Variation in Intrinsic Viscosity ϕ Parameter with Chain Topology, Hydrodynamic Interaction, and Excluded Volume

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ABSTRACT: We have surveyed normal coordinate intrinsic viscosity calculations for linear, cyclic, and branched polymer chains as functions of excluded volume and hydrodynamic interaction effects. A simple factorization of the Flory–Fox ϕ factor, of the form $\phi = 2.84 \times 10^{21} qF(\epsilon)[h^{0.94}/(e^{A} + h^{0.94})]$, gives good agreement with detailed calculations over the entire range of excluded volume parameter ϵ and hydrodynamic interaction parameter h encountered in practice. Since the variation of ϕ with chain topology and ϵ is known, standard log $[\eta]$ − log M plots can be analyzed to give the effective segment length, b, in any solvent. It is shown that b remains palpably constant for three common nonionic polymers, but increases substantially with decreasing ionic strength (increasing ϵ) for polyacrylic acid.

In 1951, Flory and Fox[1] argued that, since the intrinsic viscosity $[\eta]$ of a polymer in solution reflected its effective hydrodynamic volume, $[\eta]$ could be written in the form

$$[\eta] = \phi\langle L^2\rangle^{3/2}/M \qquad (1)$$

The molecular weight of the polymer is M; its mean-square end-to-end distance, which reflects both short-range and long-range interactions, is $\langle L^2\rangle$. ϕ is a parameter which, it was argued, "should be the same for all polymers regardless of the solvent and temperature"[1] once M has reached a (moderate) limiting value.

Since that time, research has gone along two main lines. In the first, substantial theoretical effort has been devoted to justifying the form of eq 1 and to *a priori* calculation of the magnitude of ϕ. The first calculation which was firmly grounded on statistical mechanical principles and which took account of hydrodynamic interactions was that of Kirkwood and Riseman.[2] An equivalent, but somewhat simpler, theory was developed by Zimm[3] using a normal coordinate analysis introduced by Rouse[4] and by Bueche.[5] The normal coordinate theory has since been applied to linear polymers with varying hydrodynamic interaction[6] and excluded volume effects,[7] to branched polymers,[8] and to cyclic polymers with excluded volume.[9]

The upshot of these calculations is that ϕ is not truly a universal constant, but instead depends somewhat on polymer chain topology (linear, cyclic, branched), on excluded volume effects, and on the magnitude of hydrodynamic interaction or draining effects. It is the major aim of this paper to survey these calculations and to show that ϕ can be factored, to a good approximation, into a product of terms which reflect the individual factors mentioned above.

Concurrently with these theoretical developments, many experiments have been done using eq 1 with theoretical or experimental values for ϕ, and some theory of excluded volume effects, to obtain unperturbed dimensions of polymer chains. These in turn lead to information on short-range interactions such as internal rotation hindrance potentials.[10] These treatments usually implicitly assume that short-range interactions are independent of solvent, and often[1] that ϕ is independent of solvent. These assumptions are unlikely to be true in detail,[11] and it would therefore appear to be a safer procedure to devise a method for assessing short-range interactions in any solvent, whether good or poor. The equations presented here enable the simple formulation of such a method.

Calculations and Results

In order to encompass cyclic and branched molecules as well as linear ones, we shall rewrite eq 1 as

$$[\eta] = (6g^{-1})^{3/2}\phi\langle R^2\rangle^{3/2}/M \qquad (2)$$

where $\langle R^2\rangle$ is the mean-square radius of the polymer chain and g is the ratio of the mean-square radii of nonlinear and linear chains of the same molecular weight in the absence of excluded volume effects, and has been computed for a number of special cases.[12] Equation 2 can be applied to cyclic chains, in which $\langle L^2\rangle$ is zero by definition, and to branched polymers for which $\langle L^2\rangle$ is ambiguous. Furthermore, $\langle R^2\rangle$ is less sensitive to excluded volume effects than is $\langle L^2\rangle$,[13] so that ϕ will be more nearly constant when defined as in eq 2. Finally, when ϕ is defined by eq 2, one has for two different chain topologies α and β in the absence of excluded volume effects, $[\eta]_\alpha/[\eta]_\beta = \phi_\alpha/\phi_\beta$.

