Unperturbed dimensions of branched chain, star and ring polymers

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A novel Monte Carlo method has been applied to the calculation of the unperturbed dimensions of various monodisperse polymers, e.g. star polymers, branched polymers formed by the crosslinking of linear primary chains, and linear chains with some intramolecular cycles. Where results for the parameters h^{-1} and g (representing the effect of branching upon the hydrodynamic radius and the radius of gyration, respectively) were known previously, agreement is good. The method can, however, be applied to furnish other statistical averages for polymers of any arbitrary branched structure, and the effects of polydispersity may also be included.

INTRODUCTION

Since 1949 when Flory[1] introduced the concept of the θ state for a polymer in dilute solution at a particular (θ) temperature, the statistics of polymers with unperturbed dimensions (i.e. with a 'Markovian' end-to-end distance distribution) have been well studied by, amongst others, Zimm and Stockmayer[2] and Kurata and Fukatsu[3]. In this paper we show how, by using equation (1), the so-called Zimm–Stockmayer[2] relationship (see also ref 4) and the Gaussian subchain approximation, a novel Monte Carlo method enables the statistics of star, branched chain and ring containing polymers to be calculated, without recourse to the unwieldy formulae which are required for polymers of specific architecture (see e.g. ref 3), and with a method in principle applicable to any distribution of molecular chain lengths (molecular weight distribution). We note here that Gupta and Forsman[5,6] have evaluated the complete distribution functions for the radius of gyration for both linear and branched molecules, although their elegant matrix graph theoretical method seems difficult to generalize to deal with the effect of polydispersity. The molecular parameters considered here are the mean unperturbed radius of gyration $\langle S^2\rangle_0$ and the unperturbed Stokes radius $\langle R_S{}^{-1}\rangle_0$. The latter is the minus first moment of segment end-to-end distributions and is related to frictional properties of polymer solutions. Some of the results obtained in this paper have been obtained before by analytic methods – the advantage offered by the Monte Carlo method is its generality and simplicity. To illustrate this, the data of Allen, Burgess, Edwards and Walsh[7] for cyclization of linear polymers is satisfactorily fitted, without the use of the sophisticated self-consistent field (*SCF*) method[8].

THEORY

The Zimm–Stockmayer formula[2,4] relates the radius of gyration of unperturbed monodisperse polymer chains to the distance between the ith and jth segments of the chains R_{ij}:

$$\langle S^2\rangle_0 = \frac{1}{2n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\langle R_{ij}^2\rangle_0 = \frac{1}{n^2}\sum\sum_{j>i}\langle R_{ij}^2\rangle_0 \qquad (1)$$

where n is the number of segments. For Gaussian subchains, (each subchain obeying random flight statistics) we have:

$$\langle R_{ij}^2\rangle_0 = |i-j|b^2 \qquad (2)$$

with b the intersegmental distance (or more generally the length of a Kuhn *statistical* segment). From equations (1) and (2):

$$\langle S^2\rangle_0 = \frac{1}{n^2}\sum_{i}^{n}\sum_{j}^{n}|i-j|b^2 \qquad (3)$$

Replacing the sums by integrals we easily obtain:

$$\langle S^2\rangle_0 = \frac{nb^2}{6} \qquad (4)$$

for a linear monodisperse chain.

Kirkwood's[9] general expression for the frictional constant of a macromolecule of n chain elements may be written:

$$\Xi_0 = (n\xi_0)^{-1} + (3\pi\eta_s n^2)^{-1}\sum\sum_{j>i}\langle R_{ij}{}^{-1}\rangle_0 \qquad (5)$$

where Ξ_0 is the frictional constant, ξ_0 the friction constant of a single chain element, and η_s the solvent viscosity. For long chains (where the effect of hydrodynamic shielding is dominant) we may neglect the term $(n\xi_0)^{-1}$, and the effective Stokes radius may be written:

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$$\langle R_s^{-1}\rangle_0 \equiv 6\pi\eta_s\Xi_0^{-1} = \frac{2}{n^2}\sum_{j>i}\sum \langle R_{ij}^{-1}\rangle_0 \qquad (6)$$

