References and Notes

(1) (a) Adelphi University; (b) Bar Ilan University.
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A Study of the Segmental Distribution of a Polymer Chain Terminally Attached to a Surface

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I. Introduction

Recently[1-3] attention has been focused on the behavior of a polymer chain terminally attached to a surface. A terminally attached chain is defined as one that is anchored to the surface at either one end (tail) or at both ends (loop). In particular Meier[3] and Hesselink[2] have obtained results using random walk statistics for the distribution of segments of tails and loops on the cubic lattice.

Such information is important in understanding the behavior of random walks near barriers, the stability of colloid dispersions, the size of the fold surface in polymer crystals, and the thickness of polymer films near weakly attracting interfaces. The effects caused by self-exclusion between chain elements have not been considered in either of these studies. Nevertheless it is apparent that such effects alter the relative location of polymer segments with respect to one another and hence may seriously alter the form of the distribution with respect to the surface.

In this paper we report a study of the distribution of segments for self-avoiding walks terminally attached to a surface generated on the diamond lattice by the method of exact enumeration.

II. Results and Discussion

The methods used to generate such walks are similar to those described previously.[1] In this particular study a count of the number of self-avoiding open walks (tails), i.e., those which do not return to the surface of size i, $C_{nr}(i,k,z)$ (where i is the number of segments $i-1$ being the number of bonds), having segment k in level z were obtained. In addition, the number of self-avoiding loops $C_{rr}(i,k,z)$, i.e., loops which return to the surface *randomly* for the *first time*, and the number of self-avoiding loops $C_{ar}(i,k,z)$, i.e., loops which return for the first time adjacent to their starting point, having segment k in level z were also obtained. These counts are reported in Tables I, II, and III, respectively. It should be noted that in Tables II and III only certain values of $C(i,k,z)$ are listed. The remaining values of $C(i,k,z)$ may be computed using the symmetry relationship.

$$C(i,k,z) \equiv C(i,i-k+1,z)$$

In addition all walk counts listed in Tables I–III are reduced by a factor of 2 due to symmetry considerations.

(1) Walk Probabilities. One defines the conditional probability for finding a walk of size i with segment k in level z and its first segment in level zero by

$$P_{nr}(i,k,z) \equiv C_{nr}(i,k,z)/C_{nr}{}^{S} \quad (1)$$

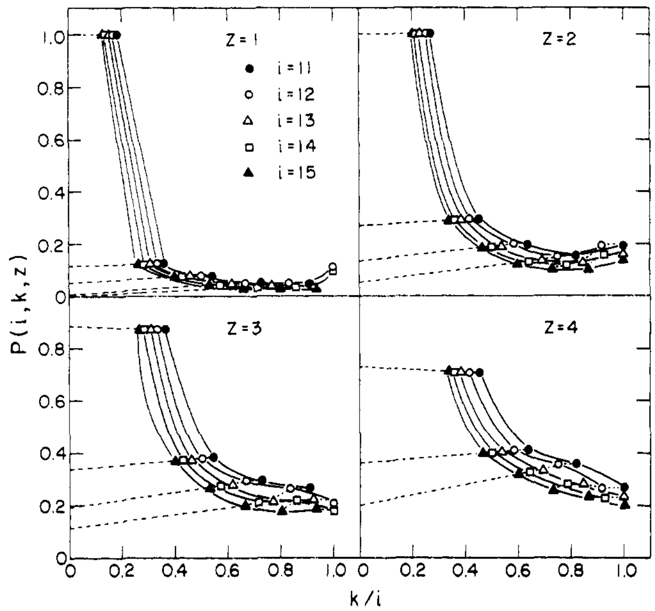

Figure 1. Plots of probability $P_{nr}(i,k,z)$ vs. k/i.