In the subsequent treatment we characterize the

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TABLE I

VALUES OF γ AND A IN EQUATION 7 AS FUNCTIONS OF ϵ FOR LINEAR, CYCLIC, AND BRANCHED POLYMERS

	Linear		Cyclic		Branched			
					$f = 4$		$f = 8$	
ϵ	γ	A	γ	A	γ	A	γ	A
0.0	0.876	0.190	0.884	0.457	0.914	0.476	0.881	1.05
0.1	0.937	−0.169	0.926	0.0758				
0.2	0.996	−0.533	0.932	−0.291				
0.33	0.949	−0.933	0.967	−0.703				

excluded volume effect by a parameter ϵ[7,9] defined such that for linear chains with N statistical segments of length b

$$\langle L^2\rangle = b^2N^{1+\epsilon} \tag{3}$$

or

$$\langle L^2\rangle/\langle L^2\rangle_0 = N^\epsilon \tag{4}$$

where $\langle L^2\rangle_0$ is the mean-square length in a θ solvent, when $\epsilon = 0$.

Hydrodynamic interaction is characterized by a parameter[7,9]

$$h(\epsilon) = 2^{\epsilon/2}N^{(1-\epsilon)/2}\zeta/(12\pi^3)^{1/2}b\eta_0 \tag{5}$$

where ζ is the translational frictional coefficient of a segment and η_0 is the solvent viscosity. It will be noticed that h is a function of N; for spherical segments of radius $b/2$, and no excluded volume ($\epsilon = 0$), $h(0) = 0.489N^{1/2}$.

Intrinsic viscosities have been calculated from the equation[8]

$$[\eta] = (N_Ab^2\zeta/6M\eta_0)\sum_k \omega_k\lambda_k^{-1} \tag{6}$$

where N_A is Avogadro's number, ω_k is the degeneracy and λ_k the eigenvalue of the kth normal mode.

In all cases we have combined eq 2 and 6 with the appropriate eigenvalues and degeneracies to calculate $\phi(\epsilon, h)$, and have fit our results by linear least squares analysis to the form

$$\phi(\epsilon, h) = 2.843 \times 10^{21}qF(\epsilon)[h^\gamma/(e^A + h^\gamma)] \tag{7}$$

In eq 7 the factor 2.843×10^{21} is ϕ ($\epsilon = 0$, $h = \infty$) for linear chains.[3] q is the ratio of $\phi(0, \infty)$ for the chain topology under consideration to $\phi(0, \infty)$ for linear chains

$$q = \phi(0, \infty)/2.843 \times 10^{21} \tag{8}$$

$F(\epsilon)$ is taken to be a quadratic in ϵ, while γ and A are numbers which may depend on ϵ.

1. Linear Chains. Calculations of ϕ_L for linear chains, as a function both of ϵ and h, have been made by Tschoegl.[7] We have found that his results can be expressed in the form of eq 7, where

$$q_L = 1 \tag{9}$$

$$F_L(\epsilon) = 1 - 2.531\epsilon + 2.273\epsilon^2 \tag{10}$$

The values of γ and A are given as functions of ϵ in Table I. Deviations between ϕ_L as given by eq 7 with these numbers, and as calculated by Tschoegl,[7] are never more than 5% for $h \geqslant 2.5$, corresponding to a very short polymer with $N = 25$ if $\epsilon = 0$.

2. Cyclic Chains. For cyclic chains the factor g in eq 2 is $^1/_2$.[12] The eigenfunctions are rigorously the sum of free-draining and nondraining eigenfunctions[9]

$$\lambda_k = (4\pi^2/N^2)[k^2 + h(\epsilon)\lambda_k'/\pi^2] \tag{11}$$

where the nondraining eigenvalues are related to zero-order Bessel functions J_0

$$\lambda_k' = (-1)^k\sqrt{2}\pi^3k^2J_0(\pi k) \tag{12}$$

All degeneracy factors ω_k are equal to 2.

The value of the ϕ_c factor for rings has already been calculated[9] as a function of ϵ at infinite h (the nondraining limit). We can then compute ϕ_c at finite values of h by using eq 2, 6, and 11.

$$\phi_c(\epsilon, h) = \phi_c(\epsilon, h = \infty)\left(\sum_{k=1}^{\infty}\frac{2}{[\lambda_k' + \pi^2k^2/h(\epsilon)]}\right)\Bigg/\left(\sum_{k=1}^{\infty} 2/\lambda_k'\right) \tag{13}$$

The procedure used for evaluating the summation in the numerator of this equation is detailed in the Appendix. A good numerical approximation to the results obtained from eq 13 is given by eq 7, where the least-squares values of γ and A are given in Table I, and

$$q_c = 0.6514 \tag{14}$$

$$F_c(\epsilon) = 1 - 2.840\epsilon + 3.218\epsilon^2 \tag{15}$$

3. Branched Chains. Zimm and Kilb[8] have determined free-draining and nondraining eigenvalues for a variety of branched polymer configurations. We have considered only those branched molecules with f branches of equal length, where f is 4 and 8. The g values for these two cases are 0.625 and 0.344, respectively. Calculations have been made only for the θ solvent case, $\epsilon = 0$.

