2130 Macromolecules **1997,** *30,* 2130−2134

Shapes and Sizes of Gaussian Macromolecules. 2. Stars and Combs in Three Dimensions

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Received July 9, 1996; Revised Manuscript Received October 29, 1996[⊗]

ABSTRACT: The shapes and sizes of star- and comblike macromolecules in the framework of Gaussian models have been analytically and numerically investigated in terms of shape factors (approximately), asphericity and prolateness parameters and factors, and shrinking factor. It is found that the general size and shape features of these macromolecules persist from two dimensions to three. For regular stars and a special class of irregular stars with f infinitely long arms, both shape asymmetry and shrinking factor decrease as the number f of arms increases from 2 to 12 with perfect symmetry and zero shrinking factor at $f = \infty$. For a large irregular star whose arms have two or three different lengths, the well-known "maximum shape asymmetry" effect, i.e., having greater values of the largest shape factor and asphericity or prolateness 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 regular combs with both equal and unequal length arms and spacers, a "minimum shape asymmetry" effect appears for certain values of f. The large shape asymmetry of the end-linked chains in three dimensions may have important implications for improving rheological and other shape-dependent properties of the existing linear macromolecules, and it is, therefore, highly desired that this finding can also be verified for excluded-volume or rotational isomeric state models of end-linked chains and, through experiments, for real end-linked linear macomolecules.

Introduction

Many theoretical analyses[1−30] and computer simulations[31−42] of the configurational properties of regular stars in three dimensions have been carried out in the past. However, shapes of regular combs and H-combs in three dimensions (3D) have been only slightly studied,[4,5,19,38−40] while those of 3D irregular stars have not yet been investigated at all. As is well known,[22] exact evaluations of shape factors δ_i ($i = 1, 2, 3$), i.e., the averaged principal components of shape or gyration tensor **S** divided by mean square radius of gyration $\langle s^2\rangle$, for 3D Gaussian or Edwards or Flory macromolecules have encountered great difficulties. We therefore focus our study here on approximate calculations of shape factors for regular combs and both regular and irregular stars by use of the general approximation method recently developed by us,[22] which generalizes the Koyama−Yang−Yu method[12,13,43] to arbitrary space dimensionality and an arbitrary architectural type of Gaussian, Edwards, Flory, and any other reasonable model of macromolecules. The asphericity and prolateness parameters and factors will, however, be calculated exactly here for the above-mentioned two types of macromolecules.

As in our previous study[44] of the exact shapes and sizes of 2D irregular stars and regular combs, the general theoretical background is first presented. Numerical results are then given, and finally, the results obtained are discussed and some conclusions are drawn from the discussion.

Theory

It is well known that exact analytic evaluations of shape factors for any model of macromolecules in three dimensions are extremely difficult in spite of the fact that the 3D shape distribution function for any Gaussian macromolecule has been explicitly formulated in complete generality[9,17,18] and numerically evaluated and graphically represented for chains and rings of finite lengths.[17,45−47] Recently, we have presented a general formalism for approximately evaluating shape factors δ_i ($i = 1, 2, ..., d$) for any model of macromolecules in any d-dimensional space.[22] For $d = 2$, for example, one has for the larger shape factor,

$$\delta_1 \cong [1 + (1 - 4a_1)^{1/2}]/2 \tag{1}$$

where $a_1 = \langle S_1S_2\rangle/\langle s^2\rangle^2$ and s is the radius of gyration or $s^2 = \mathrm{tr}(\mathbf{S}) = S_1 + S_2$ with the S_i ($i = 1, 2, ..., d$) denoting the d eigenvalues or principal components of the shape or gyration tensor **S** of an N-bead macromolecule in d dimensions. For Gaussian macromolecules in particular, one has $\delta_1 \cong [1 + \mu_{2,N}{}^{1/2}(0)]/2$ with $\mu_{m,N}(x)$ defined in ref 44. In the case of $d = 3$, we have

