is in qualitative agreement with the behavior of experimental rate constants, which, nevertheless, are always much smaller.

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Ideal Polymer Chains of Various Architectures at a Surface

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ABSTRACT: We study the macroscopic behavior of ideal polymer chains of various architectures in the vicinity of a surface, by considering that at least one of the units of the chains is in contact with the surface. The probability that any unit will be in contact with the surface is employed and the macroscopic properties are determined as averages over this probability. The present model is an amendment to the model used previously with the one end of a linear chain fixed at the surface, and though it is a simplification to the full problem where the chains can move freely in the whole space, it is free from the necessity to include the volume and the polymer concentration in order to describe chains in the vicinity of the surface. We estimate the mean number of contacts between a chain and the surface for the cases of linear, ring, regular star, and regular comb polymers as the basic quantity for the description of both the thermodynamics of chains at a surface and the degree of adsorption of polymers of various architectures.

1. Introduction

The study of the macroscopic behavior of polymer chains at surface finds applications in numerous fields such as the stabilization of colloid suspensions,[1] chromatography,[2] adhesion,[3] and restriction of flow in capillaries.[4] A number of theoretical[5,6] and experimental[7] works have been done on the subject but they mainly concern the adsorption of linear chains. Only few works deal with polymers of various architectures at an interacting surface,[8-10] though interest in the synthesis[11] and the study of the solution properties[12,13] of such macromolecules is increasing. We present in this work a model capable of describing the role of architecture on the behavior of chains at an interacting surface, and we apply it to the cases of ideal linear, ring, regular star, and regular comb polymers.

In the vicinity of an interacting surface the conformational behavior of a polymer chain in a solvent is governed by two kinds of mean interactions: the two-body interactions between all pairs of units far along the contour length of the chain but close in space and the interactions between the units of the chain and the surface. The probability of a specific configuration determined by the M position vectors ($\mathbf{R}_i$, $i = 1, 2, ..., M$) of the units of the chain can be written as

$$P(\mathbf{R}_i) = P_0(\mathbf{R}_i) \exp\{-u_e \sum_{i=1}^{M} \sum_{\substack{j=1 \\ i \neq j}}^{M} \delta^3(\mathbf{R}_i - \mathbf{R}_j) - u_a \sum_{i=1}^{M} \delta(z_i)\} \tag{1.1}$$

where $P_0(\mathbf{R}_i)$ is the ideal probability representing the connectivity term of the chain. The two δ function pseudopotentials obtain significant values, the first one when two units come close in space and the second one when a unit approaches the surface. The exponential form of these pseudopotentials is realized through its expansion where the terms to all orders in a perturbation theory scheme are produced. The interaction parameters u_e and u_a are proportional to the binary cluster integrals of the two mean potentials in the presence of the solvent, between two units and a unit and the surface, respectively. They express the intensity of the corresponding interactions

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and they are positive values in the case of repulsions and negative values in the case of attractions, while they become zero at the Θ temperature and the adsorption–desorption transition temperature T_a. This dependence of u_e and u_a on the mean potentials gives the model of freedom to describe cases with different Θ's and T_a's by changing the form of the potentials in order to incorporate the different characteristic temperatures. This is useful sometimes for comparison with experiment and other models.

The probability distribution, eq 1.1, represents a chain free to move in the whole space of volume V, and in order to describe a system of n such chains in the thermodynamic limit, the concentration n/V of the polymer chains has to be employed.