The distribution over $\langle R_{ij}^2\rangle_0$ is usually preaveraged so that we obtain from equation (2):

$$\langle R_{ij}^{-1}\rangle_0 = \frac{1}{|i-j|^{1/2}b} \qquad (7)$$

and replacing the double sum

$$\sum_{j>i}\sum$$

by integrals we find[10]:

$$\langle R_s^{-1}\rangle_0 = \left(\frac{6}{\pi}\right)^{1/2}\left(\frac{8}{3}n^{-1/2}\right) \qquad (8)$$

Equations (1), (2) and (6) may be applied to non-linear polymers when the segments are labelled in the correct order. Thus Zimm and Stockmayer[2] and Kurata and Fukatsu[3] have derived formulae for g defined by:

$$g \equiv \frac{\langle S^2\rangle_{0,br}}{\langle S^2\rangle_{0,l}} \qquad (9)$$

(when n is constant) where the subscripts *br* and *l* refer to branched and linear polymers.

Similarly, using the Ham[11] and Zimm–Kilb[12] theories various workers, e.g. Stockmayer and Fixman[13], Kurata and Fukatsu[3] and Ptitsyn[14], obtained values for the parameter h:

$$h \equiv \frac{\langle R_s^{-1}\rangle_{0,l}}{\langle R_s^{-1}\rangle_{0,br}} \qquad (10)$$

The parameters h and $g^{1/2}$ were believed to be equal but Kurata and Fukatsu showed theoretically that for their randomly branched and comb polymers the function $hg^{-1/2}$ was greater than unity. Zimm and Kilb[12] assumed that the ratio of the intrinsic viscosities of branched to linear polymers (with the same number of segments) was:

$$\frac{[\eta]_{br}}{[\eta]_l} \simeq g^{1/2} \qquad (11)$$

(in contradiction to the Flory–Fox theory[15] which predicts a $g^{3/2}$ dependence). The effect of branching on the intrinsic viscosity is thus expected to be greater than on the frictional constant.

All the above discussion is strictly valid only for constant n, i.e. monodisperse molecular weight distribution, and in the words of Flory[16] 'in seeking to observe the influence on a given physical property of the introduction of polyfunctional units into an otherwise linear polymer, the resulting broadening of the distribution is likely to be of much greater consequence than the alteration of the average dimensions of molecules of a given degree of polymerisation'. For random f-functional polycondensates the method of Dobson and Gordon[17] using Kramer's theorem[18] is useful, and using the path weighting generating function method, Kajiwara[19,20] calculated the Stokes radius for the same system. For random crosslinking of primary chains of known molecular weight distribution, Gordon and Kajiwara[21] were able to calculate $\langle S^2\rangle_0$, but because of the mathematical difficulties inherent in their method they could not obtain $\langle R_s^{-1}\rangle_0$, because of the unavoidable inversion necessary to obtain the first negative moment of the path distribution.

COMPUTATIONAL METHODS

Sampling

The computational method we have developed for the calculation of $\langle S^2\rangle_0$ is based upon equation (3), and as an illustration we consider the construction of a random star molecule of functionality, f. This macromolecule has f branches, with a total of n segments. For convenience n is chosen to be 6×10^4, and b the statistical segment is taken to be unity. This gives $\langle S^2\rangle_{0,l}$, the radius of gyration of the linear polymer molecule with the same number of segments, to be equal to $6 \times 10^4/6$ (equation 4) = 10^4 units, and g values are found directly.

The random number generator is used to produce $f-1$ integers, X_i, $i = 1,2 \ldots f-1$, in the range $1-n$. X_f is defined to have the value n. The X_i represent the $f-1$ 'cuts' to produce f sections of chain. These sections are then reassembled to form an f-functional star. The segments are numbered serially so that that particular segment with index X_k represents the segment on the kth arm of the star, which is connected to the other $f-1$ arms of the nucleus of the star. Two more integers, I and J (ordered so that $J > I$), representing the indices of the segments denoted j and i, respectively, are then selected in the same range $1 < I < J < n$, so that if e.g. $X_1 < I < X_2$, then segment i is on the second arm of the star, and the path from i to the centre of the star is X_2-I segments in length. Similarly if $X_2 < J < X_3$, the total length of the path from the segment denoted i to j is given by:

