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Cycles within Micronets and at the Gel Point

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ABSTRACT: The formation of cycles during the reaction of an $\mathbf{A}_2$ monomer with an $N\mathbf{B}_3$ monomer has been modeled in a new manner on a lattice, each component of the residues being placed upon different lattice sites and the functional groups being allowed to react by chance with their neighbors. The Monte Carlo method differs from previous percolation models in providing smooth distributions of cycles of different size in quantities similar to those found by experiment without any adjustable parameter, and differs from mean field treatments in placing the different and nonphantomlike structures properly within three-dimensional space. Not only may cycles form in competition with branching growth, but if the statistics require it, segments of one cycle may be shared with those of any number of others, as Houwink indicated in 1935. After a small number of simple cycle-containing micronet molecules are considered, a new measure of cycle number, C, is introduced to cope with issues intractable with cycle rank, c, alone. For an equimolar mixture of $\mathbf{A}_2$ and $\mathbf{B}_3$ monomers a simulation found that 22% of the two-node molecules at the end of a reaction contained cycles, and reported their proportions, to show that in these the cycles were remote from each other. At the gel point identified by the extent of reactions between molecules an analytical method identified all the cycles present in the system up to a certain size, and found that when the number of cycles of m nodes, R_m, is examined in terms of the relationship $R_m = Km^{-k}$, k has the initial value of 2.50 as for difunctional monomers, but k then falls, an effect permitted by the trifunctional residues and attributed to cycles sharing segments to an increasing extent as m increases. By the time m rises to about 8, k has fallen to 2.00, which is a critical value, as the total weight of C cycles in the system, $K'\zeta(k-1)$, is then unbounded if that trend persists—from the property of the Riemann ζ function, $\zeta(1.00)$—for m may rise to infinity in a gel. It appears that at the gel point this critical behavior applies and that it is enhanced, as k falls further to about zero, when $m \cong 24$. The periodic boundaries of the model were not large enough to provide the exact behavior of the cycle number as m becomes larger, but an explosion is certainly indicated by k becoming negative. A resilient product is predicted at the gel point.

Introduction

As Stockmayer recently disclosed,[1] when Flory and he first considered network formation, an issue "vexed"[2] by the simultaneous development of a high molecular weight product and the formation of cycles, the latter process was neglected, probably because molecular weights were more readily measured. In doing this they were following Carothers, who had earlier extended his equation relating degree of polymerization to extent of reaction to the case of monomers which had an average functionality greater than 2.[3] Despite being only an initial and temporary approach,[4,5] this strategey has survived, to become almost a doctrine with some. Subsequently several broadly equivalent methods have been provided: for example there has been a cascade theory,[5] a recursive method,[7] and a Smoluchowski coagulation kinetic model.[8] They are mean field theories,[9−11] they are concerned with phantom[12] chains and trees, they are directed at describing how the molecular weights rise to infinity, and they suffer from the unrealistic characteristic that in three dimensions the density rises with the molecular weight.[10] This is because the Cayley trees follow the pattern described by Pólya,[12] whose theorem does not allow for the congestion that occurs in real highly branched structures. Such congestion is generally recognized as limiting the formation of regular dendrimers above a certain generation, and is relieved in one two-dimensional system by the branches slipping, at the third generation, into the third dimension.[14] In hyperbranched polymers tipped with functional groups it is the approach to just this physical congestion in three dimensions that promotes and is inevitably relieved by chemical cyclization.

While the divergence of molecular weight and its polydispersity is well provided by these accounts, experiments have found that the formation of cycles does consume a proportion of the functional groups, so that the gel point occurs later than the theory predicts, a small delay enhanced by dilution[1,15] and several attempts at describing this, essentially as a side reaction, have been made. During the last half of the 20th century the formation of cycles within polymers has received a growing attention. For example, cycles in natural polymers have been recognized,[16] much work has been done on cyclization of linear polymers,[17−19] and the tadpole structure, a cycle linked to a tail, has now been synthesized,[20] having been invoked first in modeling studies.[21] Molecules with two cycles have been obtained: in one a tetravalent atom links the two rings,[22] in another two remote rings are linked by a segment,[19,20] and in the third each ring shares a short segment with the other,[23] so in fact there are three distinguishable