$$\delta_k \cong [1 + 2a_2 \cos(\theta_k/3)]/3 \tag{2}$$

where $\delta_1 = 1 - \delta_2 - \delta_3 \in [1/3,1]$, $\theta_k = 2(k - 1)\pi + \varphi$, $a_2 = (1 - 3a_3)^{1/2}$, $\cos\varphi = [1 + 9(3a_4 - a_3)/2]/a_2{}^3$, $a_3 = \langle S_1S_2+S_2S_3+S_1S_3\rangle/\langle s^2\rangle^2$ with $s^2 = \mathrm{tr}(\mathbf{S}) = S_1 + S_2 + S_3$, and $a_4 = \langle S_1S_2S_3\rangle/\langle s^2\rangle^3$. For the special case of Gaussian macromolecules, we find that $a_2 = \mu_{2,N}{}^{1/2}(0)$, $\cos\varphi = \mu_{3,N}(0)/\mu_{2,N}{}^{3/2}(0)$, and the δ_k are also approximately the three real roots of the following polynomial:

$$W_3(x) = x^3 - x^2 + \gamma_1 x/3 - \gamma_2/27 \tag{3}$$

where $\gamma_1 = 1 - \mu_{2,N}(0)$ and $\gamma_2 = 1 - 3\mu_{2,N}(0) + 2\mu_{3,N}(0)$. We note that eqs 1−3 have been used to obtain approximate shape factors for both Gaussian and Edwards chains, i.e., random walks (RW's) and self-avoiding walks (SAW's),[21,22] rings and end-looped chains,[21,22] H-combs,[19] regular stars and starbursts,[20] rooted Cayley trees,[48] linear and circular multiple rings or twisted random walks,[49,50] and di- and triblock copolymer molecules.[51]

For asphericity parameter $\langle A\rangle$ and prolateness parameter $\langle P\rangle$, where $A = (3/2)\ \mathrm{tr}(\Delta^2)/s^4 \in [0,1]$ with $\Delta = \mathbf{S} - (s^2/3)\mathbf{U}$ and **U** being a $d \times d$ unit matrix and $P = (9/2)\ \mathrm{tr}(\Delta^3)/s^6 \in [-1/8,1]$ with the interval $[-1/8,0]$ or $[0, 1]$ corresponding to oblate or

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

Table 1. Shape Parameters for 3D Regular Stars with *f* Infinitely Long Arms

f	δ_1	δ_1/δ_3	$\langle A\rangle$	δ	$\langle P\rangle$	ζ
2	0.750 384	10.554 7	0.394 274	0.526 316	0.237 475	0.443 740
3	0.655 530	7.153 38	0.304 419	0.360 885	0.142 948	0.208 127
4	0.603 928	5.121 11	0.242 690	0.273 159	0.092 058	0.120 069
5	0.570 695	4.134 54	0.200 616	0.219 503	0.063 579	0.078 010
6	0.547 095	3.562 67	0.170 595	0.183 398	0.046 354	0.054 722
7	0.529 255	3.189 49	0.148 235	0.157 467	0.035 223	0.040 495
8	0.515 174	2.925 98	0.130 984	0.137 949	0.027 643	0.031 173
12	0.478 935	2.352 87	0.089 219	0.092 202	0.012 990	0.014 033
∞	0.333 333	1.000 00	0.000 000	0.000 000	0.000 000	0.000 000

Table 2. Shape Parameters for 3D *f*-Long-Arm Irregular Stars with $n_i = in_1$

f	δ_1	δ_1/δ_3	$\langle A\rangle$	δ	$\langle P\rangle$	ζ
2	0.750 384	10.554 7	0.394 274	0.526 316	0.237 475	0.443 740
3	0.705 113	8.288 76	0.340 445	0.442 575	0.183 310	0.335 843
4	0.663 956	6.733 75	0.295 487	0.369 812	0.141 488	0.242 651
5	0.632 069	5.639 07	0.259 506	0.315 063	0.111 318	0.179 971
6	0.607 174	4.885 79	0.230 745	0.273 605	0.089 494	0.137 777
7	0.587 249	4.350 53	0.207 460	0.241 447	0.073 375	0.108 486
8	0.570 914	3.954 83	0.188 312	0.215 891	0.061 192	0.087 474
12	0.526 753	3.058 75	0.137 297	0.151 291	0.033 669	0.043 842
∞	0.333 333	1.000 00	0.000 000	0.000 000	0.000 000	0.000 000