If we make the approximation, which has also been made for the linear case,[6] that the eigenfunctions are pure sine and cosine functions for all degrees of hydrodynamic interaction, then we may write the eigenvalues as a sum of free-draining and nondraining eigenvalues

$$\lambda_{fk} = \frac{\pi^2f^2k^2}{4N^2} + \frac{4h}{N^2}\left(\frac{f}{2}\right)^{3/2}\lambda_{fk}' \tag{16}$$

where the λ_{fk}' are given by Zimm and Kilb.[8] The eigenvalues with odd k have $\omega_k = f - 1$, while those with even k are nondegenerate.

Proceeding as in the case of the cyclic chain, we now use eq 2, 6, and 16, and follow Zimm and Kilb[8] in approximating λ_{fk}' by λ_{2k}' for all k. As before, the results are reproduced with good accuracy by eq 7, with

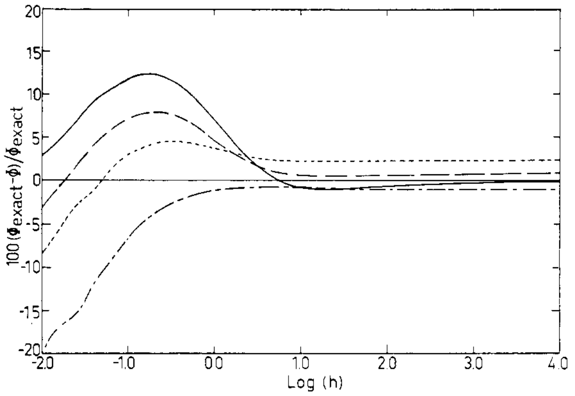

Figure 1. Percentage difference between ϕ calculated by eq 7 and 18–20, and ϕ_{exact} calculated by Tschoegl,[7] for linear chains: h is the hydrodynamic interaction parameter defined in eq 5; ϵ is the excluded volume parameter defined in eq 3; ——, $\epsilon = 0.0$; — —, $\epsilon = 0.1$; - - -, $\epsilon = 0.2$; — - — -, $\epsilon = 0.33$.

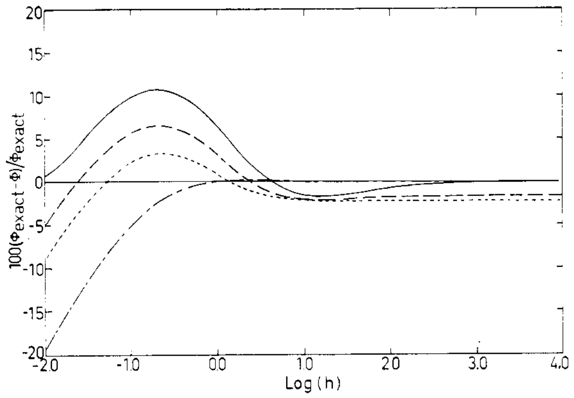

Figure 2. Percentage difference between ϕ as calculated by eq 7 and 18–20, and as calculated by eq 13, for cyclic chains: ——, $\epsilon = 0.0$; — —, $\epsilon = 0.1$; - - -, $\epsilon = 0.2$; — - — -, $\epsilon = 0.33$.

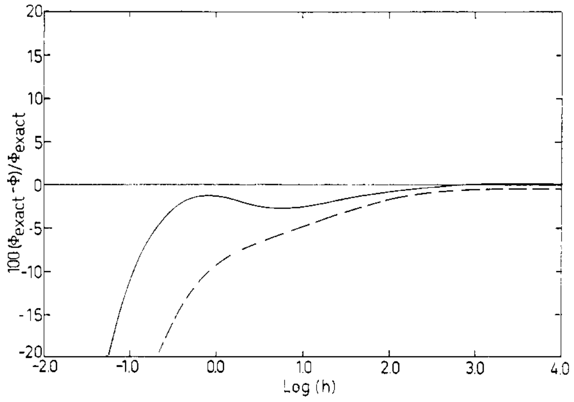

Figure 3. Percentage difference between ϕ as calculated by eq 7 and 18–20, and as calculated by method of Zimm and Kilb,[8] for chains with four and eight branches; number of branches of equal length: ——, $f = 4$; — —, $f = 8$.

