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Shapes and Sizes of Gaussian Macromolecules. 1. Stars and Combs in Two Dimensions

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ABSTRACT: The shapes and sizes of star- and comblike macromolecules in the framework of Gaussian models and confined to a plane have been analytically and numerically investigated in terms of shape factors, shape variance factors, asphericity parameter and factor, and shrinking factor. It is found that for regular stars and a special class of irregular stars with very long arms, both shape asymmetry and shrinking factor decrease as the number f of arm chains increases from 2 to 12 with perfect symmetry and zero shrinking factor at $f = \infty$. For a large f-arm irregular star whose arms have two or three different lengths, the well-known "maximum shape asymmetry" effect, i.e., having greater values of the larger shape factor and asphericity parameter or factor than the corresponding ones for linear chains, occurs when the stars are chains end-linked with two or more shorter chains. For large f-arm regular combs with both equal and unequal length arms and spacers, a "minimum shape asymmetry" effect appears for certain values of f, while the shrinking factor decreases with increasing f or, for fixed f, increases with increasing length of the spacer relative to the arm. The large shape asymmetry of the end-linked chains studied here may have important implications for improving rheological and other shape-dependent properties of the existing linear macromolecules confined to surfaces.

Introduction

Since Kuhn's pioneering theoretical work on polymer shape,[1] the field of polymer configuration statistics has witnessed great progress.[2−41] Recently, we have obtained an exact analytic solution to the average principal components of shape or gyration tensor **S** for an arbitrary Gaussian macromolecule in two dimensions,[38] which is regarded as a major step forward from Šolc and Gobush's work on rings[10] in two dimensions (2D) and makes the present theoretical study of both sizes and shapes of 2D irregular stars and regular combs feasible.

Star- and comblike polymers are now readily available in polymer synthesis laboratories worldwide as they represent two simplest types of branched polymer molecules. As applications of polymers at surfaces become wider and wider, theoretical study on stars and combs confined to a plane is assuming greater importance. Unfortunately, there is an obvious lack of both theoretical and experimental work in this regard except for a few computer simulation results.[42] This paper is thus intended to fill this gap.

In what follows, theoretical background is first given on exact evaluations of such shape and size parameters as shrinking factor g, shape factors δ_i ($i = 1, 2$) or the averaged individual principal components of shape tensor divided by mean square radius of gyration, asphericity parameter $<A>$, and asphericity factor δ for a given type of polymer molecules in the framework of a Gaussian model. Numerical results are then presented followed by a discussion of the results and a few conclusions.

Theory

We have recently presented a general formalism for calculating exactly shape factors and asphericity parameters and factors of arbitrary random walks or Gaussian macromolecules in two dimensions.[37−39] It is a generalization of Šolc and Gobush's treatment of rings[10] and Diehl and Eisenriegler's work on both rings and chains.[22]

From this formalism, the larger shape factor δ_1 is given by $\delta_1 = 1 - \delta_2 = 1/2 - \chi_{1,N}$, where $\chi_{m,N}$ for $m = 1$ or 2 is defined as