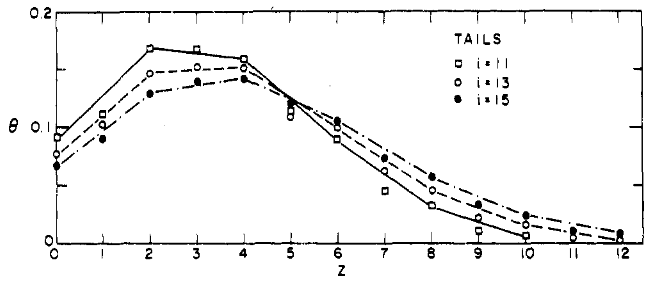

Figure 2. Plots of fraction of segments vs. normal to the surface distance for tails.

where $C_{nr}{}^{S}$ is the total number of self-avoiding tails obtained. These probabilities are normalized so that

$$\sum_{z=0}^{z=i-1} P_{nr}(i,k,z) = 1 \quad (2)$$

and also

$$\sum_{z=0}^{z=i-1} \sum_{k=1}^{k=i} \rho_{nr}(i,k,z) = 1 \quad (3)$$

where

$$\rho_{nr}(i,k,z) \equiv P_{nr}(i,k,z)/i \quad (4)$$

It is apparent that $P_{nr}(i,k,z)$ can also be looked upon as the average number of kth segments per chain located in level z, whereas $P_{nr}(i,k,z)/i$ represents the fraction of kth segments in level z. In addition one may compute the average number of segments per chain, $i\theta(i,z)$, where $\theta(i,z)$ is the fraction of segments in any level, by summing the $P_{nr}(i,k,z)$ over k, i.e.,

$$i\theta(i,z) = \sum_{k=1}^{k=i} P_{nr}(i,k,z)$$

Figure 1 is a normalized plot of $P_{nr}(i,k,z)$ vs. k/i for various z levels. By connecting points corresponding to the same value of k one obtains curves of constant k, and extrapolating to $k/i = 0$ one obtains an estimate for $P_{nr}(\infty,k,z)$. It is seen that for most values of k straight lines are obtained; only for large k/i does curvature appear due

Table I
A List of the Number of Self-Avoiding Walks of Size i (Which Have One End Only Attached to a Surface), $C_{nr}(i,k,z)$, Having Segment k in Level z

k,z	$C(4,k,z)$	$C(5,k,z)$	$C(6,k,z)$	$C(7,k,z)$	$C(8,k,z)$	$C(9,k,z)$	$C(10,k,z)$	$C(11,k,z)$	$C(12,k,z)$	$C(13,k,z)$	$C(14,k,z)$
1,0	14	42	106	314	818	2398	6374	18638	50250	146438	398754
2,1		42	106	314	818	2398	6374	18638	50250	146438	398754
4,1	2	6	14	42	102	306	794	2330	6182	18098	48766
6,1		10	10	30	70	198	486	1450	3774	10990	29294
8,1				54	50	142	322	934	2270	6694	17374
10,1						330	310	886	1958	5626	13558
12,1								2098	1966	5558	12102
14,1										13966	13166
3,2	4	42	106	314	818	2398	6374	18638	50250	14638	39874
5,2	6	18	34	102	250	730	1878	5502	14578	42510	114562
7,2			34	98	182	526	1266	3718	9550	27814	73698
9,2					194	558	974	2830	6734	19606	49866
11,2							1230	3550	6130	17598	41446
13,2									8090	23358	39806
15,2											55234
4,3	12	36	92	272	716	2096	5580	16308	44068	128340	349988
6,3		196	48	140	324	956	2448	7140	18844	54952	147828
8,3				100	288	840	1888	5500	14032	40784	107196
10,3						596	1712	4968	10888	31556	79452
12,3								3948	11264	32576	70428
14,3										26596	75888
5,4	8	24	72	212	568	1668	4496	13136	35672	103928	284192
7,4			40	120	348	1024	2620	7632	20220	58924	158528
9,4					272	784	2280	6632	16644	48364	127456
11,4							1720	4944	14280	41512	102256
13,4									11760	33520	96600
15,4											81136
6,5		16	48	144	424	1244	3440	10048	27632	80496	221632
8,5				96	288	840	2468	7228	19372	56416	153248
10,5						704	2048	5968	17356	50536	134280
12,5								4720	13660	39504	114736
14,5										33364	95700
7,6			32	96	288	848	2488	7288	20480	59700	116528
9,6					224	672	1968	5784	16920	49316	136344
11,6							1760	5152	15056	43840	127660
13,6									12480	36312	105356
15,6											91248
8,7				64	192	576	1696	4976	14576	42544	120936
10,7						512	1536	4512	13264	38816	113160
12,7								4288	12608	36928	107728
14,7										32064	93680
9,8					128	384	1152	3392	9952	29152	85088
11,8							1152	3456	10176	29920	87584
13,8									10240	30208	88640
15,8											80512
10,9						256	768	2304	6784	19904	58304
12,9								2360	7680	22656	66624
14,9										24064	71168
11,10							512	1536	6784	13568	39808
13,10									7680	16896	49920
15,10											55808
12,11								1024	4608	9216	27136
14,11									5632	12288	36864
13,12									3072	6144	18432
15,12											26624
14,13									2048	4096	12288
15,14											8192