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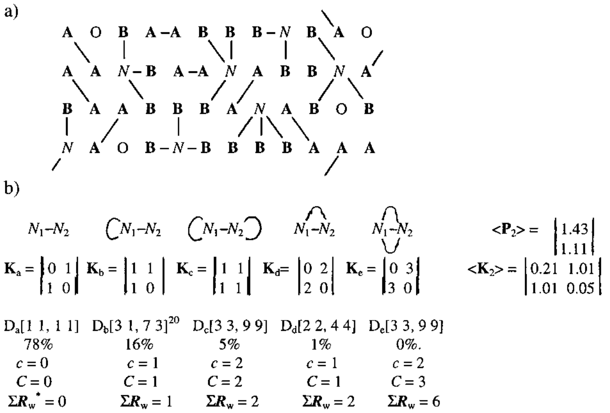
cycles. These bicyclic models presents a new issue, rarely if ever faced by those concerned with cycles within networks, of how they are arranged with respect to each other:[24] indeed, when discussing the concept of cycle rank, Flory's diagram did not contain a single cycle,[12] though it was stated that many of the chains were linked at infinity, and, within a review, to illustrate current theory[15] of the relative sizes of cycles that may form, a diagram indicating the potential for cycle formation had no cycle present. The assumption, often unstated, is that cycles may not be of much consequence, if they are present they will be isolated and mainly of a small size, and that they may be neglected, at least until the gel point is reached, and certainly so within the sol at all times.[1,5,7,25] It is not quite clear how isolated cycles envisaged as capable, as in the spanning tree approximation,[26,27] of being absorbed within a tree to produce a huge "floppy" branched molecule, will ever provide structures that have a permanent shape and resilience in real space, even if their branches do extend to infinity.

The New Lattice-Based Simulation Method

We here present some early results on a gelling system of a new method[27−29] for simulating step-growth reactions which has provided "a sound theoretical basis" to the results of experiments when applied to the closely related and previously avoided[4] issue of cycle formation by $\mathbf{AB}_2$ systems.[31] In the model, each of the molecules are placed at several sites and may move and react upon a three-dimensional lattice. There is an expression of excluded volume—hugely branched molecules cannot form as there would be too much congestion—and by using several sites for each monomer, in contrast to standard percolation models,[9−11] a loop involving a single branch point is shown explicitly on three or more sites, and larger cycles are clearly recognized. In this way a realistic representation in space is obtained of the competition between growth and cycle formation. Whereas on a cubic lattice cycles have only 4, 6, 8, ... nodes, in our system their distribution is not sparse, for all cycles of 1, 2, 3, ... nodes may form,[30] and furthermore, smooth number distributions are obtained.[28−32] The chains are not phantoms:[12] knots are encountered and recognized,[33] as may be entanglements. Periodic boundaries apply. When employed to simulate the growth of $\mathbf{AB}_f$ monomers, on completion of the polymerization, it obtained one cycle within each molecule,[29,30] a prediction[34] confirmed by later-reported experiments with some flexible[31,35] and even some stiff monomers.[36] Cycle formation under kinetic control came to limit the fractallike growth of high polymers to a finite size, and transformed the distribution functions for molecular sizes to the initial terms of ζ functions,[29,30] the extent of the series being limited by cyclizations.