$F(0) = 1$, since no calculations have been made for $\epsilon \neq 0$. Values of γ and A are given in Table I, while

$$q_f = (2/f)^{3/2}[0.390(f - 1) + 0.196]/0.586 \qquad (17)$$

4. A General Expression. We have found, in the above calculations, that the dependence of the ϕ parameter on chain topology, excluded volume, and hydrodynamic interaction can be represented adequately by eq 7. Comparison of eq 10 and 15 indicates that the coefficients of ϵ and ϵ^2 in $F(\epsilon)$ do not depend strongly on topology; and inspection of Table I leads to the same conclusion about γ, which is also not strongly dependent on ϵ. Furthermore, A varies in a similar manner with ϵ for linear and cyclic chains.

Consequently, we are led to propose a set of simple expressions for the parameters in eq 7, which will apply to all types of chains, regardless of topology. These are

$$F(\epsilon) = 1 - 2.68\epsilon + 2.74\epsilon^2 \qquad (18)$$

$$\gamma = 0.94 \qquad (19)$$

and

$$A = (0.175/q^2) - 3.38\epsilon \qquad (20)$$

where q is given by eq 9, 14, and 17 for linear, cyclic, and f-branched chains, respectively. Zimm and Kilb[8] have conjectured that the simple relation (in our notation)

$$q = g^{1/2} \qquad (21)$$

holds with sufficient accuracy for all branched molecules, regardless of detailed shape.

In Figures 1, 2, and 3 we have plotted the percentage deviation, $100(\phi_{exact} - \phi)/\phi_{exact}$, for linear, cyclic, and branched chains, respectively, as a function of log h for various values of ϵ. The ϕ's were calculated from eq 7 and 18–20, while the ϕ_{exact} values were computed as described above. Except in the case of the eight-branched polymer, the percentage deviation is never greater than 5% for log $h > 0.2$, corresponding to $N = 10$ if $\epsilon = 0$. It would appear that ϕ calculated from the general expression is of quite sufficient accuracy for almost all practical situations.

At very low h (log $h < -1.0$), the percentage deviation becomes substantial. In these cases, however, $\phi_{exact} \times 10^{-21}$ is very small, so the absolute magnitude of the discrepancy is also small.

Applications

The value of an expression such as eq 7 is very clear, since it enables accurate estimation of ϕ parameters, and thus of average chain dimensions, for chain topologies and values of ϵ and h for which detailed normal coordinate calculations may not have been done.

For high molecular weight linear chains, when h is effectively infinite, combination of eq 1, 3, 7, 9, and 18 gives

$$[\eta] = 2.843 \times 10^{21}(1 - 2.68\epsilon + 2.74\epsilon^2)b^3M_0^{-(3+3\epsilon)/2}M^{(1+3\epsilon)/2} \qquad (22)$$

M_0 is the monomer molecular weight. This is of the familiar Mark–Houwink–Sakurada form

$$[\eta] = KM^a \qquad (23)$$

with $a = (1 + 3\epsilon)/2$.

Equation 22 presents a simple way, embodying the most accurate results of calculations of $[\eta]$ for random chains, for calculating the segment length b in any polymer–solvent system. The slope of the standard log–log plot of $[\eta]$ *vs.* M gives ϵ; the intercept gives K, which depends on ϵ. Knowing M_0, one can then obtain b.

Results for four polymers are shown in Figure 4. Values of K and a for the three nonionic polymers, polyisobutylene, atactic polystyrene, and polyethylene oxide, were taken from the compilation of Kurata and Stockmayer.[10] Data for the polyelectrolyte, polyacrylic acid, comes from the work of Takahashi, *et al.*[14] In this case, ϵ was increased by decreasing the ionic strength of the solvent. We observe that b remains palpably constant for the three nonionic polymers over the entire range of solvent conditions. On the other hand, b increases substantially with increasing ϵ for polyacrylic acid, presumably reflecting a redistribution among rotational isomeric states so as to minimize electrostatic repulsions as the ionic strength decreases.