$$\langle R_{ij}^2\rangle_0 = (X_2 - I) + (X_3 - J) \qquad (12)$$

If, however, both i and j are on the same arm of the star, i.e. for example, $X_3 < I < J < X_4$, then $\langle R_{ij}^2\rangle_0$ is simply $(J - I)$. Then, writing:

$$\langle S^2\rangle_0 = \frac{1}{2n^2}\sum_I^{\text{all paths}}\sum_J \langle R_{ij}^2\rangle_0 \qquad (13)$$

we replace the double sum

$$\sum^{\text{all paths}}\sum \langle R_{ij}^2\rangle_0$$

by $n^2\langle\overline{R_{ij}{}^2}\rangle_0$, with $\langle\overline{R_{ij}{}^2}\rangle_0$ the mean value of $\langle R_{ij}^2\rangle_0$ over, say, p Monte Carlo cycles:

$$\langle\overline{R_{ij}{}^2}\rangle_0 = \frac{1}{p}\sum^{p}\langle R_{ij}^2\rangle_0 \text{ and } p \ll n^2$$

The value of $\langle S^2\rangle_0$ is then given by:

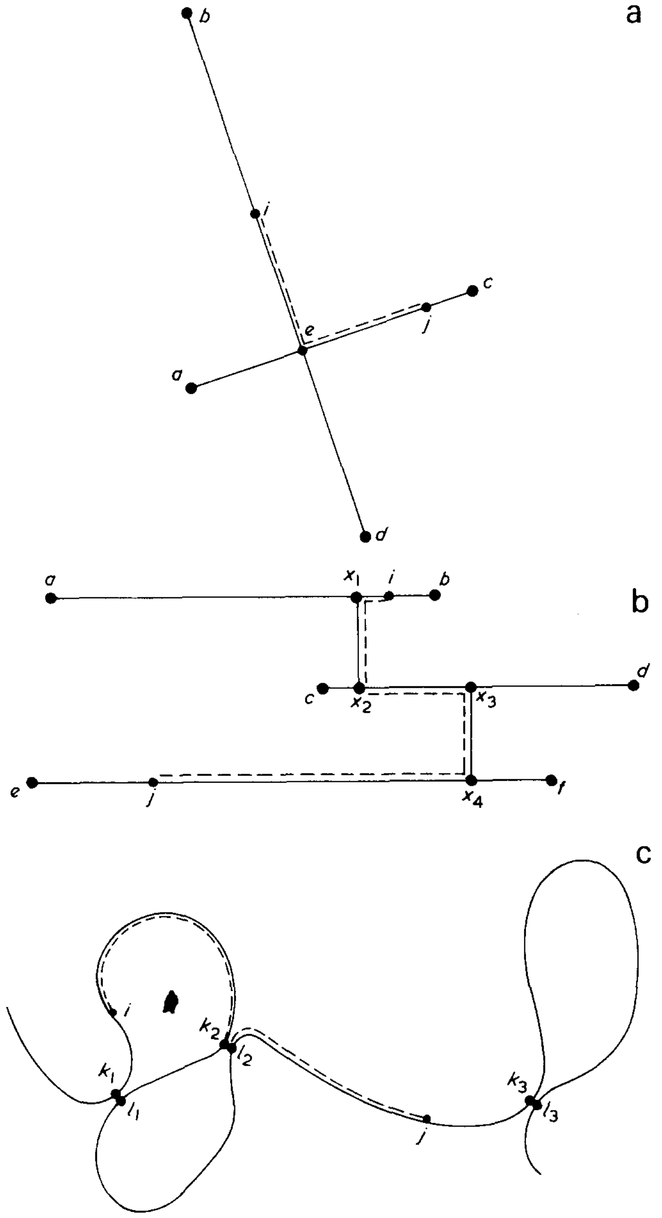

Figure 1 Graph-like representation of polymer molecules: (a) four branch random star, (b) branched polymer formed by the crosslinking of three linear polymer chains, (c) linear polymer with three intramolecular cycles. The dashed line represents a path from the segment denoted i to that denoted j. Other details as in text

$$\frac{\langle \overline{R_{ij}}^2\rangle_0}{2} = \frac{1}{2}\,\overline{|I - J|}$$

That this preaveraging is valid readily checks for a linear chain when $\overline{|I - J|} = n/3$, and $\langle S^2\rangle_0 = n/6$ as it should be.