In the presence of a surace, penetrable or impenetrable, the constant average concentration of the homogeneous bulk is changed in the vicinity of the surface because of the extra interactions between the surface and the chains. The conformational behavior of a chain near the surface is different from that of a chain in the bulk. Recognizing this difference, early attempts describe linear chains at surfaces by employing the model with the one end of the chain fixed at the surface,[6,14] thus circumventing the necessity to include the volume and the concentration of the chains in the treatment of the full problem. In the real system the chains at the surface may or may not have one of their ends adsorbed at the surface. The model with the one end of the chain fixed at the surface misses all the conformations of the chain adsorbed with some other units but with neither of their ends being at the surface. Moreover, the units of the chain are not equivalent and fixing one of them at the surface brings an artificial distortion. The case is even worse for chains of complicated architectures, such as stars where the nonequivalence between special units like the core of the star and the end of a branch is larger. In the real problem any unit of the chain can be at the surface. If we use the model with at least one unit, any unit, at the surface[15] and express macroscopic properties as averages over all states with different units in contact with the surface, we will be closer to the real situation. At the same time we will get rid of the necessity to solve the full problem by inclusion of volume and concentration effects. This model will be useful when the study of the concentration effects is not the object, but other aims like the comparison between the behaviors of chains of various architectures in the vicinity of the surface are the main themes. In the case of polymers made from the same monomer, in the same system of solvent and substrate, the mean potentials between a monomer and the surface can be considered the same and so u_e and u_a can be taken as the same regardless of the architecture of the chain.

Under this assumption the probability distribution is given by eq 1.1 with u_e and u_a independent of the architecture.

2. The Model

The probability distribution $P(i)$ of the model can be taken from eq 1.1 if we force at least one monomeric unit, the ith unit, to be at the surface.

$$P(i) = P_0(\mathbf{R}_j)\delta(z_i) \exp\{-u_e \sum_{i=1}^{M}\sum_{\substack{j=1\\ i\neq j}}^{M} \delta^3(\mathbf{R}-\mathbf{R}_j) - u_a \sum_{i=1}^{M} \delta(z_i)\} \quad (2.1)$$

The z axis is perpendicular to the xy plane representing the surface, and z_i is the component of the position $\mathbf{R}_i$ of the ith unit along this axis. The presence of the extra function $\delta(z_i)$ in front of the exponential ensures that the ith unit is in contact with the surface. Macroscopic properties are mean quantities with respect to $P(i)$ after performing averages over states with all different M units of the chain in contact with the surface. In the long-chain limit the real discrete chain can be treated as a continuous line and the summations over the M units of the chain can be replaced with integrations over the contour length M of the chain. A macroscopic property χ is then given by

$$\chi = \int_0^M \mathrm{d}i\, \chi(i)P(j) / \int_0^M \mathrm{d}i\, P(i) \quad (2.2)$$

where $\chi(j)$ is the corresponding property when the ith point of the chain is at the surface.

Increasing u_a the repulsive character of the interactions between the surface and the chain increases and more units of the chain are pushed away into the solution. For $u_a \leq 0$ the chain exists in an adsorbed state with the majority of its units adsorbed at the surface while for $u_a > 0$ the chain goes to a desorbed state with the majority of the units belonging to the solution. These two states have been described for both penetrable[16] and impenetrable[17] surfaces by means of the characteristic fixed-point values $u_a^* = 0$ and $u_a^* = \epsilon/2$ where $\epsilon = 2 - d + d_\parallel$ (d is the dimensionality of the space and $d_\parallel$ is the dimensionality of the surface[18]) is treated as small in the frame of the perturbation theory. Similarly the increase of u_e expands the chain and the two characteristic values $u_e^* = 0$ and $u_e^* = \epsilon/16$ ($\epsilon = 4 - d$) describe the ideal and the expanded chains. This description concerns the chain when the two different potentials act independently. The simultaneous presence of both u_a and u_e decreases the fixed-point value of u_a^* for the desorbed expanded state. While it gives the value $u_a^* = \epsilon/2$ in the absence of excluded-volume interactions, it decreases to the value $u_a^* = 3\epsilon/8$ in the presence of excluded-volume interactions. This means that the expanded chain reaches the desorbed state easier with the majority of its units away from the surface, and conversely that shrunk conformations can have more units at the surface and therefore can be adsorbed more readily than expanded ones. We will see that this increase in the capability of adsorption with the compactness of the chain applies to polymers of various architectures too where the architecture characteristic of a chain is an extra factor influencing its compactness.