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

type	δ_1	δ_1/δ_3	$\langle A\rangle$	δ	$\langle P\rangle$	ζ
1	0.625 380	5.163 64	0.237 415	0.300 654	0.102 684	0.176 760
2	0.594 710	4.566 41	0.217 235	0.253 744	0.079 628	0.118 039
3	0.503 883	2.705 08	0.114 371	0.121 914	0.022 634	0.026 644

prolate asymmetric ellipsoids, we have[22]

$$\langle A\rangle = (15/2)\int_0^\infty x^3 S_{2,N}(x)\, D_N^{-3/2}(x)\, \mathrm{d}x \qquad (4)$$

and

$$\langle P\rangle = (105/8)\int_0^\infty x^5 S_{3,N}(x)\, D_N^{-3/2}(x)\, \mathrm{d}x \qquad (5)$$

where $S_{m,N}(x)$ and $D_N(x)$ are the same as defined in ref 44. Similarly, for asphericity factor $\delta \equiv (3/2)\langle \mathrm{tr}(\Delta^2)\rangle/\langle s^4\rangle \in [0,1]$ and prolateness factor $\zeta \equiv (9/2)\langle \mathrm{tr}(\Delta^3)\rangle/\langle s^6\rangle \in [-1/8,1]$, one can write

$$\delta = 5/[2 + 3/\mu_{2,N}(0)] \qquad (6)$$

and

$$\zeta = 35/\{8 + 9[1 + 2\mu_{2,N}(0)]/\mu_{3,N}(0)\} \qquad (7)$$

by use of the Wei–Eichinger method.[16] Again, all that is needed in characterizing mathematically the shapes and sizes of 3D Gaussian macromolecules is the function $D_N(x)$ or $D(x) \equiv D_\infty(x)$ as in the 2D case.

Numerical Results

Irregular Stars. For the large irregular star or irregular-star-branched random walk described in ref 44, the analytic expressions for $S_m(0)$ are found to be,

$$S_1(0) = (3\nu_2 - 2\nu_3)/6 \qquad (8)$$

$$S_2(0) = (10\nu_3^{\,2} + 15\nu_4 - 24\nu_5)/90 \qquad (9)$$

$$S_3(0) = -(35\nu_3^{\,3} - 126\nu_3\nu_5 - 63\nu_6 + 153\nu_7)/945 \qquad (10)$$

and

$$S_4(0) = (350\nu_3^{\,4} - 1680\nu_3^{\,2}\nu_5 + 1008\nu_5^{\,2} + 2040\nu_3\nu_7 + 765\nu_8 - 2480\nu_9)/28350 \qquad (11)$$

which reproduce the results for $m \le 3$ first obtained by Solc.[5] Here, $\nu_k = (N-1)^{-k}\sum_{1\le i\le f} n_i^{\,k}$, which becomes f^{1-k} for regular stars for which $S_m(0)$ takes the following simple forms:

$$S_m(0) = \begin{cases} (3f-2)/(6f^2) & (m=1) \\ (15f-14)/(90f^4) & (m=2) \\ (63f-62)/(945f^6) & (m=3) \\ (255f-254)/(9450f^8) & (m=4) \end{cases} \qquad (12)$$

Use of eqs 2–12, together with the analytic expressions for $D(x)$ and $S_m(x)$ given in ref 44, allows the shape parameters δ_1, δ_1/δ_3, $\langle A\rangle$, δ, $\langle P\rangle$, and ζ to be both analytically and numerically evaluated for both regular and irregular stars (the shrinking factor takes the same values as in the 2D analogues). The results are summarized in Tables 1–5.

