Macromolecules **1992,** *25,* 3307–3308

Are Ring Polymers Adsorbed on a Surface More Than Linear Polymers?

G. Stratouras and M. Kosmas*

Chemistry Department, University of Ioannina, Ioannina, Greece

Received August 28, 1991
Revised Manuscript Received December 17, 1991

The architecture of polymers is a determining factor for their adsorbance on a surface.[1,2] Comparing ring and linear chains of the same molecular weight in the neighborhood of a surface, we found that cyclic macromolecules under the same conditions are adsorbed more than the linear ones.[2] Recent experiments though on the adsorption of linear and cyclic polystyrene on two surfaces of mica at a distance D apart led to the opposite conclusion,[3] and it is the purpose of this note to investigate this contradiction. We will show that the two different behaviors can be explained by means of the solution of the problem of a localized chain interacting with a surface via a potential of the form[4,5] $u_a\delta(z)$, where z is the perpendicular distance of the monomers from the surface. The ideal Gaussian distribution, which allows a large number of monomers of the chains to adsorb at the surface, is affected by u_a, which, defined as the binary cluster integral $u_a = \int[1 - \exp(-V(r)/kT)]\ \mathrm{d}r$, expresses the intensity of the unit–surface interactions.[6] Close to its zero it is proportional to $1 - T_a/T$, where T_a is a characteristic adsorption temperature and has the same temperature dependence as the Flory χ parameters. The second experimental behavior of chains between two surfaces corresponds to chains localized on one surface while interacting with the second surface where some of their units are adsorbed. Finding the amount of adsorbed units on a surface for chains localized at a distance z_0 from it, we will be able to see how, for the two architectures of linear and ring polymers, the distance of localization z_0 affects their adsorption and give an answer to the above question.

Before addressing the adsorption of localized linear and ring chains, let us compare their coil density distributions $\tilde{\rho}_l(\rho)$ and $\tilde{\rho}_r(\rho)$ when they are far away from the surface ($u_a = 0$) as a function of the distance $\rho_s = |\mathbf{R} - \mathbf{R}_0|$ from the point $\mathbf{R}_0$ of their localization. This will help us in understanding their behaviors while they approach and interact with the surface. We have already studied the linear chain[5] and found that

$$\tilde{\rho}_l(\rho) = N\left(\frac{3}{2\pi Nl^2}\right)^{3/2}\frac{2\pi^{1/2}}{\rho}\operatorname{erfc}\left(\frac{\rho}{2}\right) \tag{1}$$

where Nl is the length of the chain made of N units each of length l and $\rho = 6^{1/2}\rho_s/(lN^{1/2})$ is a reduced distance. With the same method the density $\tilde{\rho}_r(\rho)$ of a ring can be determined, and it is equal to

$$\tilde{\rho}_r(\rho) = N\left(\frac{3}{2\pi Nl^2}\right)^{3/2}\frac{4\pi^{1/2}}{\rho}\exp(-\rho^2) \tag{2}$$

The ratio $\tilde{\rho}_r(\rho)/\tilde{\rho}_l(\rho)$ is shown in Figure 1. It is larger than 1 for $\rho < 1.32$, which means that for a ring and a linear macromolecule localized at the same point, at small reduced distances $\rho < 1.32$ the ring has a larger density of monomers than the linear macromolecule, the reason being the more compact structures of the rings. At larger distances, $\rho > 1.32$, the extensivity of linear chains yields larger densities so that $\tilde{\rho}_r(\rho)/\tilde{\rho}_l(\rho)$ becomes smaller than 1.

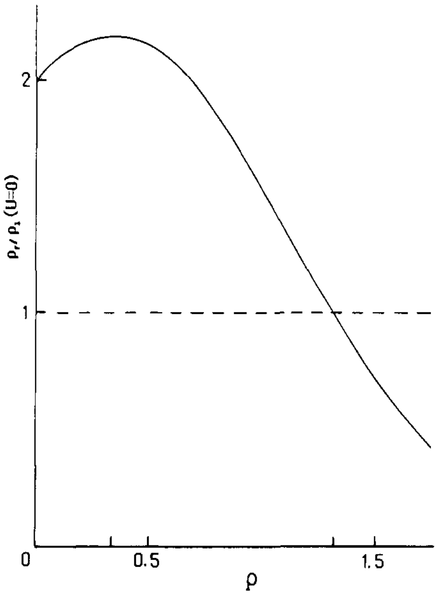

Figure 1. Ratio $\tilde{\rho}_r(\rho,U = 0)/\tilde{\rho}_l(\rho,U = 0)$ of the densities of localized chains of ring and linear polymers as a function of the distance ρ for $U = 0$. At $\rho = 0.35$ and 1.32 the ratio becomes maximum and equal to 1, respectively.

Notice also that at $\rho = 0.35$ the maximum value of the ratio is obtained, meaning that at these small distances the ring is much denser that the linear chain. Now let us study the density of monomers of the two macromolecules at the surface as they start approaching the surface from far away. First the linear chain with larger densities of monomers at larger distances will touch the surface and yield a larger number of monomers adsorbed at the surface. Then at smaller distances rings with larger densities will reach the surface and yield larger densities of adsorbed monomers. This explains the two different behaviors of the absorbances of the two macromolecules depending on the distance of localization. We will arrive at the same conclusions but in a quantitative manner by means of the exact analytical expressions of the amounts of adsorbed monomers for the two cases.