A basic quantity for the understanding and the description of adsorption phenomena is the average number $\langle\nu\rangle$ of contacts between the chain and the surface defined by $P(i)$, eq 2.1, as

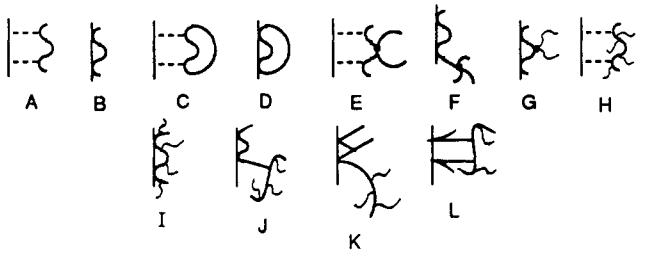
$$\langle\nu\rangle = \langle\sum\delta(z_i)\rangle = \int \mathrm{d}i \int \mathrm{d}j\, \langle\delta(z_i)P(j)\rangle / \int \mathrm{d}j\, P(j) = \int \mathrm{d}i \int \mathrm{d}j\, \langle\delta(z_i)\delta(z_j)P_0(\mathbf{R}_i) \exp(-u_e \sum\sum\delta^3(\mathbf{R}-\mathbf{R}_j) - u_a\sum\delta(z_i))\rangle / \int \mathrm{d}j\, P(j) \quad (2.3)$$

$\langle\nu\rangle$ is proportional to the average energy of adsorption and increases with the readiness of the adsorption of a chain. $\langle\nu\rangle$ is expected to decrease on increasing u_a because the repulsive character of the adsorption increases, and it is also expected to decrease on increasing u_e because the chains become more expanded. From eq 2.3 the quantitative dependence of adsorption on u_a and u_e can be found. In the frame of the perturbation theory, first-order calculations on u_e and u_a yield for example the critical exponent of the dependence of $\langle\nu\rangle$ on the molecular weight M to order ϵ.[16,17] This, though, is not the subject

of the present work, where we will address instead the question of how architecture influences the adsorption of chains. If we calculate $\langle \nu \rangle$ even to zero order in u_e and u_a for the four characteristic classes of linear, ring, regular star, and regular comb polymers, we will gain good insight into the role of the architecture of a chain in its adsorption. Calculations then to higher orders in u_e and u_a for each architecture are possible.

3. Average Number $\langle \nu \rangle$ of Contacts between a Polymer Chain and the Surface

The average number $\langle \nu \rangle$ of contacts as defined by eq 2.3 includes the product of two δ functions, which force two monomeric units to lie at the surface. $\langle \nu \rangle$ therefore is equal to the average number of bridges formed when two monomeric units are held at the surface. knowing the general trends in the dependence of $\langle \nu \rangle$ on u_a and u_e we concentrate on the calculation of $\langle \nu \rangle$ for the ideal situation ($u_a = u_e = 0$) for chains of various architectures, aiming at finding how architecture affects $\langle \nu \rangle$. The total number of bridges with two units in contact with the surface can be represented by A so that



$$\langle \nu \rangle = \mathrm{A} / \int_0^M \mathrm{d}i\, P(i) \tag{3.1}$$

Any two units can be in contact with the surface, so in the continuous line representation we have to integrate twice over the contour length of the chain to account for all bridges. The overcounting in this double integration, in the limit of zero bridge length when the two integration length variables i and j coincide, is negligible and does not affect the final N dependence for large N. For each different architecture the general diagram A produces different diagrams with specific units attached on the surface. The forms of these diagrams are taken from the probability of occurrence of a bridge of length L, which in the Gaussian model is equal to $(3/2\pi l)^{1/2}(1/L^{1/2})$, where l is the length of the effective unit of the chain. This probability is of the same form for cases of both penetrable and impenetrable surfaces with the sole difference being that the normalization constant is larger by a factor of 2 for the case of the impenetrable surface since the chain can move only in the half-space. The final values of the diagrams are found after suitable double integrations for each case. The ideal part of $P(i)$ does not include any bridge so that $\int_0^M \mathrm{d}i\, P(i) = M$ for open chains, accounting for the total number of units capable of being at the surface. For rings with a probability of occurrence proportional to $(3/2\pi l)^{3/2}/M^{3/2}$, it is equal to