Now p typically can be taken to be $\approx 10^4$ Monte Carlo cycles $1/M$ – the only restrictions being those on computer time, and on the convergence of $\langle R_{ij}^2\rangle_0$ – so that for the examples here the ratio $n^2/p \approx (10^7)$.

The sampling technique is thus extremely efficient, and the only problem is in correctly constructing algorithms to mirror the more complex one-dimensional topologies representing the non-uniform star, chain and ring copolymers.

Network topologies

Star branched molecules. To illustrate the construction of different networks, consider *Figure 1*. *Figure 1a* represents the star macromolecule with f (=4 in this case) branches. The four branches ae, be, ce and de consist respectively of A, B, C and D segments ($A + B + C + D = n$), and the segments are numbered serially so that if the index I of the segment denoted i is numerically $A < I < A + B$, then i is on branch be. For uniform stars, $A = B = C = D$, whereas for random* stars A, B, C and D are equal respectively to $n \times q(0,1)/(A + B + C + D)$; I and J are themselves equal to $n \times q(0,1)(I < J)$.

Crosslinked chain molecules. In *Figure 1(b)* is a typical three branch (i.e. $m = 3$) chain molecule with chains ax_1b, cx_2x_3d and ex_4f of length AB, CD and EF, respectively. For uniform branches, $AB = CD = EF$, whereas for random branching each is set equal to $n \times q(0,1)/(AB + CD + EF)$, so that $AB + CD + EF = n$. The lth crosslink x_l, $l = 1,2 \ldots 2(f - 1)$ is again generated at random so that e.g. $X_1 = AB \times q(0,1)$, and the position of segments i and j in the network are generated so that $I,J = q(0,1)(I < J)$. The unique path through the crosslinks $x_1 - x_2$ and $x_3 - x_4$ then enables the calculation of the mean square distance $\langle R_{ij}^2\rangle_0$. The length of the crosslinks $x_1 - x_2$ etc. was assumed throughout to be zero.

Cyclized linear polymers. The system of Allen *et al.*[7,8] consists of a linear polymer chain in which a small number of sites are preactivated at random along the chain. A very dilute solution of the polymer is made up, and then these preactivated sites allowed to react pairwise to form cycles. In this mechanism, for small numbers of cycles i.e. small numbers of activated sites, cyclization is assumed *not* to be governed by Gaussian statistics i.e. the probability $p(x)$ that a ring of, say, x units is formed is assumed independent of x. The normal Gaussian ring closure would give $p(x) \sim x^{-3/2}$ so that small rings are heavily favoured.

Molecules with (at least) m pairs (see ref 22) of rings were generated by selecting the segments k_r and l_r (contact pairs), which make up the rth ring, for example, and the segments i and j in the manner outlined above. Now equation (3) is only valid for tree molecules, in which there is a unique path between i and j, so we use the heuristic 'spanning tree' approximation of 'breaking' one bond in each cycle, so converting each graph into one of its spanning trees. A unique path is *constructed* by firstly tracing a path (i–i') along the beads from i in a direction chosen at random, until the first bead i' is encountered which is a member of a contact pair. Similarly a path ($j' - j$) is traced from j to the first encountered j' belonging to a contact pair. The *shortest* (of the many possible) path from i' to j' is found by a minimum path algorithm[23]. The mean square distance $\langle R_{ij}^2\rangle_0$ is then taken as that of the path (i–i')–(j'–j) (provided no bead on that path occurs more than once; otherwise the attempt is rejected). In a modification of the program which should produce an estimate of the lower bound for $\langle S^2\rangle_0$, the distances I–I' and J'–J were also the shortest possible paths.