Regular Combs. For the large regular comb or regular-comb-branched random walk defined in ref 44, we find the following analytic expressions for $S_m(0)$:

$$S_1(0) = [f^2 + (f-1)\lambda(3\lambda - f - 1)]/(6f^2) \qquad (13)$$

$$S_2(0) = \{2f^4 + \lambda(f^2-1)[10\lambda^2 + (2f^2+7)\lambda - 4(f^2+1)] - 15\lambda^4(f-1)^2\}/(180f^4) \qquad (14)$$

$$S_3(0) = \{8f^6 + 24\lambda(1-f^6) + \lambda^2(f^2-1)[3(8f^4 + 15f^2 + 22) - \lambda(8f^4 - 13f^2 + 29) - 105\lambda^3(f^2-1) + 63\lambda^2(f^2+3)] - 63\lambda^6(f-1)(5f-3)\}/(7560f^6) \qquad (15)$$

and

$$S_4(0) = \{24f^8 + 96\lambda(1-f^8) + \lambda^2(f^2-1)[88(18f^6 + 28f^4 + 35f^2 + 45) - 8\lambda(12f^6 + 12f^4 + 33f^2 + 63) + \lambda^2(24f^6 - 456f^4 + 251f^2 + 1081) + 4\lambda^3(160f^4 + 139f^2 - 71) - 2\lambda^4(120f^6 + 743f^4 - 1007) + 20\lambda^5(21f^2 + 75) + 5\lambda^8(f-1)(63f^3 + 63f^2 - 819f + 405)]\}/(226800f^8) \qquad (16)$$

where $\lambda = r_1 = 1/(1+\beta)$. We note that eqs 13–15 reproduce the Solc's results[5] which give the following analytic expressions for evaluating the shrinking factor for regular combs with finite n and m:

$$g = N^{-3}(N-1)\{2 + n(m-2n) + 3f[m + n(n+1)] + f^2 m(m+n)\} \qquad (17)$$

For the special case of $\lambda = 1/2 (\beta = 1)$, we find

$$S_1(0) = (2f^2 + 3f - 1)/(24f^2) \qquad (18)$$

$$S_2(0) = (8f^4 + 25f^2 + 30f - 31)/(2880f^4) \qquad (19)$$

$$S_3(0) = (64f^6 + 210f^4 + 777f^2 + 504f - 1043)/(483840f^6) \qquad (20)$$

Table 4. Shape Parameters for 3D 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	δ_1/δ_3	$\langle P\rangle$	δ_1	δ_1/δ_3	$\langle P\rangle$	δ_1	δ_1/δ_3	$\langle P\rangle$
0	0.570 695	4.134 54	0.063 579	0.603 928	5.121 11	0.092 058	0.655 530	7.153 38	0.142 948
1/5	0.567 564	4.041 57	0.061 051	0.594 463	4.766 29	0.082 856	0.631 315	5.913 05	0.115 382
1/3	0.563 774	3.935 18	0.058 069	0.584 190	4.428 05	0.073 589	0.609 244	5.054 41	0.093 315
1	0.547 095	3.562 67	0.046 354	0.547 095	3.562 67	0.046 354	0.547 095	3.562 67	0.046 354
2	0.592 973	4.271 67	0.073 818	0.592 724	4.417 98	0.076 428	0.582 390	4.279 13	0.070 446
3	0.657 323	5.507 69	0.122 519	0.638 317	5.646 84	0.114 659	0.609 244	5.054 41	0.093 315
4	0.700 605	6.704 68	0.164 692	0.665 747	6.648 67	0.141 804	0.623 273	5.572 35	0.106 985
5	0.727 065	7.761 13	0.195 621	0.682 884	7.388 77	0.160 184	0.631 315	5.913 05	0.115 382
8	0.759 422	9.951 05	0.241 921	0.708 624	8.629 30	0.189 229	0.642 237	6.433 64	0.127 435
12	0.767 738	11.16 94	0.258 093	0.722 666	9.319 56	0.205 384	0.647 462	6.707 07	0.133 448
99	0.752 248	10.73 15	0.240 384	0.746 992	10.40 96	0.233 461	0.654 742	7.109 24	0.142 016
∞	0.750 384	10.55 47	0.237 475	0.750 384	10.55 47	0.237 475	0.655 530	7.153 38	0.142 948