$$\int_0^M \mathrm{d}i\, P(i) = (3/2\pi l)^{3/2}\, M/M^{3/2} = (3/2\pi l)^{3/2}\, M^{-1/2}$$

3.A. Linear Chains. For the case of linear chains of molecular weight M the sweep of the i and j variables representing the ends of a bridge produces the following

$$\mathrm{A} = 2\mathrm{B} \tag{3.2}$$

If the contour lengths i and j are measured from the beginning of the chain, the length of the bridge is $(j - i)$ and the probability of its occurrence is equal to $(3/2\pi l)^{1/2}/(j - i)^{1/2}$. The value of the diagram becomes

$$\mathrm{B} = (3/2\pi l)^{1/2} \int_0^M \mathrm{d}i \int_i^M \mathrm{d}j\, 1/(j-i)^{1/2} = (3/2\pi l)^{1/2}(4/3)M^{3/2} \tag{3.3}$$

The number 2 in eq 3.2 is a symmetry number coming from the equivalence of the two cases $i < j$ and $i > j$. By means of eq 3.1 and the value of the diagram we take for linear polymers the result

$$\langle \nu \rangle_{\mathrm{linear}} = (3/2\pi l)^{1/2}(8/3)M^{1/2} \tag{3.4}$$

revealing that the average number of contacts is proportional to the square root of the molecular weight M and agrees with the results of previous works concerning linear chains. We will see that this molecular weight dependence is the same regardless of the architecture of the chain, but the proportionality constant differs for polymers of different architecture. A point to mention is that the i and j variables are considered distinguishable in the definition of $\langle \nu \rangle$ in eq 2.3, in the sense that i belongs to $P(i)$ and j to the second contact. Otherwise there is a double counting and a division of the second part of eq 3.4 by a factor of 2 is necessary. This constant cancels in the g ratios that are calculated below.

3.B. Ring Polymers. For the case of ring polymers the contact of two units with the surface yields the following diagram

$$\mathrm{C} = 2\mathrm{D} \tag{3.5}$$

This diagram consists of two bridges of length $(j - i)$ and $[M - (j - i)]$ and it is equal to

$$\mathrm{D} = (3/2\pi l)^2 \int_0^M \mathrm{d}i \int_1^M \mathrm{d}j\, 1/[(j-i)^{1/2}[M - (j-i)]^{1/2}M] = (3/2\pi l)^2(\pi/2) \tag{3.6}$$

We take thus for the average number of contacts between a ring polymer and the surface the value

$$\langle \nu \rangle_{\mathrm{ring}} = \mathrm{C} / \int \mathrm{d}i\, P(i) = 2(3/2\pi l)^2(\pi/2)/(3/2\pi l)^{3/2}M^{-1/2} = (3/2\pi l)^{1/2}\pi M^{1/2} \tag{3.7}$$

$\langle \nu \rangle_{\mathrm{ring}}$ is also proportional to the square root of the molecular weight M of the ring chain but now the constant of proportionality is bigger than that of the linear chain. This result indicates that ring polymers are expected to be adsorbed to a larger extent than linear chains of the same molecular weight and is in accord with the results of ref 10, which under ideal conditions give that rings are adsorbed more than linear chains. From the previous studies of the fixed points we had the first indication that more compact structures are adsorbed more. The result, eq 3.7, for rings having a larger number of contacts than those of linear chains is in accord with this rule since rings formed from linear chains after the closure of the two ends are more compact structures than linear chains of the same molecular weight. The characteristic ratio

$$g_{\nu,\mathrm{ring}} = \langle \nu \rangle / \langle \nu \rangle_{\mathrm{linear}} = \pi/(8/3) = 1.18 \tag{3.8}$$

between $\langle \nu \rangle_{\mathrm{ring}}$ and $\langle \nu \rangle_{\mathrm{linear}}$ for chains of the same molecular weights provides a number for comparison between the readiness of adsorption of the two different kinds of polymers under ideal conditions.