$$\chi_{m,N} = \int_0^\infty M_N(x)\, F_{m,N}(x)\, \mathrm{d}x \qquad (1)$$

Here, N is the total number of vertices or beads in a molecular graph or macromolecule, $M_N(x) = 1/|D_N(x+ix)|$, $D_N(x) = P_{N-1}[-(x/N)^2]$, $P_{N-1}(x) = P_R(2-x)/P_R(2)$, $P_R(\lambda) = |\mathbf{K}-\lambda\mathbf{E}|/(-\lambda)$, where $\mathbf{E}$ is an $N \times N$ unit matrix and $\mathbf{K}$ is the architecture or Kirchhoff matrix for the N-bead molecule with one zero eigenvalue and $N - 1$ non-zero eigenvalues denoted by λ_1, λ_2, ... and λ_{N-1}, $F_{1,N}(x) = \mathrm{Im}[\mu_{1,N}(x+ix)/x]$, with $\mathrm{Im}(z)$ denoting the imaginary part of the complex variable z and $\mu_{m,N}(x) = S_{m,N}(x)/S_{1,N}{}^m(0)$ for $m \geq 1$ in which $S_{m,N}(x) = \sum_{1\leq j\leq N-1} (N^2\lambda_j+x^2)^{-m}$, and $F_{2,N}(x) = x^{-1}\, \mathrm{Im}[\mu_{2,N}(x+ix)+\mu_{1,N}{}^2(x+ix)/2]$. We note that for small x one has $F_{1,N}(x) = -S_{1,N}(0)x[\mu_{2,N}(0)+O(x)]$ and $F_{2,N}(x) = -2S_{1,N}(0)x[2\mu_{3,N}(0)+\mu_{2,N}(0)\mu_{1,N}(0)+O(x)]$. For the αth shape variance factor σ_α which is defined as the ratio of the second moment of the difference between the αth principal component and its mean value to $<s^2>^2$, where s is the radius of gyration or $s^2 = \mathrm{tr}(\mathbf{S})$, we have $\sigma_\alpha = [1 + 3\mu_{2,N}(0)]/4 + (-1)^\alpha\chi_{2,N} - \delta_\alpha{}^2$. The asphericity parameter $<A>$ is given by

$$\langle A\rangle = 4\int_0^\infty x^3 S_{2,N}(x)\, D_N{}^{-1}(x)\, \mathrm{d}x \qquad (2)$$

where $A = 2\,\mathrm{tr}(\mathbf{\Delta}^2)/s^4$ in which $\mathbf{\Delta} = \mathbf{S} - (s^2/2)\mathbf{U}$, $\mathbf{U}$ is a $d \times d$ unit matrix, and $0 \leq A$, $<A> \leq 1$, with the lower (upper) bound corresponding to spheres (rods), while the asphericity factor δ defined as $2<\mathrm{tr}(\mathbf{\Delta}^2)>/<s^4> \in [0,1]$ is found to be $\delta = 2/[1 + 1/\mu_{2,N}(0)]$ with the use of Wei and Eichinger's general results.[26] The shrinking factor g, defined as $<s^2>/<s^2>_{\mathrm{chain}}$, now becomes $g = S_{1,N}(0)/S_{1,N}(0)_{\mathrm{chain}}$.

Obviously, in the above formulas for the calculations of δ_α, σ_α, $<A>$, δ, and g, a key function is $D_N(x)$ or $D(x) \equiv D_\infty(x)$, from which $S_{m,N}(x)$ or $S_m(x) \equiv S_{m,\infty}(x)$ can be analytically evaluated as follows:

$$S_1(x) = D^{(1)}(x)/[2xD(x)] \qquad (3)$$

with $D^{(k)}(x) = \mathrm{d}^kD(x)/\mathrm{d}x^k$,

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Table 1. Shape and Size Parameters for 2D Regular Stars with f Infinitely Long Arms

f	δ_1	$<A>$	δ	σ_1	σ_1/σ_2	g
2	0.832 938	0.396 400	0.571 429	0.369 214	40.6160	1.000 000
3	0.783 755	0.321 011	0.403 909	0.202 247	12.3994	0.777 778
4	0.749 535	0.263 590	0.310 811	0.133 987	7.666 21	0.625 000
5	0.724 855	0.222 090	0.252 327	0.098 432	5.784 53	0.520 000
6	0.706 136	0.191 354	0.212 291	0.077 030	4.781 19	0.444 444
7	0.691 358	0.167 867	0.183 191	0.015 126	4.157 28	0.387 755
8	0.679 330	0.149 407	0.161 094	0.052 906	3.730 85	0.343 750
12	0.646 963	0.103 507	0.108 639	0.031 791	2.845 47	0.236 111
∞	0.500 000	0.000 000	0.000 000	0.000 000	1.000 00	0.000 000

