

NOTE

**On the adsorbed mass of polymers on surfaces**

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It is shown that for ideal polymers interacting with a surface *via* the pseudo-potential of a delta function, the number of contacts between the monomer units and the surface as a function of concentration  $c_b$  is a dependence of the form  $c_b/(1 - c_b)$ . The architecture of the polymer, the degree of polymerization, the interaction energy between a monomer unit and the surface, the area of the surface and the monomer length are embodied in the parameters  $\alpha$  and  $\beta$ . The above dependence of the adsorbed mass of a polymer on the concentration is confirmed by the experimental results of Takahashi and his collaborators. For linear polystyrene of molecular weight  $134 \cdot 10^5$ , interacting with a chrome plate, the parameters  $\alpha$  and  $\beta$  are, respectively, about equal to  $(89938/273) \cdot 10^{-6}$  m and  $(-19300/273) \text{ m}^3 \text{ kg}^{-1}$ .

*Keywords:* adsorbed mass, polymer, linear, cyclic, A-B diblock copolymer.

In this work, studies on the behaviour of an ideal chain<sup>1–9</sup> are continued, since the potential of a delta function leads exactly to results which approach sufficiently well the experimental data. One of these experiments is the experiment of Takahashi and his collaborators.<sup>10</sup> They studied the adsorption of polystyrene having molecular weights from  $10^4$  to  $13 \cdot 10^6$  onto a chrome plate from a cyclohexane solution at the temperature. On the other hand, Fu and his collaborators studied the adsorption of polystyrene onto gold from dilute solutions under  $\theta$  condition.<sup>11</sup> Also, Anada and Kawaguchi studied the adsorption of binary mixtures of polystyrenes onto porous and nonporous silica surfaces.<sup>12</sup> In addition, Kawaguchi and Takahashi extended their studies to polymers of more complex architecture. They studied the adsorption of a well-characterized comb-branched polystyrene onto a chrome plate from a cyclohexane solution at the temperature.<sup>13</sup> In the above four experiments, the amount of adsorbed mass per unit surface was studied as a function of the bulk concentration  $c_b$ . The above experimental data gave the information that, independent of the architecture of the polymer, the adsorbed mass as a function of  $c_b$  is given by a dependence of the form  $x/(1 - x)$ .

The aim of this Note is to show that the average number of contacts between the monomer units and the surface bring about the above dependence as a function of  $c_b$ . So, before, handling the theoretical background of the above proposition, it is necessary to men-

tion that for a linear polystyrene of molecular weight  $134 \cdot 10^5$ , interacting with a chrome plate,<sup>10</sup> the function  $c_b/(1 - c_b)$  describes sufficiently well the adsorbed mass as a function of concentration when the parameters  $\lambda$  and  $\mu$  are about equal to  $(89938/273) \cdot 10^{-6}$  m and  $(-19300/273) \text{ m}^3 \text{ kg}^{-1}$ , respectively. Indeed, for the same mass of polystyrene of molecular weight  $134 \cdot 10^5$  dissolved in different volumes of solvent so as to give the concentrations which appear in Table I and assuming that  $\lambda = (89938/273) \cdot 10^{-6}$  m and  $\mu = (-19300/273) \text{ m}^3 \text{ kg}^{-1}$ , then the function  $c_b/(1 - c_b)$  renders the values which appear in column 3 of Table I. The corresponding experimental values<sup>10</sup> appear in column 2, which can be compared with the theoretical values of column 3. For linear polystyrene of molecular weight  $242 \cdot 10^4$ , the parameters  $\lambda$  and  $\mu$  are about equal to  $(71258/293) \cdot 10^{-6}$  m and  $(-15800/293) \text{ m}^3 \text{ kg}^{-1}$ , respectively. The theoretical values appear in column 3 of Table II, while the corresponding experimental values<sup>10</sup> appear in column 2 of Table II. In Tables I and II,  $A$  is the adsorbed mass per unit of surface.