to the limited number of data available. The asymptotic estimates for $P_{nr}(\infty,k,z)$ are reported in Table IV. Unfortunately in the case of the loop data the curves of constant k could not be satisfactorily extrapolated.

(2) Chain Density Distribution. Figures 2, 3, and 4 are plots of the fraction of segments vs. the distance normal to the surface for tails, random returning loops, and adjacently returning loops, respectively. On each figure a number of curves for different values of i are shown. It is seen that the curves can be divided into three categories according to the chain size dependence. For tails (Figure 2) one finds that for $0 < z < 4.5$, θ decreases with increasing i, for $z = 4.5$, θ is constant with increasing i, for $4.5 < z < i$, θ increases with increasing i. This crossover behavior is typical of systems[4] where the sums of the dependent variables (in this case the fraction of segments) are constrained to equal the same constant for all choices of the dependent variables; namely $\Sigma_z \theta(i,z) = 1$ for all i. It is seen therefore that at a certain distance from the surface a point exists where the density of segments for a weakly interacting chain is appreciable and independent of molecular weight. Estimates for θ vs. z dependence of the infinite chain were obtained by plotting θ vs. z/i (as was done previously) for P vs. k/i and extrapolating the curves of constant z to the point $z/i = 0$. This method was not as successful when applied to the θ vs. z data; nevertheless some estimates for the shape of the infi-

Table II
A List of the Number of Self-Avoiding Loops of Size i Segments (Which Randomly Return to the Surface for the First Time), $C_{rr}(i,k,z)$, Having Segment k in Level z

k,z	$C(4,k,z)$	$C(6,k,z)$	$C(8,k,z)$	$C(10,k,z)$	$C(12,k,z)$	$C(14,k,z)$
1,0	4	18	106	638	4126	27474
2,1	4	18	106	638	4126	27474
4,1		4	20	96	604	3796
6,1				92		2734
8,1						2088
3,2	4	18	106	638	4126	27474
5,2			52	262	1478	9284
7,2					1332	7290
4,3		14	86	542	3522	23678
6,3				342	2004	12064
8,3						11542
5,4			54	376	2648	18190
7,4					2002	12940
6,5				204	1672	12676
8,5						10784
7,6					792	7244
8,7						3060