Table 2. Shape and Size Parameters for 2D f-Long-Arm Irregular Stars with $n_i = in_1$

f	δ_1	$<A>$	δ	σ_1	σ_1/σ_2	g
2	0.832 938	0.396 400	0.571 429	0.369 214	40.6160	1.000 000
3	0.805 917	0.194 083	0.487 963	0.285 249	24.6331	0.833 333
4	0.781 781	0.308 788	0.413 212	0.218 246	16.0894	0.700 000
5	0.761 739	0.275 438	0.355 664	0.172 942	11.9370	0.600 000
6	0.745 124	0.248 013	0.311 291	0.141 554	9.577 79	0.523 810
7	0.731 174	0.225 292	0.276 390	0.118 924	8.076 17	0.464 286
8	0.719 289	0.206 253	0.248 346	0.102 007	7.042 72	0.416 667
12	0.685 072	0.153 868	0.176 217	0.063 484	4.903 79	0.294 872
∞	0.500 000	0.000 000	0.000 000	0.000 000	1.000 00	0.000 000

Table 3. Shape and Size Parameters for Three Special Types of 2D Long Arm Irregular Stars

type	δ_1	$<A>$	δ	σ_1	σ_1/σ_2	g
1	0.752 150	0.248 558	0.340 321	0.168 703	14.3997	0.402 344
2	0.736 959	0.235 104	0.289 786	0.014 936	8.498 10	0.500 000
3	0.667 730	0.130 334	0.142 815	0.046 703	3.773 08	0.264 746

$$S_2(x) = S_1^{\,2}(x) + \Delta_2(x) \qquad (4)$$

with $\Delta_2(x)$ given by

$$\Delta_2(x) = [2S_1(x) - D^{(2)}(x)/D(x)]/(4x^2) \qquad (5)$$

and

$$S_3(x) = S_1(x)[3S_2(x) - S_1^{\,2}(x)]/2 + \Delta_3(x) \qquad (6)$$

with $\Delta_3(x)$ defined as

$$\Delta_3(x) = [12x\Delta_2(x) + D^{(3)}(x)/D(x)]/(16x^3) \qquad (7)$$

For $m \geq 4$, $S_m(x)$ can be calculated analogously from $D(x)$. For analytic evaluations of $D_N(x)$ or $D(x)$, one needs either the eigenpolynomial of **K** or the characteristic function for a given type of molecules. For example, for chains (represented by $m = 1$ below) and rings ($m = 2$), we have

$$D_N(x) = \{\mathrm{sh}(ny/m)/[n\ \mathrm{sh}(y/m)]\}^m \qquad (8)$$

where $y = 2\ \mathrm{arsh}[x/(2n)]$ and

$$D(x) = [\mathrm{sh}(x/m)/(x/m)]^m \qquad (9)$$

From eqs 8 and 9, we further have for chains,

$$S_{1,N}(x) = [n\ cth(ny) - \mathrm{cth}\ y]/[2nx\ \mathrm{ch}(y/2)] \qquad (10)$$

and

$$S_1(x) = [x\ \mathrm{cth}\ x - 1]/(2x^2) \qquad (11)$$

which is also the same as $\omega_1(x)$ with $\omega_m(x)$ defined as

$$\omega_m(x) = \sum\nolimits_{1\leq k\leq\infty}[(k\pi)^2 + x^2]^{-m} \qquad (12)$$

Analogous to eq 12, one may further define

$$\omega_m(b,x) = \sum\nolimits_{-\infty\leq k\leq\infty}[(2k\pi + \arccos b)^2 + x^2]^{-m} \qquad (13)$$

with $\omega_1(b,x) = \mathrm{sh}\ x/[2x(\mathrm{ch}\ x - b)]$, which will be of use in the following treatment of stars and combs.

Numerical Results

Irregular Stars. For an irregular star consisting of f-arm chains, each of n_i ($i = 1, 2, ..., f$) segments, meeting at one central bead, the total number of beads is $N = 1 + \sum_{1\leq i\leq f} n_i$. Now let $\alpha_i = n_i/(N - 1)$ and each arm chain be infinitely long, then, we have for this large irregular star or irregular-star-branched random walk:

$$D(x) = D_S(x)\prod\nolimits_{1\leq j\leq f}\mathrm{ch}(\alpha_j x) \qquad (14)$$

from the existing expressions for the characteristic function[12,43] or the eigenpolynomial of **K**[44,45] for irregular stars. Here, $D_S(x) = \sum_{1\leq j\leq f} th(\alpha_j x)/x$. From eq 14, one can write

$$S_m(x) = S_{m,S}(x) + \sum\nolimits_{1\leq j\leq f}\alpha_j^{\,2m}\omega_m(0,\alpha_j x) \qquad (15)$$

where $S_{m,S}(x)$ may be easily evaluated from $D_S(x)$ by use of eqs 3−7.