Table 5. Shape Parameters for 3D 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	δ_1/δ_3	$\langle P\rangle$	δ_1	δ_1/δ_3	$\langle P\rangle$	δ_1	δ_1/δ_3	$\langle P\rangle$
1	0.655 530	7.153 38	0.142 948	0.684 914	7.801 66	0.165 648	0.707 408	8.508 07	0.187 036
2	0.693 277	7.836 45	0.170 980	0.722 954	8.777 28	0.200 680	0.734 378	9.376 35	0.214 843
3	0.725 155	8.665 17	0.201 349	0.742 411	9.566 69	0.223 082	0.747 113	9.984 76	0.230 400
4	0.740 855	9.343 03	0.219 954	0.750 186	10.089 6	0.233 908	0.751 855	10.349 1	0.237 308
5	0.748 494	9.844 69	0.230 558	0.753 290	10.404 2	0.239 009	0.753 548	10.550 2	0.240 284
6	0.752 274	10.191 5	0.236 545	0.754 459	10.584 7	0.241 366	0.754 043	10.656 2	0.241 488
7	0.754 133	10.422 5	0.239 915	0.754 787	10.685 1	0.242 376	0.754 052	10.709 4	0.241 872
8	0.754 996	10.573 3	0.241 782	0.754 741	10.738 7	0.242 711	0.753 866	10.733 4	0.241 874
12	0.755 071	10.789 5	0.243 374	0.753 696	10.771 2	0.241 988	0.752 846	10.726 8	0.240 905
99	0.750 603	10.576 6	0.237 824	0.750 497	10.566 3	0.237 657	0.750 460	10.562 6	0.237 598
∞	0.750 384	10.554 7	0.237 475	0.750 384	10.554 7	0.237 475	0.750 384	10.554 7	0.237 475

$$S_4(0) = (384f^8 + 1600f^6 + 5019f^4 + 15750f^2 + 6120f - 22729)/(58060800f^8) \quad (21)$$

$$S_5(0) = (15360f^{10} + 79200f^8 + 277860f^6 + 673409f^4 + 2314070f^2 + 491040f - 3359419)/(45984153600f^{10}) \quad (22)$$

and

$$S_6(0) = f^{-12}\{\sum_{1\le j\le 6}\gamma_j \sum_{1\le k\le[(f-1)/2]} \sin(\pi k/f)^{-2j} + (f/2 - 1)\gamma_7 + \gamma_8\} \quad (23)$$

where $\gamma_1 = -10\,931/638\,668\,800$, $\gamma_2 = 1613/309\,657\,600$, $\gamma_3 = -91\,177/123\,863\,040$, $\gamma_4 = 1831/245\,760$, $\gamma_5 = -11/512$, $\gamma_6 = 1/64$, $\gamma_7 = 691/319\,334\,400$, and $\gamma_8 = 70\,910\,984\,779/167\,382\,319\,104\,000$.

As in the case of 3D irregular stars, eqs 13−23, together with the analytic expressions for $D(x)$ and $S_m(x)$ given in ref 44, permit the shape parameters δ_1, δ_1/δ_3, $\langle A\rangle$, δ, $\langle P\rangle$ and ζ to be both analytically and numerically evaluated for regular combs (the shrinking factor takes the same values as in the 2D analogues). The results are presented in Tables 6−8.