3.C. Regular Star Polymers. For the case of regular stars of molecular weight $M = fN$, with f equal branches starting from the same core, each one having molecular weight N, we take the following

$$\mathrm{E} = f\mathrm{F} + f(f-1)\mathrm{G} \tag{3.9}$$

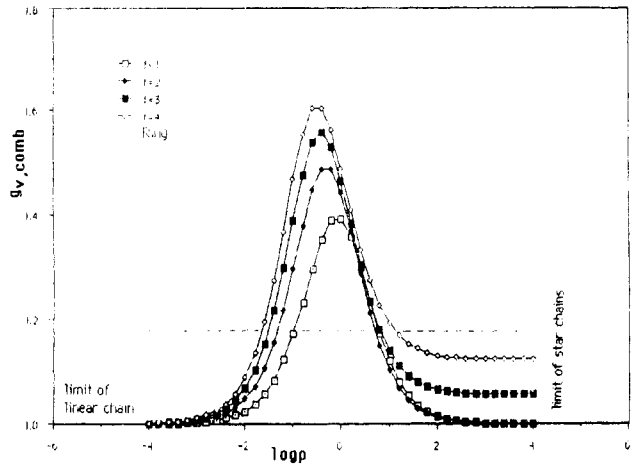


Figure 1. g factor of combs with $f = 1$, 2, 3, and 4 as a function of log ρ with ρ the ratio of the molecular weights of a branch to the backbone. The two limits $\rho \to 0$ and $\rho \to \infty$ represent the linear and star cases, respectively. The g factor of rings is equal to 1.18 and lies between the g's of stars with $f = 4$ and 5.

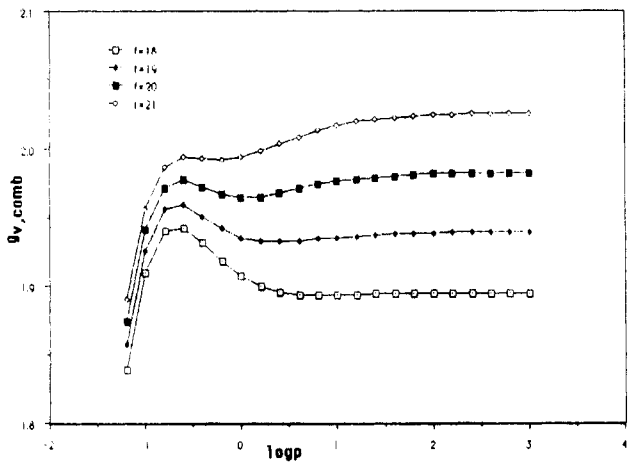


Figure 2. For $f = 18$, 19, 20, and 21, increasing ρ's the g's of combs gives small maxima accompanied by slight minima.