Table III
A List of the Number of Self-Avoiding Loops of Size i (Which Return to an Adjacent Point on the Surface for the First Time), $C_{ar}(i,k,z)$, Having Segment k in Level z

k,z	$C(4,k,z)$	$C(6,k,z)$	$C(8,k,z)$	$C(10,k,z)$	$C(12,k,z)$	$C(14,k,z)$
1,0	2	18	22	106	506	2774
2,1	2	18	22	106	506	2774
4,1		4	2	10	56	318
6,1				10	30	186
8,1						106
3,2	2	18	22	106	506	2774
5,2			6	30	126	722
7,2					114	476
4,3		14	20	96	450	2456
6,3				42	202	964
8,3						924
5,4			16	76	380	2052
7,4					228	1226
6,5				54	274	1624
8,5						1166
7,6					164	1072
8,7						578

Table IV
Conditional Probabilities for Finding a Tail with Its kth Segment in Level z

z	k	$P(\infty,k,z)$
0	1	1.000
1	4	0.115
1	6	0.050
1	8	0.005
1	10	0.000
2	3	1.000
2	5	0.270
2	7	0.133
2	9	0.050
3	4	0.888
3	6	0.340
3	8	0.195
3	10	0.115
4	5	0.730
4	7	0.360
4	9	0.200
5	6	0.600
5	8	0.385
6	7	0.505
6	9	0.390
7	8	0.400
7	10	0.395

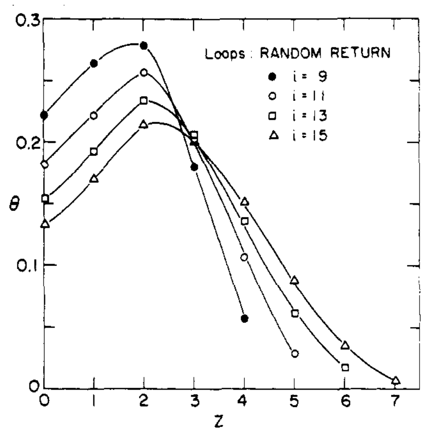

Figure 3. Plots of fraction of segments vs. normal to the surface distance for random returning loops.

nite curve can be reported. The tentative results are listed in Table V with the estimated error range. The major problem encountered was in the region of the maximum, where the curves of θ vs. z/i (at constant z) were not linear. The

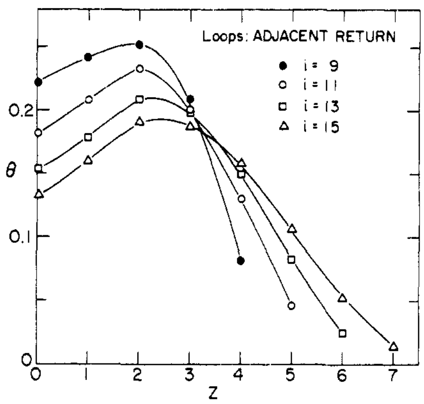

Figure 4. Plots of fraction of segments vs. normal to the surface distance for adjacently returning loops.

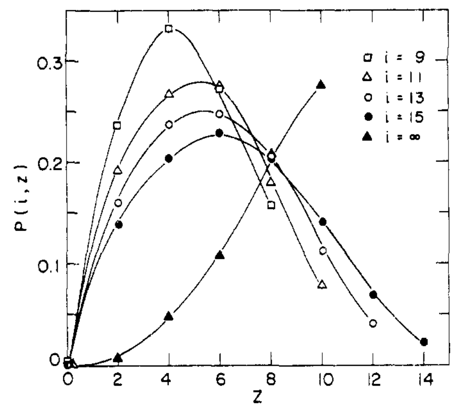

Figure 5. Plots of the probability for finding the chain end a distance z from the surface.

Table V
Estimates for the Fraction of Segments as a Function of the Distance Normal to the Surface for an Isolated Infinite Chain

z	Fraction	z	Fraction
0	0.00	4	(0.06—0.08)
1	0.01	5	(0.100—0.120)
2	0.03	6	(0.138—0.148)
3	(0.04—0.05)	7	~0.143

generalized shape is in agreement with that reported by Hesselink[2] and that computed from the data of Meier.[3] It did not seem worthwhile to make more quantitative comparisons considering the errors involved in our methods. It becomes clear that data for longer walks will be necessary to quantitatively describe the infinite chain in the vicinity of the maximum and at higher z levels. For the present we deemed it too difficult to obtain such data due to the enormous amount of computer time required.