TABLE I. Adsorption data for polystyrene of molecular weight  $134 \cdot 10^5$ . The corresponding experimental values<sup>10</sup> appear in column 2

$c_b/(\text{kg}/\text{m}^3)$	$A(\text{expt.})/(\text{g}/\text{m}^2)$	$A(\text{theoret.})/(\text{g}/\text{m}^2)$
0.01	1.93	1.93
0.03	2.13	3.17
0.1	4.08	4.08
0.3	4.59	4.45
0.5	4.70	4.53
1	4.63	4.60
3	4.66	4.64

TABLE II. Adsorption data for polystyrene of molecular weight  $242 \cdot 10^4$ . The corresponding experimental values<sup>10</sup> appear in column 2

$c_b/(\text{kg}/\text{m}^3)$	$A(\text{expt.})/(\text{g}/\text{m}^2)$	$A(\text{theoret.})/(\text{g}/\text{m}^2)$
0.01	1.58	1.58
0.05	2.63	3.29
0.1	2.95	3.80
0.2	3.96	4.13
0.4	4.31	4.31
1	4.49	4.43
3	4.51	4.48

Now, one has to consider how the above dependence of the adsorbed mass on the concentration  $c_b$  was obtained. In a previous study,<sup>1</sup> it was found that the partition function of a linear chain interacting with a penetrable surface *via* the pseudopotential of a delta function is given by the dependence

$$Z = S (L - 2(N/6)^{0.5} - 2^{-0.5} - U^{-1} + U^{-1} \exp U^2 \operatorname{erfc}(U)) \quad (1)$$

The index  $l$ , of the function  $Z$ , denotes that the polymer is linear. Also, in the case of cyclic chain interacting with a penetrable surface, it was found that the partition function is given by the dependence<sup>3</sup>

$$Z_{pc} = S (3/2 N^2)^{0.5} (L - (N/6)^{0.5} - 1 - \exp U^2 \operatorname{erfc}(U)) \quad (2)$$

On the other hand, for a reflecting impenetrable surface, it was found that the partition function of a cyclic chain is given by the dependence<sup>5,7</sup>

$$Z_{ic} = S (3/2 N^2)^{0.5} (L - (N/6)^{0.5} - 0.5 - \exp U^2 \operatorname{erfc}(U)) \quad (3)$$

where  $U = u(6N)^{0.5}/2$  is a reduced dimensionless interaction parameter. The area of

the available surface is given by  $S$  and  $V = S L$  is the volume of the system. In the case where the surface (plane  $Z = 0$ ) is penetrable, the solution extends  $L/2$  to the right of the surface and  $L/2$  to the left of the surface. Also,  $N$  is the total length of the chains and  $l$  is the effective Kuhn length. The partition functions  $Z$ ,  $Z_{pc}$  and  $Z_{ic}$ , as functions of  $L$ , are functions of the form  $aL - b$ . Also, the partition functions of star polymers and of marguerite polymers have the same form.<sup>14</sup> In other words, the partition functions, as functions of  $L$ , are independent of the architecture of the polymer. The architecture of the polymer, as well as all the other parameters of the problem are included in parameters  $a$  and  $b$ .

The average number of the monomer units touching the surface is given by

$$\bar{u} = - \frac{1}{L} \frac{d \ln Z}{d U} \quad (4)$$

Thus, if  $Z$  is given by one of the Eq. (1), Eq. (2) or Eq. (3), then the total average number of contacts between the polymer and the surface is given, correspondingly, by the following functions

$$\bar{u} = \frac{(N/L)}{2} \left[ U^{-2} - 2^{-0.5} U^{-1} + (2 - U^{-2}) \exp U^2 \operatorname{erfc}(U) \right] / \left( 1 - (2/L) (N^2/6)^{0.5} \right) \quad (5)$$

$$\bar{u}_{pc} = \frac{(N/L)}{2} \left[ -0.5 U \exp U^2 \operatorname{erfc}(U) / \left( 1 - (L/6) (N/6)^{0.5} \right) \right] / \left( 1 - \exp U^2 \operatorname{erfc}(U) \right) \quad (6)$$

and

$$\bar{u}_{ic} = \frac{(N/L)}{2} \left[ -0.5 U \exp U^2 \operatorname{erfc}(U) / \left( 1 - (L/6) (N/6)^{0.5} \right) \right] / \left( 0.5 - \exp U^2 \operatorname{erfc}(U) \right) \quad (7)$$