For this system no attempt was made to calculate $\langle R_s^{-1}\rangle_0$, the approximations involved being even more gross for the reciprocal moment of the distribution $\langle R_{ij}^{-1}\rangle$. Further, the

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* In this paper we use 'random' to mean chosen at random from a block distribution under a specific constraint. This means that each arm of the star may consist of $1,2 \ldots, n - f + 1$ segments with equal probability. The constraint is that the *total* number of segments in all f arms is equal to n. This is completely different to a Flory or most probable distribution of chain lengths (sometimes called 'random'), in which the probability that a chain consists of x-mer falls asymptotically as $\exp(-x)$ for large x.

Table 1 (a) Results for *f*-functional uniform star polymer

f	$hg^{-1/2}_{\mathrm{FOUND}}$	$hg^{-1/2}_{\mathrm{CONT}}$	$\langle S^2\rangle_0$	g_{FOUND}	g_{CONT}	$\langle R_s^{-1}\rangle_0$	h^{-1}_{FOUND}	h^{-1}_{CONT}
2	1.000	1.000	1.000×10^4	1.000	1.000	1.493×10^{-2}	1.000	1.000
3	1.075	1.074	0.777×10^4	0.777	0.777	1.577×10^{-2}	1.056	1.055
4	1.128	1.127	0.626×10^4	0.626	0.625	1.674×10^{-2}	1.121	1.121
5	1.167	1.166	0.520×10^4	0.520	0.520	1.775×10^{-2}	1.189	1.188
6	1.198	1.194	0.445×10^4	0.445	0.444	1.874×10^{-2}	1.255	1.253
8	1.237	1.236	0.343×10^4	0.343	0.344	2.063×10^{-2}	1.382	1.378
10	1.264	1.262	0.280×10^4	0.280	0.280	2.236×10^{-2}	1.498	1.495

(b) Results for *f*-functional random star polymer

f	$hg^{-1/2}_{\mathrm{FOUND}}$	$hg^{-1/2}_{\mathrm{CONT}}$	$\langle S^2\rangle_0$	g_{FOUND}	g_{CONT}	$\langle R_s^{-1}\rangle_0$	h^{-1}_{FOUND}	h^{-1}_{CONT}
2	1.000	1.000	1.002×10^4	1.000	1.000	1.50×10^{-2}	1.000	1.000
3	1.026	1.024	0.900×10^4	0.900	0.900	1.54×10^{-2}	1.027	1.029
4	1.048	1.049	0.800×10^4	0.800	0.800	1.60×10^{-2}	1.067	1.066
5	1.068	1.068	0.715×10^4	0.715	0.714	1.66×10^{-2}	1.107	1.108
6	1.082	1.083	0.643×10^4	0.643	0.643	1.73×10^{-2}	1.153	1.151
8	1.111	1.109	0.534×10^4	0.534	0.533	1.85×10^{-2}	1.233	1.235
10	1.129	1.126	0.455×10^4	0.455	0.454	1.97×10^{-2}	1.313	1.318 .

(c) Results for random crosslinking of *m* uniform primary chains

m	$hg^{-1/2}_{\mathrm{FOUND}}$	$\langle S^2\rangle_0$	g_{FOUND}	$\langle R_s^{-1}\rangle_0$	h^{-1}_{FOUND}
1	1.000	1.000×10^4	1.000	1.50×10^{-2}	1.000
2	1.077	0.749×10^4	0.749	1.61×10^{-2}	1.073
3	1.113	0.636×10^4	0.636	1.69×10^{-2}	1.127
4	1.127	0.565×10^4	0.565	1.77×10^{-2}	1.180
6	1.141	0.494×10^4	0.494	1.87×10^{-2}	1.247
8	1.147	0.455×10^4	0.455	1.94×10^{-2}	1.293