The values of b obtained in this manner are very close to those obtained in other ways by, *e.g.*, Kurata and Stockmayer;[10] but the method of data analysis we propose here is substantially simpler to apply.

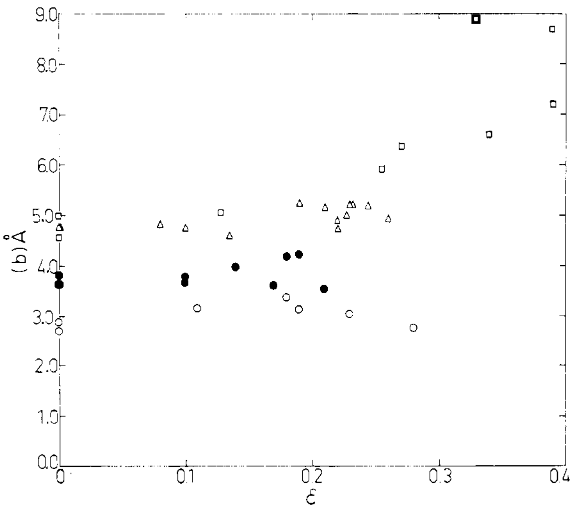

Figure 4. Segment length b as function of ϵ for polyisobutylene[10] (●), atactic polystyrene[10] (△), polyethylene oxide[10] (○), and the polyelectrolyte polyacrylic acid[14] (□).

Discussion

We have seen that the Flory–Fox[1] ϕ parameter can be factored into a product of terms: a constant which represents ϕ for a linear chain in the limit of vanishing excluded volume and infinite hydrodynamic interaction; a factor q which depends only on the topology of the polymer chain; a factor $F(\epsilon)$ which depends only on excluded volume; and a factor which depends both on ϵ and hydrodynamic interaction. This factorization is adequate to give ϕ to 5% or better in all realistic cases ($\log h > 0.2$) which have been examined thus far. This, in turn, is adequate to give the statistical segment length b to better than 2%. Experimental errors are substantially larger than this.

There are several points at which some of the details of this work might be slightly improved. Fixman and Pyun[15] have recently calculated the intrinsic viscosity of a linear Gaussian chain by normal coordinate techniques but with avoidance of premature averaging. They obtained $\phi_L(0,\infty) = 2.68 \times 10^{21}$, about 5% lower than the value used here. Fukatsu and Kurata[9] performed a similar calculation for cyclic chains, and obtained $\phi_c(0, \infty) = 1.74 \times 10^{21}$, or $q_c = 0.648$. Since the effect of this improvement is so small, we have preferred to retain the original treatment[3] for consistency with the calculations on branched chains[8] and on non-Gaussian chains.

We have used a parameter ϵ to represent excluded volume effects. This representation has the virtue that ϵ remains constant with varying molecular weight in a given solvent–polymer system, and eq 3 agrees in form with the results of machine calculations.[16] It should be noted that we have made no attempt, in contrast to other theories,[1,10] to compute ϵ from first principles.

It is an old and vexed problem, how to compute moments of a distribution afflicted with excluded volume effects. We have assumed that the second moment is given by eq 3, but the (-1) moment is also needed for hydrodynamic calculations. The distribution function which led to the results summarized here[7,9] is plausible but not firmly grounded. We[17] have investigated the effect of using instead a distribution function of the form suggested by Domb, Gillis, and Wilmers[18] on the basis of complete enumeration studies of random walks on a lattice. This distribution has the form

$$W(L) = \text{const}\; e^{-(L/\mu\langle L^2\rangle^{1/2})^{\delta}} L^{\delta} \qquad (24)$$

where δ, according to Fisher,[19] is $2/(1-\epsilon)$, and $\mu = \{\Gamma[1 + (1/\delta)]/\Gamma[1 + (3/\delta)]\}^{1/2}$, where Γ is the γ function. Use of this distribution function has the effect of multiplying $F(\epsilon)$ by a factor which is very nearly $[1 + (\epsilon/2)]$. In the common range of ϵ (see Figure 4), this will increase ϕ by 15% at most.

One factor we have neglected entirely is chain stiffness. The calculations of Hearst, Beals, and Harris[20] indicate that stiffness reduces ϕ by a few per cent, depending on ϵ and persistence length, for very long wormlike chains. For shorter, more realistic stiff chains, the chain length dependence (*i.e.*, h or N dependence) is quite complicated and difficult to subsume under the framework considered here.