Substitution of the above analytic expressions for $D(x)$ and $S_m(x)$ in the formulas for calculating δ_α, σ_α, $<A>$, δ, and g yields accurate numerical values for these shape and size parameters for both regular and irregular stars. The results are given in Tables 1−5. In Table 3, a molecule of type 1 corresponds to a large 10-arm irregular star with two long ($n_2 = 4n$) and eight short ($n_1 = n$) branches,[46] while that of type 2 or 3 corresponds to a large 6- or 12-arm irregular star with two or six long ($n_3 = 3n$), two or three ($n_2 = 2n$) middle-sized, and two or three short ($n_1 = n$) branches.

Regular Combs. For a regular comb consisting of f-arm chains, each of $n_i = n$ ($i = 1, 2, ..., f$) segments, equally spaced along a backbone chain of fm segments, the total number of beads is $N = 1 + f(m+n)$. Now let $\beta = m/n$, $r_1 = 1 - r_2 = 1/(1 + \beta)$, and both m and n be infinitely large, we then have for this large regular comb or regular-comb-branched random walk:

Table 4. Shape and Size Parameters for 2D 6-Long-Arm Irregular Stars with $K_2 = 6 - K_1$ and $\beta = n_1/n_2$

	$K_1 = 1$			$K_1 = 2$			$K_1 = 3$		
β	δ_1	<*A*>	g	δ_1	<*A*>	g	δ_1	<*A*>	g
0	0.724 855	0.222 090	0.520 00	0.749 535	0.263 590	0.625 00	0.783 755	0.321 011	0.777 78
1/5	0.722 053	0.216 717	0.487 94	0.741 518	0.247 760	0.537 94	0.765 260	0.284 464	0.592 59
1/3	0.718 727	0.210 657	0.472 66	0.732 965	0.232 032	0.501 46	0.748 384	0.253 838	0.527 78
1	0.706 136	0.191 354	0.444 44	0.706 136	0.191 354	0.444 44	0.706 136	0.191 354	0.444 44
2	0.730 044	0.220 584	0.475 22	0.733 227	0.227 054	0.484 38	0.728 942	0.222 863	0.481 48
3	0.765 796	0.267 293	0.531 25	0.762 619	0.270 818	0.544 00	0.748 384	0.253 838	0.527 78
4	0.792 524	0.306 915	0.588 48	0.780 938	0.301 525	0.597 22	0.759 050	0.272 765	0.564 44
5	0.810 200	0.336 616	0.640 00	0.792 332	0.322 066	0.641 40	0.765 260	0.284 464	0.592 59
8	0.834 110	0.384 927	0.754 21	0.808 877	0.353 428	0.733 00	0.773 721	0.301 132	0.646 09
12	0.841 897	0.406 387	0.841 24	0.817 377	0.369 572	0.802 11	0.777 737	0.309 223	0.683 10
99	0.834 317	0.399 678	0.994 67	0.831 076	0.393 392	0.970 59	0.783 186	0.319 960	0.764 58
∞	0.832 938	0.396 400	1.000 00	0.832 938	0.396 400	1.000 00	0.783 755	0.321 011	0.777 78

Table 5. Shape and Size Parameters for 2D 3-Long-Arm Irregular Stars with $\alpha = n_2/n_3$ and $\beta = n_1/n_2$