(d) Results for random crosslinking of *m* random primary chains

m	$hg^{-1/2}_{\mathrm{FOUND}}$	$\langle S^2\rangle_0$	g_{FOUND}	$\langle R_s^{-1}\rangle_0$	h^{-1}_{FOUND}
1	1.000	1.000×10^4	1.000	1.500×10^{-2}	1.000
2	1;052	0.811×10^4	0.811	1.584×10^{-2}	1.056
3	1.082	0.690×10^4	0.690	1.670×10^{-2}	1.113
4	1.103	0.614×10^4	0.614	1.735×10^{-2}	1.157
6	1.119	0.533×10^4	0.533	1.836×10^{-2}	1.224
8	1.140	0.484×10^4	0.484	1.891×10^{-2}	1.261

justification for the application of this method directly to cyclized molecules is only apparent *a posteriori*, there are no available data for $\langle R_s^{-1}\rangle_0$ for the system of Allen *et al.*

Acceptability of results. $\langle S^2\rangle_0$ and $\langle R_s^{-1}\rangle_0$ were calculated from the distribution $\langle R_{ij}^2\rangle_0$ as described above; if these had converged to within $\approx 2\%$, for 5 different Monte Carlo runs, the results were considered acceptable. Typically this required $p \sim 10^4$ cycles (see above), generally 100 choices for the segments i and j, for each of 100 chain topologies.

The pseudorandom number generator *SRAN* used was of the usual multiplicative congruential type, but with a 'stream-splitter' incorporated to restrict cycling. It performed well when subjected to the usual moment, sequence, interval and correlation ('poker') tests.

RESULTS AND DISCUSSION

Chains and stars

Results for the Monte Carlo calcultions of $\langle S^2\rangle_0$ are given in *Tables 1a–1d*. The g and h^{-1} values for stars should agree with the formulae of Zimm and Stockmayer[2], Stockmayer and Fixman[13], Ptitsyn[14] and Kurata and Fukatsu[3]. Thus, for example:

$$g_r(\text{star}) = \frac{6f}{(f+1)(f+2)} \tag{14}$$

where the subscript r refers to random (see footnote) stars and

$$h_r^{-1}(\text{star}) = \frac{3\pi^{1/2}(f+3)\Gamma(f+1)}{16\Gamma(f+3/2)} \tag{15}$$

The calculated value of $\langle S^2\rangle_{0,l}$ for linear chains was found to be 1.000×10^4 ($\pm 0.002 \times 10^4$) in excellent agreement with equation (4) ($n = 6 \times 10^4$). However, $\langle R_s^{-1}\rangle_0$ was found to be 1.498×10^{-2} ($\pm 0.005 \times 10^{-2}$) compared with the value 1.505×10^{-2} given by equation (8). This significant discrepancy (0.5%) is due to the use of integrals to approximate the double sum in passing from equations (6) and (7) to equation (8). Sums of the form:

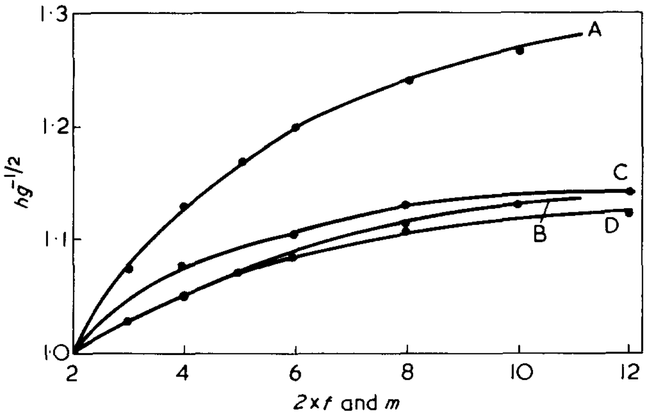

Figure 2 $hg^{-1/2}$ plotted against 2 X functionality, f, for stars or m, the number of crosslinked primary chains. A, Denotes the results for uniform stars; B, for random stars; C, for random crosslinking of uniform primary chains; D, random crosslinking of random primary chains

$$\sum_{i=1}^{n} i^{-x}$$

are not well approximated by:

$$\int_{i}^{n} i^{-x}\,di$$

when n is small (or x becomes large). Thus

$$\sum_{i=1}^{100} i^{-1/2} = 18.59$$

whereas

$$\int_{1}^{100} i^{-1/2}\,di = 18.00$$

an error of ~3%. In *Tables 1a* and *1b* the results for g, h^{-1} and $hg^{-1/2}$ found by the computer (denoted e.g. g_{FOUND}) and from the continuum integral formulation (denoted e.g. g_{CONT}) which gives equation (15), are compared for the star polymer models of different functionality. The agreement is encouraging, the error in g, h^{-1} and $hg^{-1/2}$ being in all cases less than 0.2%.