Table 6. Shape Parameters for 3D f-Long-Arm Regular Combs with $\beta = m/n = 1$

f	δ_1	δ_1/δ_3	$\langle A\rangle$	δ	$\langle P\rangle$	ζ
1	0.750 384	10.554 7	0.394 274	0.526 316	0.237 475	0.443 740
2	0.693 277	7.836 45	0.328 510	0.421 450	0.170 980	0.307 800
3	0.675 324	6.921 60	0.303 169	0.388 204	0.149 889	0.271 816
4	0.675 518	6.636 82	0.295 931	0.386 632	0.146 651	0.278 236
5	0.680 187	6.615 44	0.296 065	0.393 813	0.149 354	0.291 975
6	0.685 627	6.699 18	0.299 180	0.403 003	0.153 904	0.305 747
7	0.690 801	6.825 58	0.303 416	0.412 102	0.158 835	0.318 026
8	0.695 449	6.967 45	0.307 952	0.420 472	0.163 612	0.328 653
10	0.709 101	7.516 87	0.324 302	0.445 815	0.179 106	0.358 556
∞	0.750 384	10.554 7	0.394 274	0.526 316	0.237 475	0.443 740

Table 7. Shape Parameters for f-Long-Arm Regular Combs in Three Dimensions

	$\beta = 1/5$			$\beta = 5$		
f	δ_1	δ_1/δ_3	$\langle P\rangle$	δ_1	δ_1/δ_3	$\langle P\rangle$
2	0.730 038	9.462 37	0.212 120	0.730 038	9.462 37	0.212 120
3	0.650 125	6.725 30	0.134 818	0.735 814	9.468 73	0.216 807
4	0.609 269	5.160 89	0.094 574	0.739 396	9.634 18	0.221 106
5	0.586 980	4.418 89	0.073 896	0.741 625	9.775 89	0.224 107
6	0.574 960	4.027 90	0.063 146	0.743 119	9.885 03	0.226 229
7	0.569 090	3.811 04	0.057 751	0.744 184	9.969 20	0.227 788
8	0.567 044	3.691 19	0.055 423	0.744 980	10.035 3	0.228 975
12	0.575 548	3.625 81	0.058 900	0.746 818	10.198 5	0.231 784
15	0.587 206	3.741 25	0.065 990	0.747 545	10.266 8	0.232 919
∞	0.750 384	10.554 7	0.237 475	0.750 384	10.554 7	0.237 475

Discussion and Conclusion

For 3D regular stars with f infinitely long arms, it can be seen from Table 1 that shape asymmetry decreases as f increases from 2 to 12, with perfect symmetry (spheres) at $f = \infty$. It is also seen that our exact results for $\langle A\rangle$ for $f = 2-6$ confirm Jagodzinski's earlier results,[30] and those for both $\langle A\rangle$ and other shape parameters indicate a good accuracy in the simulation results of Solc[5] for δ_α ($n \le 80$ and $f \le 8$, see also refs 12 and 13 for a comparison with approximate analytic results for finite n), Cannon et al.[35] for $\langle A\rangle$, δ, $\langle P\rangle$, and ζ ($n = 31$ and $\langle P\rangle$ or $\zeta = 0.240$ or 0.448, 0.137 or 0.192, and 0.090 or 0.114 for $f = 2$, 3, and 4, respectively), Bishop et al.[36] for $\langle A\rangle$ and δ ($f = 2-6$ and extrapolated), and Zifferer[42] for $\langle A\rangle$, δ, and δ_α ($f \le 96$ and extrapolated). For δ_1 in particular, our approximate results are in good agreement with the simulation results of Solc[5] ($\delta_1 =$ 0.656, 0.604, 0.547, and 0.516 for $f = 3$, 4, 6, and 8, respectively) and Zifferer[42] ($\delta_1 = 0.7646$, 0.6905, 0.6416, 0.5826, 0.5475, and 0.5063 for $f = 2$, 3, 4, 6, 8, and 12, respectively).

For 3D 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 asymmetry on f. Table 3 shows the effects of the architecture of 3D irregular stars on shape parameters. We note that for