For an $\mathbf{A}_2 + \mathbf{B}_3$ reaction the simplest lattice representation has each **A** group on a lattice site, with the trifunctional molecule being placed as $N(-\mathbf{B})_3$ on four sites (Scheme 1a). The lattice is cubic, but bonds may be directed and form on plane and space diagonals, as well as on a lattice spacing: chemistry takes place on a 26-choice fluctuating-bond lattice, the lattice coordination number and the residue functionality differing by an order of magnitude and presenting a sensible representation of real molecules in space[30] as well as readily allowing many types of movement[30,33] and avoiding the difficulties identified by Gordon in normal bond percolation models.[37] When the polymerization proceeds, the new method allows cycles to form remote from and next to each other—and thereby sharing segments—as pairs of **A** and **B** groups adjacent on the lattice are selected to be linked, if they turn out by chance to be within the same molecule. If (as for the results shown here) an equal number of each type of monomer is present at the start of the reaction, it is possible to show that the cycle rank within the system is equal to the number of molecules that remain when all the **A** groups have reacted.[38] The questions arise as to how these cycles are distributed within the sol molecules and the gel, and also how many different cycles may be distinguished, for, as we shall show, the cycle rank provides a conservative count of cycles when they have segments in common. The lattice model naturally operates in three dimensions, as opposed to the one-dimensional graphs favored by others (we do not doubt the elegance of such ideas, merely their relevance to three-dimensional gels). In the lattice model the excluded volume factor might be varied by varying the number of sites used to represent each residue, but certain results for $\mathbf{AB}_2$ systems on the distributions of molecular and ring sizes are apparently independent of the manner of mapping the residues onto the lattice.[29,30] Stiffness might be expressed by restricting the angles at the ends of the **A**−**B** and N−**B** bonds. Lattice models are of course insensitive to the conformational details that are expressed within rotational isomeric state treatments[39] and have drawbacks,[4] but have provided useful indications of the behavior of polymers in other circumstances,[40−42] and perhaps configurational effects might be included once the broad nature of the problem is properly understood.

Scheme 1. (a) $\mathbf{A}_2$ and $N\mathbf{B}_3$ Molecules Dispersed Randomly on a Sample of the Lattice in Two Dimensions before the Reaction Took Place (the Calculations used a 3-D Lattice), Where Vacant Sites Are Represented as O and (B) Some Two-Node Molecules or Dimers, Their Structures, Mean Extent of Reaction Vector, P, Kirchhoff Matrices for Individual Dimers and, at the End of an $\mathbf{A}_2 + N\mathbf{B}_3$ Lattice Simulation, the Mean Value of K, Priority Values [ ],[30] and Proportions[a]



[a] They are ordered by their occurrence among the sol molecules at the end of a simulation when random bead movements[30,33] were allowed; the lines represent −**A**−**A**− segments. c is the cycle rank,[44,45] C Is the cycle number, and $\sum R_w$ is the total weight of segments in the C cycles *per molecule*. Note that no D_es were obtained, so among the two-node molecules −**A**−**A**− segments were not shared. The asterisk indicates that only −**A**−**A**− segments (or nodes) are counted.

Structures of Two-Node Molecules[43]