	$\alpha = 1$			$\alpha = 2$			$\alpha = 3$		
β	δ_1	<*A*>	g	δ_1	<*A*>	g	δ_1	<*A*>	g
1	0.783 755	0.321 011	0.777 78	0.796 465	0.336 769	0.808 00	0.807 916	0.353 104	0.842 57
2	0.799 301	0.339 184	0.812 50	0.814 852	0.361 496	0.860 06	0.821 971	0.373 920	0.892 00
3	0.815 110	0.360 361	0.856 00	0.825 893	0.378 829	0.901 24	0.829 461	0.386 502	0.926 26
4	0.824 311	0.374 893	0.888 89	0.831 059	0.388 494	0.927 87	0.832 720	0.392 987	0.947 27
5	0.829 411	0.384 234	0.912 54	0.833 473	0.393 828	0.945 38	0.834 125	0.396 335	0.960 64
6	0.832 257	0.390 201	0.929 69	0.834 596	0.396 799	0.957 33	0.834 705	0.398 069	0.969 57
7	0.833 859	0.394 035	0.942 39	0.835 091	0.398 454	0.965 81	0.834 903	0.398 949	0.975 81
8	0.834 754	0.396 510	0.952 00	0.835 270	0.399 358	0.972 01	0.834 921	0.399 362	0.980 32
12	0.835 580	0.400 168	0.973 76	0.834 998	0.400 031	0.985 37	0.834 514	0.399 340	0.989 88
99	0.833 106	0.396 817	0.999 42	0.833 026	0.396 623	0.999 71	0.832 998	0.396 552	0.999 80
∞	0.832 938	0.396 400	1.000 00	0.832 938	0.396 400	1.000 00	0.832 938	0.396 400	1.000 00

$$D(x) = D_C(x)\ \mathrm{ch}(r_1 x/f)^{f-1}\ \mathrm{sh}(x/f)/(x/f) \qquad (16)$$

where $D_C(x) = U_{f-1}[y(x/f)/2]/f$, $U_n(x)$ is the Chebyshev polynomials of the second kind,[47] and $y(x) = \mathrm{ch}(r_2 x) + \mathrm{ch}\ x/\mathrm{ch}(r_1 x)$. Here, as in the case of irregular stars, one can write from eq 16,

$$S_m(x) = S_{m,C}(x) + f^{-2m}[\omega_m(x/f) + (f-1)r_1^{\,2m}\omega_m(0,r_1 x/f)] \qquad (17)$$

where $S_{m,C}(x)$ can be evaluated from $D_C(x)$ with the use of eqs 3−7.

As in the previous treatment of irregular stars, substitution of the above analytic expressions for $D(x)$ and $S_m(x)$ in the formulas for calculating δ_α, σ_α, <*A*>, δ, and g yields accurate numerical values for these shape and size parameters for regular combs. The results are tabulated in Tables 6−8.

Discussion and Conclusion

For 2D f-arm regular stars with infinitely long arms, it can be seen from Table 1 that both shape asymmetry and shrinking factor decrease as the number f of arm chains increases from 2 to 12 with perfect symmetry (spheres) and zero shrinking factor at $f = \infty$. The larger shape variance factor also decreases as f increases. It is further seen that the earlier exptrapolated simulation results[42] for asphericity parameter <*A*> of regular stars with f = 2-6 are in good agreement with our exact results in Table 1.