No comparison can be made with the results obtained from our crosslinked primary chain and those of Kurata and Fukatsu, (the latter being given in unwieldy algebraic form), because the models are different. We regard ours as more realistic (and adaptable) than theirs, although the calculations of Kajiwara[19,20] for randomly branched homopolycondensates most clearly approach an easily synthesizable physical system[24,25] by introducing the molecular weight heterogeneity.

The results for our two branch random intermolecularly crosslinked primary chain polymer (m = 2) are expected to be close to that for the f = 4 random star; for the monodisperse 2-branch polymer the results should lie between those for random and uniform 4-branch stars. (The differences are due to the correlations inherent in the generation of lengths of the two connected chains). This is indeed observed. Kajiwara[20] has shown that the effect of molecular weight heterogeneity decreases $\langle R_s^{-1}\rangle_{0w}$ and $\langle R_s^{-1}\rangle_{0z}$ the weight-average and z-average Stokes radius with increasing functionality f. Our results and those of other coworkers[2,4,26] show the opposite result for monodisperse polymers; this same counter effect of polydispersity and increasing functionality has been found in calculations of the z-average particle scattering factor for random polycondensates[27]. The effect of branching is further exemplified by the plot of the function $h/g^{1/2}$ against functionality (for stars) and 2 × number of chains for our crosslinked chain model. This function lies between 1.0 (trivially for f = 1,2) and an upper limit of 1.394[26]. For randomly branched polymers $h/g^{1/2} \approx 1.335$[3,19] independent of functionality for high enough chain length. In *Figure 2* the results for the uniform star, random star, monodisperse randomly crosslinked chains and random chain length, randomly crosslinked networks are plotted against f and m, respectively. The uniform stars yield the highest values of $hg^{-1/2}$, followed by the uniform chains crosslinked at random. The random stars and chains lie close together (they should yield similar results for f = 4 and m = 2, respectively, as explained above) and as f and m increase the results for the chains fall below those for the stars. This is expected, because for the stars the g values decrease faster than for the chains, because the centre of mass lies close to the 'nucleus' of the star. All the curves show the usual curvature, although we have not investigated the asymptotic behaviour at high f (or m).

Cyclized chains

Allen *et al.*[7] prepared samples of linear narrow molecular weight distribution polystyrenes containing a proportion (~4%) of chloromethylated units, of which a selection were covalently paired by diisocyanate. *Figure 3* shows their data (triangles), with unperturbed radius of gyration $\langle S^2\rangle_0$ plotted against number-average intramolecular crosslinks $\bar{m}_n$. In a previous publication[22] we showed incidentally that, whilst the theory of Edwards[8] gives:

$$\langle S^2\rangle_{0,m} \approx \frac{nb^2}{6(m+1)} \tag{16}$$

(for large $\bar{m}_n$). The empirical equation:

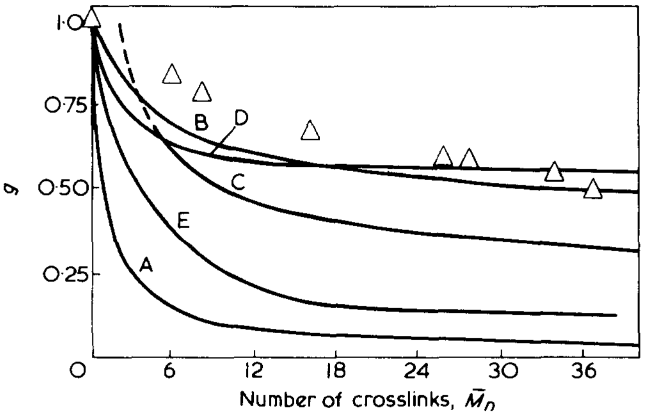

Figure 3 g values for linear chains with $\bar{m}_n$ crosslinks (intramolecular cycles). The triangles represent the data of Allen *et al.* (see ref 7); for the significance of curves A, B, C, D and E, see text