Based on the probability of the occurrence of a bridge of length L, being proportional to $(3/2\pi l)^{1/2}/L^{1/2}$, these become

$$F = (3/2\pi l)^{1/2}(4/3)N^{3/2} \tag{3.10a}$$

$$G = (3/2\pi l)^{1/2}\int_0^N di \int_0^N dj\, 1/(i+j)^{1/2} = (3/2\pi l)^{1/2}(8/3)(2^{1/2}-1)N^{3/2} \tag{3.10b}$$

Using the values of these diagrams, we take for the average number of contacts

$$\langle \nu \rangle_{star} = E/\int di\, P(i) = (3/2\pi l)^{1/2}(8/3)[f^{-1/2} + (2^{1/2}-1)(f^{1/2}-f^{-1/2})]M^{1/2} \tag{3.11}$$

The proportionality constant depends now on the number f of branches, which is the new architecture parameter, and increases as f increases, Figures 1–3. For $f = 1$ or 2 we recover as expected the result of the linear chain. The ratio $g_{\nu,star}$ between the average numbers of contacts of a star and a linear chain of the same molecular weights is equal to

$$g_{\nu,star} = \langle \nu \rangle_{star}/\langle \nu \rangle_{linear} = f^{-1/2} + (2^{1/2}-1)(f^{1/2}-f^{-1/2}) \tag{3.12}$$

and increases with f. This result is in accord with the general rule that by increasing the compactness of the stars by increasing f while keeping the total molecular weight M constant, the number of contacts with the surface and the adsorption increase. The number $g_{\nu,star}$ capable of being checked experimentally together with g's of other architectures appears in Figures 1–3.

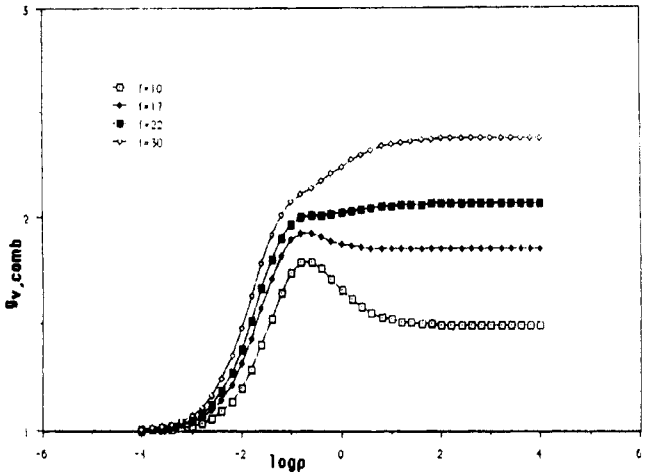


Figure 3. For $f > 21$ the g's of combs increase from the linear limit to the star limit monotonously.

3.D. Regular Comb Polymers. Regular comb polymers consist of a backbone of molecular weight N_{bb} and f branches of N_{br} molecular weight each at equal intervals of length $\alpha = N_{bb}/(f+1)$ along the backbone.[13] The total molecular weight is $M = N_{bb} + fN_{br}$ and the characteristic ratio $\rho = N_{br}/N_{bb}$ varies between the two limits $\rho \to 0$ of the linear chain and $\rho \to \infty$ of the star chains.

We take for combs the following bridge diagrams:

$$H = I + fJ + 2\sum_{k=1}^{f} K + 2\sum_{m=1}^{f}(f-m)L, \qquad m = k - k' \tag{3.13}$$

with values equal to

$$I = (3/2\pi l)^{1/2}(4/3)N_{bb}^{3/2} \tag{3.14a}$$

$$J = (3/2\pi l)^{1/2}(4/3)N_{br}^{3/2} \tag{3.14b}$$

$$K = 2\,(3/2\pi l)^{1/2}\int_0^{k\alpha} di \int_0^{N_{br}} dj\, 1/(i+j)^{1/2} = (3/2\pi l)^{1/2}(4/3)M^{3/2}\{[(\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} - [\rho/(1+f\rho)]^{3/2} - [k/(1+f)(1+f\rho)]^{3/2}\} \tag{3.14c}$$

$$L = (3/2\pi l)^{1/2}\int_0^{N_{br}} di \int_0^{N_{br}} dj\, 1/(i+j+m\alpha)^{3/2} = (4/3)M^{3/2}\{[(2\rho/(1+f\rho)) + (m/(1+f)(1+f\rho))]^{3/2} - 2[(\rho/(1+f\rho)) + (m/(1+f)(1+f\rho))]^{3/2} + [m/(1+f)(1+f\rho)]^{3/2}\} \tag{3.14d}$$