From a study of the functions  $\bar{u}$ ,  $\bar{u}_{pc}$  and  $\bar{u}_{ic}$ , the following can be noticed: firstly, the functions  $\bar{u}$ ,  $\bar{u}_{pc}$  and  $\bar{u}_{ic}$  are analogous to the corresponding density profiles when  $Z = 0$ , see Refs. 1, 3 and 7; secondly, the functions  $\bar{u}$ ,  $\bar{u}_{pc}$  and  $\bar{u}_{ic}$  have the same dependence on the variable  $L$ ; thirdly,  $\bar{u}$ ,  $\bar{u}_{pc}$  and  $\bar{u}_{ic}$  present the same dependence on variable  $N$ . Also, in the above functions, the terms  $N^{1/2}/L$  and  $N^{0.5}/L$  can be written as  $S/V$  and  $NS/VN^{0.5}$ , respectively. The ratio  $N/V$  expresses the concentration of the monomer units of one chain in the solution, and it will be symbolized by  $c_b$ . Then, from the above transformations, the function  $\bar{u}$  takes the form

$$\bar{u} = c_b / (1 - c_b) \quad (8)$$

also the asymptotic value of  $\bar{u}$  is  $c_b$ . The parameters  $c_b$  and  $c_b^*$  are given by the following types of dependencies:

$$c_b = \frac{S}{2} \left[ U^{-2} - 2^{-0.5} U^{-1} + (2 - U^{-2}) \exp U^2 \operatorname{erfc}(U) \right] \quad (9)$$

$$c_b^* = \frac{S}{2} \left[ (S/(6N)^{0.5}) \left( 2^{-0.5} - U^{-1} + U^{-1} \exp U^2 \operatorname{erfc}(U) \right) \right] \quad (10)$$

The asymptotic value of  $\bar{u}$  depends on the interaction energy between the monomer units and the surface, as well as on the degree of polymerization of the chain, while

it is independent of the monomer length and of the area of the surface with which the polymer interacts. Obviously, the functions  $\nu_{pc}$  and  $\nu_{ic}$  of a cyclic chain have the same dependence on the concentration  $c_b$  as the function  $\nu_{lc}$  and consequently these behave as  $\nu_{lc}$ . Also, the average number of contacts  $\nu_{A-B}$  of a A-B diblock copolymer which interacts with a penetrable (or impenetrable) surface, has the same dependence on the concentration  $c_b$ . For an A-B diblock copolymer which interacts with a plane penetrable surface, the parameters  $\nu_{lc}$  and  $\nu_{pc}$  are given by the following types of dependencies:

$$\begin{aligned} \nu_{A-B} = & S [0.5U_a^{-2} + 0.5U_b^{-2} - 2(U_a^2 + U_b^2) (0.5 U_a U_b (U_a + U_b))^{-1} + \\ & 2(U_a - U_b) (0.5 U_b (U_a + U_b))^{-1} T(U_b/2^{0.5}) + 2(U_b - U_a) (0.5 U_a (U_a + U_b))^{-1} \\ & T(U_a/2^{0.5}) + (1 - 2(U_a + U_b)^{-2}) T(U_a/2^{0.5}) T(U_b/2^{0.5}) + (0.5 U_b^{-2} - (U_a + U_b)^{-2} \\ & - U_a (U_a + U_b)^{-1}) T^2 (U_b/2^{0.5}) + (0.5 U_a^{-2} - (U_a + U_b)^{-2} - U_b (U_a + U_b)^{-1}) \\ & T^2 (U_a/2^{0.5}) - 2(0.5 U_b^{-2} - (U_a + U_b)^{-2} - U_a (U_a + U_b)^{-1}) T(U_b) - 2(0.5 U_a^{-2} - \\ & (U_a + U_b)^{-2} - U_b (U_a + U_b)^{-1}) T(U_a) \end{aligned} \quad (11)$$

$$\nu_{A-B} = 2 ( S/(6N)^{0.5} ) ( U_a, U_b ) \quad (12)$$

$\nu_{A-B}(U_a, U_b)$  is a symmetrical function of the variables  $U_a$  and  $U_b$ , which was calculated in a previous work.<sup>8</sup> Also  $T(U_a) = \exp(U_a^2) \operatorname{erfc}(U_a)$ . The Eqs. (11) and (12) are valid for A-B diblock copolymer where the blocks A and B have the same degree of polymerization,  $N_A = N_B = N/2$ . Also,  $U_a$  and  $U_b$  are the interaction energies of the monomer units of the A and B blocks with a plane surface, respectively.