Figure 5 is a plot for chain ends. It should be noted that whereas the maximum density of chain segments for finite chains of size $i = 15$ are located in level 4, the maximum probability for finding the end point is in level 6. This means that in general the thickness of the chain film at distances beyond where the maximum density of segments occurs is determined primarily by chain ends.

The distribution of segments for a chain which may touch a surface with any of its segments has also been considered. The results for this particular model are being published separately.

References and Notes

(1) M. Lax, *Macromolecule*, 7, 660 (1974).
(2) F. Th. Hesselink, *J. Phys. Chem.*, 10, 3488 (1969).
(3) D. J. Meier, *J. Phys. Chem.*, 71, 1861 (1967).
(4) A similar phenomenon is the well-known isosbestic point.

Communications to the Editor

Hydrogen-Transfer Polymerization of Hydroxyalkyl Acrylates

The present communication reports a base-catalyzed hydrogen-transfer polymerization of hydroxyalkyl acrylates (1) to produce polymers having an ester–ether type structure 2 (eq 1). Monomers examined were 2-hydroxyethyl

$$CH_2{=}CHCO_2{-}Y{-}OH \xrightarrow{B:} {-}\!(CH_2CH_2CO_2{-}Y{-}O)\!_n{-} \qquad (1)$$

1a, Y = CH_2CH_2 (2-HEA) **2a**
1b, Y = $CH_2CH_2CH_2$ (3-HPA) **2b**
1c, Y = CH_2CHCH_3 (2-HPA) **2c**

(2-HEA), 3-hydroxypropyl (3-HPA), and 2-hydroxypropyl (2-HPA) acrylates. This polymerization is regarded as being closely related to the base-catalyzed hydrogen-transfer polymerization of acrylic acid (eq 2) recently reported by us.[1]

$$CH_2{=}CHCO_2H \xrightarrow{B:} {-}\!(CH_2CH_2CO_2)\!_n{-} \qquad (2)$$

A typical example of polymerization is as follows. A mixture of 1.64 g (15 mmol) of 2-HEA and 2.4 mg (2.0 mol % for 2HEA) of LiH was placed in a sealed tube under nitrogen and kept at 50°. As the reaction proceeded the system became viscous. After 100 hr the tube was opened and the polymeric material was dissolved in 8 ml of $CHCl_3$. The solution was washed twice with 1 ml of H_2O, dried on K_2CO_3, and poured into a large amount of diethyl ether–hexane (50:50) mixture to precipitate the polymeric material. The polymer was isolated by decantation and dried in vacuo (1.52 g, 93% yield). It is a colorless paste, soluble in $CHCl_3$, DMF, and other polar solvents but insoluble in H_2O and diethyl ether.

An ir spectrum of the polymer (Figure 1) shows the presence of ester (1735 cm^{-1}) and ether (1180 cm^{-1}) groups. It should be noted that the intensity of $\nu_{O\text{-}H}$ at 3200–3500 cm^{-1} was greatly decreased in the polymer. The NMR spectrum of the polymer (Figure 2) shows a triplet (peak A at δ 2.58, CCH_2CO_2, 2 H), a multiplet and triplet (peaks B and C at 3.54 and 3.70, respectively, OCH_2C, 4 H), a multiplet (peak D at 4.25, CO_2CH_2C, 2 H), and a multiplet (peak E at 6.4–5.5, $CH_2{=}CHCO_2$). These data strongly indicate the polymer structure of **3a**. Based on the assumption that

$$CH_2{=}CHCO_2CH_2CH_2O{-}\!(CH_2CH_2CO_2CH_2CH_2O)\!_{n-1}H$$
3a