Finally, we note that several theories[21] of the intrinsic viscosity of finite chains have proposed N (or h) dependences similar to that exhibited in eq 7. How-

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[16] For an extensive list of references, see P. Mark and S. Windwer, *ibid.*, **47**, 708 (1967).

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[21] See, *e.g.*, A. Isihara, *J. Polym. Sci., Part A-1*, **5**, 2883 (1967), and references cited therein.

ever, for Gaussian chains usually $N^{1/2}$ (or h) appears, rather than $h^{0.94}$. We are unable to provide a rationale for this unusual dependence, but just note that it fits the calculations significantly better than does a first-power dependence.

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Appendix

The sums are of the form

$$\sum_{k=1}^{\infty} A/(\lambda_k' + Bk^2)$$

where A and B are constants. This can be broken up into

$$\sum_{k=1}^{\nu} A/(\lambda_k' + Bk^2) + \sum_{k=\nu+1}^{\mu} A/(\lambda_{k,\mathrm{app}}' + Bk^2) + \sum_{k=\mu+1}^{\infty} A/(\lambda_{k,\mathrm{app}}' + Bk^2)$$

where $\lambda_{k,\mathrm{app}}'$ is the approximate analytical form for the kth nondraining eigenvalue.[8,9] The first ν eigenvalues have been tabulated numerically.[8,9]

We have therefore evaluated the first sum numerically, and summed the second out to fairly large μ ($\approx 10^3$) by digital computer. The third sum was replaced by an integral according to the Euler–MacLaurin procedure

$$\sum_{k=\mu+1}^{\infty} f_k = \int_{\mu+1}^{\infty} f(k)dk + {}^1/_2 f(\mu + 1)$$

and evaluated by numerical integration.

Adsorption of Polystyrene on Porous and Nonporous Adsorbents[1]

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ABSTRACT: A study was made of the adsorption of polystyrene from cyclohexane solution onto aluminum and aluminum oxide surfaces. Four polystyrene fractions, ranging in molecular weight from 67,000 to 1,800,000, were used. Brief studies were also made of the adsorption of polyisobutylene from benzene onto aluminum and of ethylbenzene from cyclohexane onto aluminum oxide. The surface areas of the two solids and the pore-size distribution of the aluminum oxide were measured by low-temperature nitrogen adsorption. The aluminum was essentially nonporous. For adsorption on aluminum, equilibrium appeared to be reached in a matter of hours; it is doubtful that true equilibrium was established even after 25 days in the case of aluminum oxide. Adsorption on aluminum is typical of the behavior of a variety of polymers adsorbed on nonporous adsorbents, exhibiting, for example, an increase of adsorbance with increasing molecular weight. The molecular weight dependence of adsorption on aluminum oxide was the reverse of normal behavior, the fraction of lowest molecular weight being adsorbed to the greatest extent. This is interpreted as a result of steric hindrance to penetration of the pore structure of the solid by large molecules. The estimated radius of the smallest pores penetrated by each fraction is approximately equal to the radius of gyration of the molecules in the solution. A study of the adsorption of ethylbenzene, a monomeric analog of polystyrene, from cyclohexane gives a value of −4220 cal/mol as the lower limit of the heat of adsorption of polystyrene segments. Polyisobutylene was not adsorbed from benzene onto aluminum, a result attributed to preferential adsorption of the solvent.

Current theories[3–7] of the adsorption of polymer molecules on solid surfaces use the idealized picture of a smooth plane at which the polymer chains are attached by many[4] or few[3] of the chain segments. While such a simplification is desirable for purposes of focusing attention on the types of conformations that are typical of chains, the fact remains that many common adsorbents for polymers are not well represented by the smooth surface model. There are the "porous" adsorbents, which have very large specific surface areas, a large fraction of which is present in inner recesses of the solid. Adsorption studies of polymers on porous adsorbents to date have shown that the time required for adsorption can be very long, and that the extent of adsorption is larger for smaller molecular weights than for larger molecular weights.[8–17] This has been

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(1) (a) Based on the Ph.D. thesis of Harris Burns, Jr., Georgia Institute of Technology, 1964. (b) Presented in part at the 148th National Meeting of the American Chemical Society, Polymer Division, Chicago, Ill., Sept 1964. An abstract is given in *Polym. Preprints*, **5**, 516 (1964).

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