The fact that the adsorbed mass of a polymer is described by a function of the form  $\nu_{lc}/(1 - c_b)$  irrespective of whether the polymer is linear or cyclic, an A-B diblock copolymer, or a star or marguerite polymer, leads to the conclusion that  $\nu_{lc}/(1 - c_b)$ , is a univer-

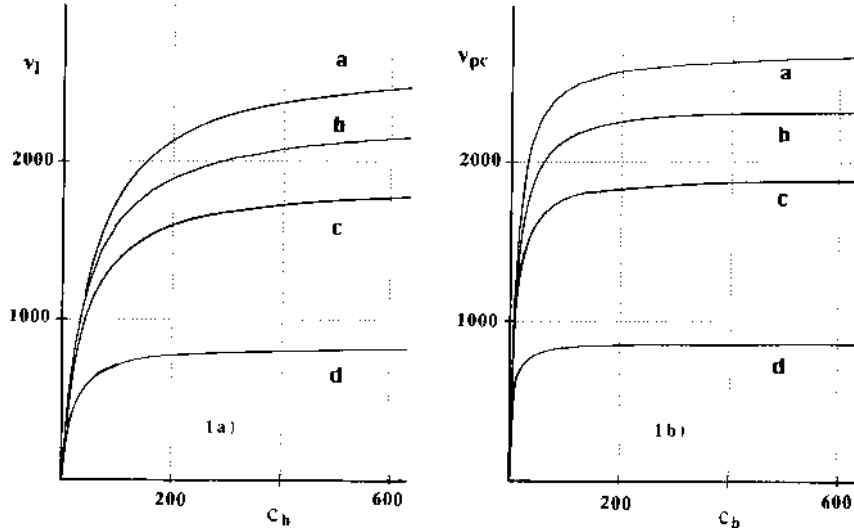


Fig. 1:  $\nu_{lc}$  (1a) and  $\nu_{pc}$  (1b) as functions of concentration  $c_b$  for  $N = 4 \cdot 10^4$  (curve a), for  $N = 3 \cdot 10^4$  (curve b), for  $N = 2 \cdot 10^4$  (curve c) and for  $N = 4 \cdot 10^3$  (curve d) when  $U = -5.5$  (attractions). The parameter  $S = 10^{-12} \text{ m}^3$ . The concentration  $c_b$  is expressed in monomer units of one chain per  $\text{m}^3$ .

sal function, since its general form is independent of the architecture of the polymer. The architecture of the polymer, the degree of polymerization, the interaction energy between the monomer units and the surface, the area of the surface and the monomer length are embodied in the parameters  $\alpha$  and  $\beta$ . Also, another interesting factor, on which the adsorbed mass depends, is the polydispersity of the polymeric sample. The problem of polydispersity, in the present theory, is confronted *via* sums of the form  $\sum_{i=1}^k n_i c_{bi} / (1 - c_{bi})$ , where  $n_i$  is the multitude of the chains with degree of polymerization  $N_i$ , and  $k$  is the number of chains with different degrees of polymerization. Obviously, in the case of  $n$  chains of the same degree of polymerization, which do not interact with each other, the number of contacts as a function of concentration keeps its form.

In Fig. 1a and 1b, the average numbers of contacts  $\alpha$  and  $\rho_{pc}$  are shown as a function of concentration  $c_b$  for four values of  $N$ , when the reduced energy  $U = -5.5$  (attractions). Remember that the reduced energy  $U$  is defined as  $U = u(6N)^{0.5}/2$ . In both Figures, the number of contacts as a function of  $c_b$  increases asymptotically in agreement with the experimental result.<sup>10</sup> Also, it can be observed that the asymptotic values become larger as  $N$  increases.

In Fig. 2, the asymptotic values of the functions  $\alpha$  and  $\rho_{pc}$  are shown as a function of the degree of polymerization  $N$  for two values of the energy parameter  $u$  (small  $U$ ). For a given value of  $u$ , the asymptotic values of the functions  $\alpha$  and  $\rho_{pc}$  are increasing functions of  $N$ . Also, for given values of  $N$  and  $u$ , the asymptotic values of the function  $\rho_{pc}$  (cyclic chain) are bigger than the asymptotic values of  $\alpha$  (linear chain) which is in accordance with previous results.<sup>1,3</sup> In addition, for a given value of  $N$ , the asymptotic values are larger as  $u$  becomes more negative (for larger attractions).