As far as linear chains are concerned, we have already studied the behavior of a chain localized with one of its ends at a distance z_0 from an interacting surface. By means of the summation of the effects to all orders of interactions, we have described analytically the linear density of monomers at the surface, which is defined to be equal to the summation of the densities from all points of the surface and expresses the amount of adsorbed units at the surface. For a linear chain localized with one of its ends at a distance z_0 from the surface, the linear density $\tilde{\rho}_{ll}(z_0,u_a)$ at the surface as a function of z_0 and the interaction parameter u_a is given by[5]

$$\tilde{\rho}_{ll}(Z_0,U) = N\left(\frac{3}{2\pi Nl^2}\right)^{1/2}\left[2\exp\left\{-\frac{Z_0{}^2}{4}\right\} - \pi^{1/2}(2U + Z_0)\exp\{U^2 + UZ_0\}\operatorname{erfc}\left(U + \frac{Z_0}{2}\right)\right]\bigg/\left[1 - \operatorname{erfc}\left(\frac{Z_0}{2}\right) + \exp\{U^2 + UZ_0\}\operatorname{erfc}\left(U + \frac{Z_0}{2}\right)\right] \tag{3}$$

where $Z_0 = 6^{1/2}|z_0|/(lN^{1/2})$ and $U = u_a(6N^{1/2})/2$ are reduced dimensionless distance and interaction parameters, respectively. By means of the same method the linear density of monomers at the surface for a ring localized

0024-9297/92/2225-3307$03.00/0

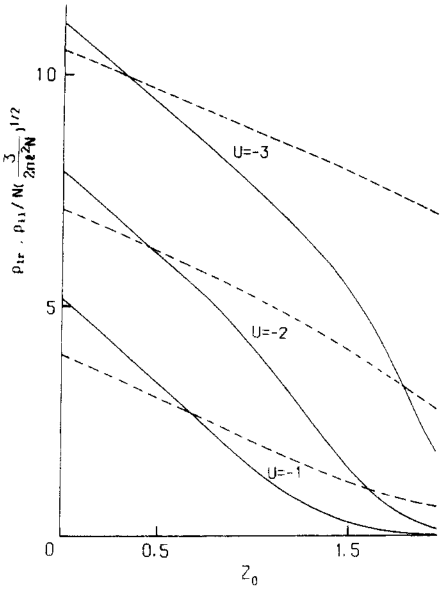

Figure 2. Linear densities $\tilde{\rho}_{lr}(Z_0,U)$ (—) and $\tilde{\rho}_{ll}(Z_0,U)$ (- - -) on the surface of a ring and a linear chain, respectively, as a function of their localization distance Z_0 for various attractive energies U. The distance Z_{0k} of crossing of pairs of graphs reduces on increasing the attractions.

with one of its points at Z_0 is found as

$$\tilde{\rho}_{lr}(Z_0,U) = N\left(\frac{3}{2\pi N l^2}\right)^{1/2}[\pi(2U^2 + 1 + 2UZ_0)\exp\{U^2 + 2UZ_0\}\operatorname{erfc}(U + Z_0) - 2U\pi^{1/2}\exp\{-Z_0^2\}]/[1 - U\pi^{1/2}\exp\{U^2 + 2UZ_0\}\operatorname{erfc}(U + Z_0)] \quad (4)$$

Plots of the two densities for attractions ($U < 0$) are shown in Figure 2. The densities $\tilde{\rho}_{ll}(Z_0,U)$ and $\tilde{\rho}_{lr}(Z_0,U)$ on the surface for the linear and ring chains respectively increase as the localized distance Z_0 becomes smaller and as the attractions become larger (U more negative). We see that, for each attractive energy U, there is a point of localization Z_{0k} where the graphs for the chains of the two architectures cross. At larger localizations $Z_0 > Z_{0k}$ the linear molecules are adsorbed more while for smaller Z_{0k} the opposite is true and rings are adsorbed more. Z_{0k} becomes smaller for larger attractions. The largest value of $Z_{0k} = 0.72$ is obtained at the limit $U \to 0$, which corresponds to a distance $z_0 = 0.286\, lN^{1/2}$ almost equal to the radius of gyration $R_g = 0.288 lN^{1/2}$ of the ring. This behavior remains the same for all attractive energies U up to the $U = 0$ case and describes experiments of adsorption even if they correspond to small adsorption energies.

The results from experiments on two surfaces of mica[3] at distances larger and smaller than the radii of gyration of the coils have been performed under conditions of small negative U. These conditions correspond to points at the right of the crossing of the two curves where the adsorption of linear chains is larger,[7] and the experimental results are not contradictory to those giving larger adsorption to rings which deal with chains closer to the surface, corresponding to points at the left of the crossings.

References and Notes

(1) Vant Lent, B.; Scheutjens, J.; Cosgrove, T. *Macromolecules* **1987**, *20*, 366.
(2) Kosmas, M. K. *Macromolecules* **1990**, *23*, 2061. Stratouras, G.; Kosmas, M. K. *Macromolecules* **1991**, *24*, 6754.
(3) Yerushalmi-Rozen, R.; Hostetter, B. J.; Fetters, L. J. Klein, J. *Macromolecules* **1990**, *23*, 2984.
(4) Stratouras, G. Kosmas, A. M.; Kosmas, M. K. *J. Phys. A: Math. Gen.* **1990**, *23*, L1317.
(5) Stratouras, G.; Kosmas, M. K. *J. Chem. Phys.* **1991**, *95*, 4656.
(6) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656. Edwards, S. F. *Proc. Phys. Soc. London* **1965**, *85*, 613. Freed, K. F. *Adv. Chem. Phys.* **1972**, *22*, 1. Kosmas, M. K. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 563.
(7) de Gennes, P.-G. *C.R. Acad. Sci., Ser. 2* **1990**, *310*, 1327.