For 2D f-long-arm irregular stars, it is seen from Table 2 that when the length of the jth arm chain is j times that of the shortest arm, i.e., $n_j/n_1 = j$, then they show similar dependences of shape and size parameters on f. Table 3 shows the effects of the architecture of 2D irregular stars on shape and size parameters. We note that for the large 10-arm irregular star with two long and eight short branches (type 1) which was first studied by Zimm and Kilb[46] and later reinvestigated by Yang and Yu,[45] we have succeeded in obtaining exact analytic results for its shrinking factor, i.e., $g = 103/256 \cong 0.402\,344$, in addition to the first calculations of its shape factors, shape variance factors, and asphericity parameter and factor. For a large 2D 6-arm irregular star with two length types of arm chains, i.e., $K_1 + K_2 = 6$, where K_1 is the number of arms for the first length type while K_2 for the second, it is seen from Table 4 that as $\beta = n_1/n_2$ increases from 0 to 1, the shape and size parameters decrease from the values for 5-, 4-, and 3-arm regular stars with K_1 = 1, 2, and 3, respectively, to those for 6-arm regular stars and that as β increases from 1 to ∞, these parameters increase monotonously from the values for a 6-arm regular star to those for linear chains (K_1 = 1 and 2) or 3-arm regular stars (K_1 = 3), except for the shape parameters for the K_1 = 1 case, i.e., a long chain end-linked with five shorter chains, which shows maxima around $\beta = 12$ and at $\beta = 12$ are 0.841 897 for δ_1 and 0.406 387 for <*A*>, all greater than the corresponding values for linear chains. This "maximum shape asymmetry" effect appears also in the chain end-linked with shorter loops[38] or both shorter and heavier chains, i.e., di- or triblock copolymers.[40] Finally, for a large 2D 3-arm irregular star with three length types of arm chains ($\alpha = n_2/n_3$ and $\beta = n_1/n_2$), we see from Table 5 that as β increases from 1 to ∞, the shrinking factor increases monotonously from the values for 3-arm regular stars (α = 1) or symmetric Y-stars (α = 2 and 3) to those for linear chains, while shape asymmetry shows maxima around β = 8 or 12, that is, a long chain end-linked with two shorter chains both of which may or may not have the same length also shows the "maximum shape asymmetry" effect as in the case of chains end-linked with five shorter chains as discussed above.

For large 2D f-arm regular combs with equal length arms and spacers ($\beta = 1$ or $m = n$), it is seen from Table

Table 6. Shape and Size Parameters for 2D *f*-Long-Arm Regular Combs with $\beta = m/n = 1$

f	δ_1	$<A>$	δ	σ_1	σ_1/σ_2	g
1	0.832 938	0.396 400	0.571 429	0.369 214	40.6160	1.000 000
2	0.799 301	0.339 184	0.466 425	0.264 634	21.3139	0.812 500
3	0.786 673	0.314 892	0.432 282	0.236 759	18.9587	0.722 222
4	0.784 025	0.306 241	0.430 657	0.238 874	20.9296	0.671 875
5	0.785 096	0.304 632	0.438 072	0.247 704	23.7257	0.640 000
6	0.787 465	0.306 218	0.447 532	0.257 401	26.4452	0.618 056
7	0.790 186	0.309 221	0.456 867	0.266 433	28.8097	0.602 041
8	0.792 884	0.312 788	0.465 426	0.274 459	30.7692	0.589 844
12	0.801 743	0.326 953	0.491 182	0.297 832	35.5316	0.560 764
∞	0.832 938	0.396 400	0.571 429	0.369 214	40.6160	0.500 000

Table 7. Shape and Size Parameters for 2D *f*-Long-Arm Regular Combs

	$\beta = 1/5$			$\beta = 5$		
f	δ_1	$<A>$	g	δ_1	$<A>$	g
2	0.820 712	0.373 971	0.895 833	0.820 712	0.373 971	0.895 833
3	0.778 462	0.309 424	0.722 222	0.822 913	0.375 425	0.870 370
4	0.750 818	0.263 215	0.609 375	0.824 971	0.378 564	0.859 375
5	0.733 149	0.232 489	0.533 333	0.826 421	0.381 220	0.853 333
6	0.721 923	0.212 197	0.479 167	0.827 451	0.383 289	0.849 537
7	0.714 960	0.198 846	0.438 776	0.828 210	0.384 901	0.846 939
8	0.710 880	0.190 194	0.407 552	0.828 789	0.386 178	0.845 052
12	0.709 245	0.179 904	0.331 597	0.830 161	0.389 358	0.840 856
15	0.714 304	0.183 363	0.300 000	0.830 715	0.390 701	0.839 259
∞	0.832 938	0.396 400	0.166 667	0.832 938	0.396 400	0.833 333