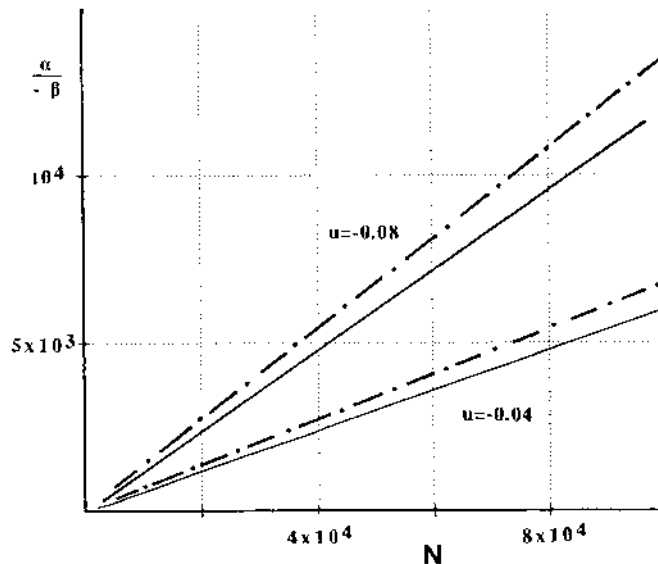


Fig. 2. The asymptotic values of  $\alpha$  (continuous line) and  $\rho_{pc}$  (broken line) as functions of  $N$  for  $u = -0.04$  and  $u = -0.08$ . The parameter  $S = 10^{-12} \text{ m}^3$ .

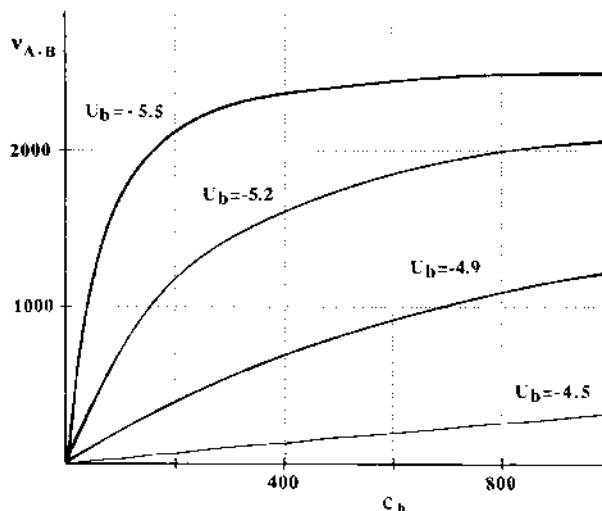


Fig. 3:  $v_{A-B}$  as function of concentration  $c_b$  for various values of reduced energy  $U_b$  when  $U_a = -5.5$  and  $N = 4 \cdot 10^4$ . The parameter  $S = 10^{-12} \text{ m}^3$ . The concentration  $c_b$  is expressed in monomer units of one chain per  $\text{m}^3$ .

In Fig. 3, the average number of contacts  $v_{A-B}$  of an A-B diblock copolymer, which interacts with a penetrable surface, is shown as a function of concentration  $c_b$  for a given value of  $N$  and for various values of energy  $U_b$  when the energy  $U_a = -5.5$  (attractions). For the same concentration,  $v_{A-B}$  increases as the attractions between the monomers units of the B block and the surface become larger. Also, it can be observed that, as the attractions become larger, the plateau region starts at lower concentrations.

#### ИЗВОД

#### О МАСИ АДСОРБОВАНИХ ПОЛИМЕРА НА ПОВРШИНАМА

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Показано је да је код идеалних полимера, који реагују са површином преко псеудо-потенцијала делта функције, зависност броја контаката мономерних јединица и површине у функцији концентрације облика  $c_b/(1 - c_b)$ . Архитектура полимера, степен полимеризације, енергија интеракције мономерних јединица и површине, дужина мономера и његова површина обухваћени су параметрима  $\delta$  и  $S$ . Наведена зависност адсорбоване масе полимера од концентрације потврђена је експерименталним резултатима Takahashi-ја и сарадника. За линеарни полистирен моларне масе  $134 \cdot 10^5$  који остварује интеракцију са хромном плочом  $\delta = (89938/273) \cdot 10^{-6} \text{ m}$ , а  $S = (-19300/273) \text{ m}^3 \text{ kg}^{-1}$ .

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