Finally the number of contacts $\langle \nu \rangle_{comb}$ of comb polymers depends both on f and ρ. It is equal to

$$\langle \nu \rangle_{comb} = (3/2\pi l)^{1/2}(8/3)M^{1/2}\{[1/(1+f\rho)]^{3/2} + f[\rho/(1+f\rho)]^{3/2} + 2\sum_{k=1}^{f}\{2[(\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} - 2[\rho/(1+f\rho)]^{3/2} - 2[k/(1+f)(1+f\rho)]^{3/2} + [[(2\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} - 2[(\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} + [(k/(1+f)(1+f\rho))]^{3/2}] \times [(f-k)/2]\}\} \tag{3.15}$$

The characteristic ratio $g_{\nu,\text{comb}} = \langle\nu\rangle_{\text{comb}}/\langle\nu\rangle_{\text{linear}}$ of chains of the same molecular weight is given by

$$g_{\nu,\text{comb}} = ([1/(1+f\rho)]^{3/2} + f[\rho/(1+f\rho)]^{3/2} + 2\sum_{k=1}^{f}\{2[(\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} - 2[\rho/(1+f\rho)]^{3/2} - 2[k/(1+f)(1+f\rho)]^{3/2} + [[(2\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} - 2[(\rho/(1+f\rho)) + (k/(1+f)(1+f\rho))]^{3/2} + [(k/(1+f)(1+f\rho))]^{3/2}][(f-k)/2]\} \quad (3.16)$$

We have calculated $g_{\nu,\text{comb}}$ on a computer and plot it as a function of ρ in Figures 1–3 for characteristic values of f. It is always bigger than one, indicating more, adsorption of comb than linear chains in accordance with the experimental findings of Cawaguchi and Takahashi;[8] in that work maxima are observed for $f \leq 20$. This last observation agrees to a large extent with the results of the present work. As appears in the figures we have sharp maxima up to $f < 18$, smaller maxima accompanied by slight minima for $f = 18$, 19, 20, and 21, and a monotonous transition from the linear limit ($\rho \to 0$) to the star limit ($\rho \to \infty$) for $f > 21$.

4. Conclusion

The average number $\langle\nu\rangle$ of contacts of polymer chains of various architectures with a surface has been determined. It was found that $\langle\nu\rangle$ increases with the square root of the molecular weight in agreement with previous results for linear chains, as well as with the compactness of the chain. Comparing chains of the same molecular weight, linear chains have the smaller $\langle\nu\rangle$ and stars with $f = 3$ and 4 follow. $\langle\nu\rangle$ of rings lies between those of stars with $f = 4$ and 5, while for stars of general f it is found that $\langle\nu\rangle$ increases with the number f of branches. $\langle\nu\rangle$ of combs depends also on the ratio ρ of the molecular weights of a branch to the backbone and varies between that of a linear chain ($\rho \to 0$) and those of star chains ($\rho \to \infty$). The characteristic ratio $g = \langle\nu\rangle/\langle\nu\rangle_{\text{linear}}$ of the average number of contacts to that of a linear chain of the same molecular weight is independent of the molecular weight and depends on the architecture of the chain. It increases with the readiness of adsorption, so it is suitable for experimental verification. The g ratios of stars with $f = 3$ and 4 and a ring are bigger than one due to the more compact structure of these macromolecules compared to that of a linear chain. The g's of regular stars with larger f follow and the g's of regular combs depend on both f and ρ. Their values vary between those of a linear chain ($\rho \to 0$) and those of star chains ($\rho \to \infty$). As ρ is varied, for $f < 18$ maxima are observed, for $f = 18$, 19, 20, and 21 the maxima become smaller and are accompanied by slight minima, and for $f > 21$ the transition between the two limits is monotonous.

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