Table 8. Shape and Size Parameters for 2D 6-Long-Arm Regular Combs

β	δ_1	$<A>$	δ	σ_1	σ_1/σ_2	g
0	0.706 136	0.191 354	0.212 291	0.077 030	4.781 19	0.444 444
1/3	0.721 923	0.212 197	0.254 751	0.105 531	7.072 15	0.479 167
1/2	0.737 303	0.232 402	0.299 517	0.138 109	10.2529	0.505 208
1	0.787 465	0.306 218	0.447 532	0.257 401	26.4452	0.618 056
2	0.812 582	0.351 586	0.517 833	0.319 698	35.7204	0.722 222
3	0.821 290	0.369 565	0.541 198	0.341 120	38.2952	0.782 986
4	0.825 283	0.378 348	0.551 706	0.350 849	39.2630	0.822 222
5	0.827 451	0.383 289	0.557 354	0.356 098	39.7191	0.849 537
8	0.830 232	0.389 822	0.564 528	0.362 779	40.2208	0.897 119
12	0.831 452	0.392 765	0.567 649	0.365 688	40.4078	0.927 679
∞	0.832 938	0.396 400	0.571 429	0.369 214	40.6160	1.000 000

6 that as f increases from 1 to ∞, the shrinking factor decreases monotonously from 1 to 1/2 which corresponds to the size of a large ring, while the shape parameters begin with the values for chains, then reach minima around $f = 4$, and finally fall back to the values for chains. Contrary to the end-linked chains (irregular stars, dumbbells, and multiblock chains) discussed before, here we see a "minimum shape asymmetry" effect in regularly branched chains (regular combs). For $f = 6$, we find $g = 89/144 \cong 0.618\,056$, which is very close to the value for the same comb with $m = n = 20$, i.e., $8\,717\,280/241^3 \cong 0.622\,773$ first obtained by Šolc.[43]

For large 2D f-arm regular combs with unequal length arms and spacers, e.g., $\beta = 1/5$ or 5, we see from Table 7 that as f increases from 2 to ∞, only those combs with arms longer than spacers ($\beta = 1/5$) show the "minimum shape asymmetry" effect (around $f = 12$) and the shrinking factor decreases monotonously and that although the shapes of regular combs with $\beta = 1/5$ or 5 reach those of linear chains at $f = \infty$, their sizes do not, with g taking its maximum value of 1/6 or 5/6 (these values may also be obtained by use of Šolc's analytic results[43] for g at $f = \infty$). For a large 6-arm regular comb in two dimensions, it is seen from Table 8 that as β increases from 0 to ∞, its shape and size parameters all increase monotonously from values for 6-arm regular stars to those for linear chains, and hence, no "minimum shape asymmetry" effect occurs in this case.

In conclusion, the shapes and sizes of large regular combs and both regular and irregular stars with infinitely long arms in two dimensions have been both analytically and numerically investigated in terms of shape factors, shape variance factors, asphericity parameter and factor, and shrinking factor. It is found that for f-arm regular stars, both shape asymmetry and shrinking factor decrease as f increases. Similar dependences of them on f are found for a special class of f-arm irregular stars each with its jth arm chain j times as long as its shortest arm. For an irregular star with its f arm chains having two or three length types, the well-known "maximum shape asymmetry" effect is found to occur for the chain end-linked with two or more shorter chains. For large f-arm combs with both equal and unequal length arms and spacers, a "minimum shape asymmetry" effect appears for certain values of f, while the shrinking factor decreases with increasing f or, for fixed f, increases with increasing length of the spacer relative to the arm. The large shape asymmetry of the end-linked chains studied in this paper may have important implications for improving rheological and other shape-dependent properties of the existing linear macromolecules confined to surfaces or interfaces, and it is, therefore, highly desired that this finding can also be verified for excluded-volume (Edwards or Lennard–Jones model) end-linked chains confined to a plane and, through experiments, for real end-linked linear macromolecules in two dimensions. The remaining question as to whether the conclusions drawn here apply also to 3D stars and combs will be addressed in the paper immediately following this one.