Table 2 g values for monodisperse linear chains with m cycles

m	$\langle S^2\rangle_{0,\mathrm{mn}}$†	g_{mn}	$\langle S^2\rangle_{0,\mathrm{min}}$‡	g_{min}
0	1.00×10^4	1.00	1.00×10^4	1.000
1	8.41×10^3	0.84	7.77×10^3	0.78
2	7.48×10^3	0.75	6.35×10^3	0.64
4	6.78×10^3	0.68	4.57×10^3	0.46
8	6.10×10^3	0.61	3.07×10^3	0.31
16	5.68×10^3	0.57	1.84×10^3	0.18
32	5.35×10^3	0.54	1.09×10^3	0.11

† mn = Mean path (uses most probable path); ‡ min = minimum path

$$\langle S^2\rangle_{0,m} \approx \frac{nb^2}{6(m+1)^q} \quad \text{with } q \sim 0.2 \tag{17}$$

fits the data better. Here m is the mean number of cycles (intramolecular crosslinks). With their modified theory, including such physical refinements as finite chain thickness, and length of crosslinks, Edwards and coworkers improved the fit to their data, but we show here that a good part of the correction required may be deduced from the purely graph theoretical treatment we use here.

Equation (16) is expected to be a strong lower bound on the estimate of $\langle S^2\rangle_{0,m}$, because for $m = 1$ it gives $g = 0.5$ (although the theory is not expected to be valid for such small m values). This corresponds to the g value of a cycle formed by joining together the two *ends* of a linear chain[2,18]. A simplistic argument enables us to deduce that a more realistic result is that $0.9 > g > 0.8$ (i.e. g lies between the results for random 3- and 4-branched stars with the same number of segments). Our Monte Carlo calculations have been carried out (see above) using either a random path in a graph, or the minimum path (see *Table 2*). These calculations give $g \approx 0.84$ and 0.78, respectively, and for high values of m produce the curves denoted D and E, respectively. Curve D is seen to fit the data adequately, and has no empirical parameters unlike fit B (based upon equation 17), the other curve E generates a (weaker) lower bound than curve A, but lies below curve C (the improved Edwards' theory). The Monte Carlo calculations used to generate D and E are expected to be invalid for large m values, but all the theoretical curves have decreasing curvature, and vary little with m, for m (and $\bar{m}_n$) ~ 40. In the region of interest $6 < \bar{m}_n < 40$, the validity of our approximations (and the agreement with experiment) is satisfactory.

The relationship between these permanent (chemical) contact pairs (rings in polymer chains) and temporary physical contact pairs and excluded volume theory have been pointed out in a recent publication[22].

DISCUSSION

The application of our computer method is not limited to calculation of $\langle S^2\rangle_0$ and $\langle R_s^{-1}\rangle_0$. For example some workers[27,28] have included the effect of excluded volume by modifying equation (2) to read:

$$\langle R_{ij}^2\rangle = |i-j|^{1+\epsilon}\, b^2 \tag{18}$$

where ϵ is a parameter $0 \leqslant \epsilon \leqslant 0.2$ to account for the expansion of the polymer coil in good solvents.

As a further example, the particle scattering factor of polymer chains is conventionally found by[29]:

$$P(\theta) = \frac{1}{2n^2} - \sum_{j>i}\sum \frac{\sin(\mu R_{ij})}{\mu R_{ij}} \tag{19}$$

with μ the scattering vector equal to $(4\pi/\lambda)\sin(\theta/2)$, with θ the scattering angle and λ the wavelength of light in the medium.

Both these expressions are easily incorporated into our programs, and results produced for any arbitrary distribution of $|i-j|$ (molecular weight distribution). We hope to investigate such problems in a later publication.

CONCLUSION

A Monte Carlo method has been used to calculate unperturbed dimensions of branch chain, star and cyclized polymers. Agreement with previous theory and experiment is satisfactory, and the method may be readily extended to more difficult averages over configurations and molecular chain length distributions.

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