Table 8. Shape Parameters for 6-Long-Arm Regular Combs in Three Dimensions

β	δ_1	δ_1/δ_3	$\langle A\rangle$	δ	$\langle P\rangle$	ζ
0	0.547 095	3.562 67	0.170 595	0.183 398	0.046 354	0.054 722
1/5	0.574 960	4.027 90	0.193 304	0.221 706	0.063 146	0.093 469
1/3	0.602 692	4.527 88	0.216 061	0.262 712	0.081 674	0.140 118
1	0.685 627	6.699 18	0.299 180	0.403 003	0.153 904	0.305 747
2	0.722 613	8.428 41	0.348 359	0.472 288	0.197 505	0.384 907
3	0.734 755	9.227 23	0.367 165	0.495 712	0.214 033	0.410 820
4	0.740 198	9.643 35	0.376 175	0.506 311	0.221 887	0.422 363
5	0.743 119	9.885 03	0.381 186	0.512 025	0.226 229	0.428 531
8	0.746 825	10.213 1	0.387 743	0.519 300	0.231 879	0.436 317
12	0.748 436	10.364 2	0.390 671	0.522 471	0.234 388	0.439 684
∞	0.750 384	10.554 7	0.394 274	0.526 316	0.237 475	0.443 740

the large 3D 10-arm irregular star with two long and eight short branches (type 1), which was first studied by Zimm and Kilb[2] and later reinvestigated by Yang and Yu,[11] we have obtained an exact analytic result[44] for its shrinking factor, i.e., $g = 103/256 \cong 0.402\ 344$, and given in Table 3 are the first numerical results for its shape factors and asphericity and prolateness parameters and factors. For a large 3D 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 is for the second, it is seen from Table 4 that as β ($\equiv n_1/n_2$) increases from 0 to 1, the shape 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 show maxima around $\beta = 12$ and at $\beta = 12$ are 0.767 738 for δ_1 and 0.258 093 for $\langle P\rangle$, all greater than the corresponding values for linear chains. This "maximum shape asymmetry" effect appears also in the chain end-linked with shorter loops[22] or both shorter and heavier chains, i.e., di- or triblock copolymers.[51] Finally, for a large 3D 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 ∞, shape asymmetry shows maxima around $\beta = 7$ 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 previously discussed.

For large 3D f-arm regular combs with equal length arms and spacers ($\beta = m/n = 1$), it is seen from Table 6 that as f increases from 1 to ∞, 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 $f = 6$, our approximate result for δ_1 or $\langle S_1\rangle:\langle S_2\rangle:\langle S_3\rangle$, ie., 0.685 627 or 6.699 18:2.071 71:1, is very close to the Monte Carlo result of Solc[5] for $m = n = 20$ (0.698 or 7.42:2.21:1).

For large 3D f-arm regular combs with unequal length arms and spacers, e.g., $\beta = 1/5$ or 5, that is, with arms 5 or 1/5 times as long as spacers, 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 $f = 8$) and that although the shapes of regular combs with $\beta = 1/5$ or 5 reach those of linear chains at $f = \infty$, their sizes[44] do not, with g taking its maximum value of 1/6 or 5/6 (these values may also be obtained by use of Solc's analytic results[5] for g at $f = \infty$). For a large regular comb with six infinitely long arms in three dimensions, it is seen from Table 8 that as β increases from 0 to ∞, its shape 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 as in the 2D case.

To conclude, the shapes and sizes of large regular combs and both regular and irregular stars with infinitely long arms in three dimensions have been both analytically and numerically investigated in terms of shape factors (approximately), asphericity and prolateness parameters and factors, and shrinking factor which is the same as in the 2D case. It is found that the general size and shape features of these macromolecules persist from two dimensions to three. For large f-arm regular stars, both shape asymmetry and shrinking factor decrease as f increases. Similar dependences of the shape and size parameters on f are found for a special class of large f-arm irregular stars each with its jth arm chain j times as long as its shortest arm. For a large 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 as in the 2D case. The large shape asymmetry of the end-linked chains in three dimensions may have important implications for improving rheological and other shape-dependent properties of the existing linear macromolecules, and it is, therefore, highly desired that this finding can also be verified for Edwards' or Lennard and Jones' excluded-volume or Flory's rotational isomeric state (RIS) model of end-linked chains and, through experiments, for real end-linked linear macromolecules.

Acknowledgment. This work was supported in part by the Peking University Fangzheng Excellent Young Scholar Fund and by the National Natural Science Foundation and FEYUT, SEDC, China.

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MA960991U