable, it is improbable that it could account for the large value of d ln d/dT.

(ii) Let us consider the opposite case, d ln d/dT = 0. We find d ln M_L/dT $\simeq -1.9 \times 10^{-3}$ deg^{-1}, corresponding to a decrease of 10% in M_L for ΔT = 50 °C. For cellulose derivatives, M_L at 25 °C agrees, within reasonable limits,[2,4,15] with the value calculated as $M_L = M_0/l_u$ where M_0 is the molecular weight of the chain repeat unit and l_u is the projection of the length of this unit on the chain axis. A decrease in M_L should be associated with an increase in l_u.

(iii) When we evaluated the d and M_L values of some stiff-chain polymers, use was made of the assumption[4,18] that the hydrodynamic volume occupied by 1 g of the wormlike cylinders is approximately equal to the partial specific volume $\bar{v}$ of the polymer so that

$$\bar{v} = (\pi N_A/4)(d^2/M_L) \quad (26)$$

It has been emphasized that the diameter in eq 26 need not be identical with the effective hydrodynamic diameter, and the same reservation is valid for the variation of d with temperature. Anyway, since the above assumption led to reasonable estimates of d and M_L with many polymers, we combine eq 16 with the quotient d ln $\bar{v}$/dT

$$\mathrm{d}\ln\bar{v}/\mathrm{d}T = 2(\mathrm{d}\ln d/\mathrm{d}T) - \mathrm{d}\ln M_L/\mathrm{d}T \quad (27)$$

to simulate an intermediate case where both M_L and d vary with temperature.

As no $\bar{v}$ values are known for CTC in benzophenone, we employ d ln $\bar{v}$/dT = 1×10^{-3} deg^{-1} evaluated from the $\bar{v}(T)$ data for solutions in acetone and tetrahydrofuran.[19] We obtain d ln M_L/dT = -2×10^{-3} deg^{-1} and d ln d/dT = -0.5×10^{-3} deg^{-1}.

While the former value is nearly the same as that estimated in (ii), the latter is small and negative, i.e., quite the opposite to that obtained with d ln M_L/dT = 0 in (i). Anyway, an explanation can be proposed for this case, too. The diameter d is assumed to be dependent on solvation,[20] and a decrease in solvation at a higher temperature could induce a reduction of the diameter.

Concluding Remarks

The discussion in (i)–(iii) leads us to conclude that, while the [η](T,M) data for stiff-chain polymers allow a fairly reliable estimation of the quotient d ln $(\langle R^2\rangle_0/M)_\infty$/d$T$, interpretation of the S_1 and Q_1 parameters, which are connected with the temperature effects on the shift factor and chain diameter, remains open for further investigation.

Registry No. Ethylcellulose, 9004-57-3; cellulose nitrate, 9004-70-0; cellulose tributyrate, 39320-16-6; cellulose tricarbanilate, 9047-07-8.

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