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References and Notes

(1) Kuhn, W. *Kolloid Z.* **1934**, *68*, 2.
(2) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 306.
(3) Edwards, S. F. *Proc. Phys. Soc. (London)* **1965**, *85*, 613.
(4) Koyama, R. *J. Phys. Soc. Jpn.* **1968**, *24*, 580.
(5) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.
(6) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(7) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(8) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 335.
(9) Mazur, J.; Guttman, C. M.; McCrackin, F. L. *Macromolecules* **1973**, *6*, 872.
(10) Šolc, K.; Gobush, W. *Macromolecules* **1974**, *7*, 814.
(11) deGennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(12) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.
(13) Eichinger, B. E. *Macromolecules* **1985**, *18*, 211.
(14) Yang, Y.; Yu, T. *Makromol. Chem.* **1985**, *187*, 441.
(15) Theodorou, D. N.; Suter, U. W. *Macromolecules* **1985**, *18*, 1206.
(16) Oono, Y. *Adv. Chem. Phys.* **1985**, *61*, 301.
(17) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(18) Aronovitz, J. A.; Nelson, D. R. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 1445.
(19) Shy, L. Y.; Eichinger, B. E. *Macromolecules* **1986**, *19*, 838.
(20) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987.
(21) Rudnick, J.; Gaspari, G. *Science* **1987**, *237*, 384.
(22) Diehl, H. W.; Eisenriegler, E. *J. Phys. A: Math. Gen.* **1989**, *22*, L87.
(23) Yang, Y. *Makromol. Chem.* **1989**, *190*, 2833.
(24) des Cloizeaux, J.; Jannink, G. *Polymers in Solution: Their Modelling and Structure*; Oxford University Press: Oxford, 1990.
(25) Wei, G. Y.; Eichinger, B. E. *Macromolecules* **1990**, *23*, 4845.
(26) Wei, G. Y.; Eichinger, B. E. *J. Chem. Phys.* **1990**, *93*, 1430.
(27) Wei, G. Y.; Eichinger, B. E. *Comput. Polym. Sci.* **1991**, *1*, 41.
(28) Jagodzinski, O.; Eisenriegler, E.; Kremer, K. *J. Phys. I* **1992**, *2*, 2243.
(29) Wei, G. Y.; Eichinger, B. E. *Ann. Inst. Statist. Math. (Tokyo)* **1993**, *45*, 467.
(30) Eichinger, B. E. *Polym. Preprints*; American Chemical Society: Washington, DC, 1994; p 114.
(31) Jagodzinski, O. *J. Phys. A: Math. Gen.* **1994**, *27*, 1471.
(32) Liverpool, T. B.; Edwards, S. F. *J. Chem. Phys.* **1995**, *103*, 6716.
(33) Wei, G. Y. The First Conference for Worldwide Young Chinese Chemists and The Third National Conference of China for Young Chemists, Beijing, China, 1995; Preprints, p 103.
(34) Wei, G. Y.; Wang, D.; Wang, Y. International Microsymposium on Polymer Physics, Xi'an, China, 1995; Preprints, p 38.
(35) Wei, G. Y. The First East-Asian Polymer Conference, Shanghai, China, 1995; Preprints, p 28.
(36) Wei, G. Y. *Polym. Preprints (Beijing)*; CCS: Guangzhou, China, 1995; p 1137.
(37) Wei, G. Y. *Chin. J. Polym. Sci.* **1995**, *13*, 204.
(38) Wei, G. Y. *Physica A* **1995**, *222*, 152.
(39) Wei, G. Y. *Physica A* **1995**, *222*, 155.
(40) Wei, G. Y. IUPAC International Symposium on Macromolecular Condensed State, Beijing, China, 1996; Preprints, p 93.
(41) Wei, G. Y. *Polym. Adv. Tech.*, in press.
(42) Bishop, M.; Clarke, J. H. R.; Rey, A.; Freire, J. J. *J. Chem. Phys.* **1991**, *94*, 608.
(43) Šolc, K. *Macromolecules* **1973**, *6*, 378.
(44) Yang, Y.; Yu, T. *Makromol. Chem.* **1985**, *186*, 513.
(45) Yang, Y.; Yu, T. *Makromol. Chem.* **1985**, *186*, 609.
(46) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(47) Gradshteyn, I. S.; Ryzhik, I. M. *Tables of Integrals, Series, and Products*; Academic Press: New York, 1965.

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