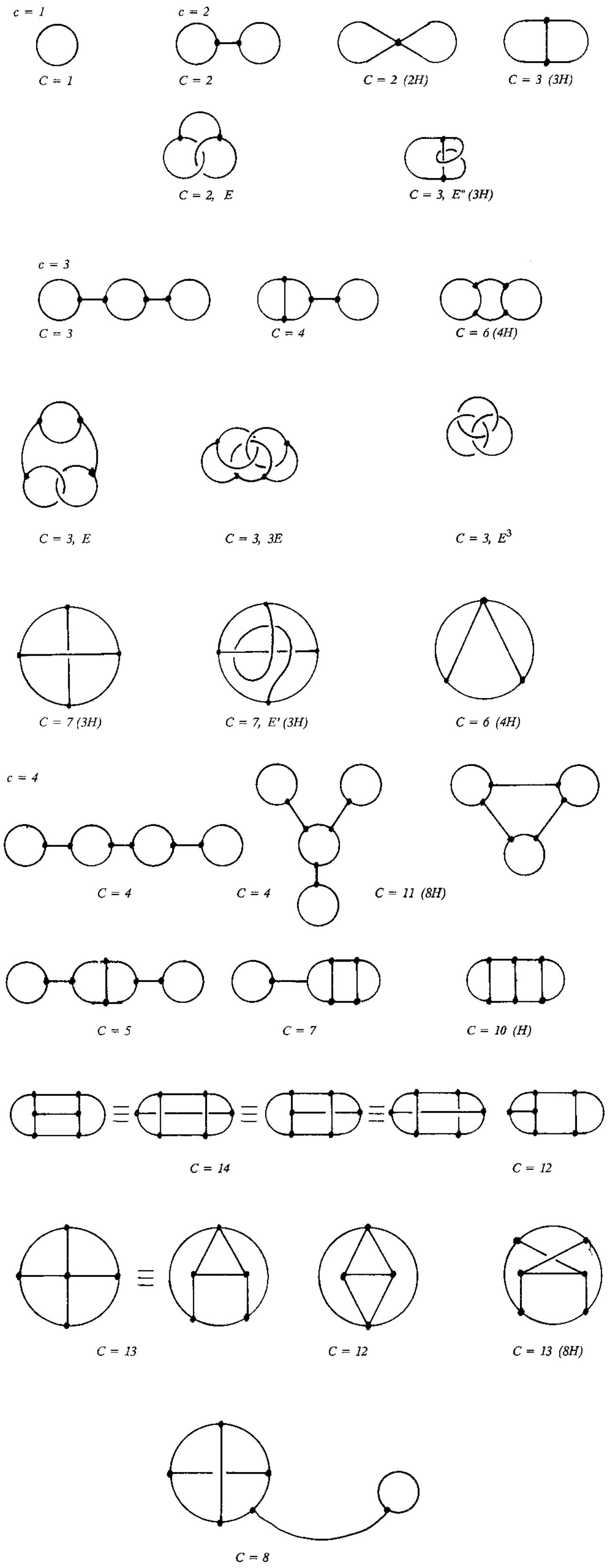
Within the two-node molecules some structures that might be envisaged are shown in Scheme 1b.[20,22,23] In these there are no **A** groups, so they may be anticipated within the sol at the end of the reaction of an equimolar mixture of flexible $\mathbf{A}_2$ and $N\mathbf{B}_3$ molecules. The first topology has two nodes linked by a single segment, and the second is a tadpole, formed from two trifunctional monomers and two $\mathbf{A}_2$ monomers. Each cycle involves a single node—a structure we term a loop. A third molecule might form from two trifunctional monomers and three $\mathbf{A}_2$ monomers, D_b being the topological precursor—and contains two loops, but the fourth, formed from two trifunctional monomers and two $\mathbf{A}_2$ monomers has a single cycle containing two nodes. The fifth molecule, D_e, formed from two trifunctional monomers and three $\mathbf{A}_2$ monomers, as did D_c, and like it has a cycle rank,[12,44,45] c, of 2, for the number of residues is unaltered if two $\mathbf{A}-\mathbf{B}$ links are severed, yet the two molecules are clearly different (just as are naphthalene and biphenyl). However flexible the links between the two nodes, the molecules have a different set of configurations. Within D_e[22,23] it is possible to trace three different cycles, which causes us to introduce the term cycle number, C, to count these in the oligomers, micronets and on a larger scale in representative parts of networks.

When our analysis scheme[46] reported the fractions of dimers—two-node molecules, they were identified by their node priority values,[30,43] and from these and the mean Kirchhoff matrixes[30] reported, the fractions of the dimers of each topology were obtained (Scheme 1). An entry of 1, 2, or 3 in $\mathbf{K}[i,j] =$ indicates the number of $-\mathbf{A}-\mathbf{A}-$ segments linking the ith and jth nodes. A simulation was performed with a random distribution of equal proportions of $\mathbf{A}_2$ and $N\mathbf{B}_3$ molecules, so that at the end only **B** tails remained.[47] At that end 22% of these sol molecules contained cycles, 5% having a cycle rank of two, but no significant proportion of these had $C = 3$. Per hundred molecules there were 28 $-\mathbf{A}-\mathbf{A}-$ segments found to be in cycles. These statistics differ from those obtained[30] and experimentally verified[31,35] for the closely related $\mathbf{A}-X-X-N(-\mathbf{B})_2$ system because the starting line was different. If cycles are present in these dimers, it is hardly possible that they will not be present in larger sol molecules. We suggest that there are no grounds (except of convenience) for excluding the formation of cycles within small molecules before or after the gel point unless the residues and the links between them are particularly stiff. As the number of $\mathbf{A}_2$ and $N\mathbf{B}_3$ molecules was the same at the start of the polymerization, it follows that the numbers of molecules and of cycles present at the end of the polymerization should also be equal.[38] Since many of these *sol* dimers lack a cycle, to compensate several cycles may be present in each of the larger size molecules, so we consider how this might be.

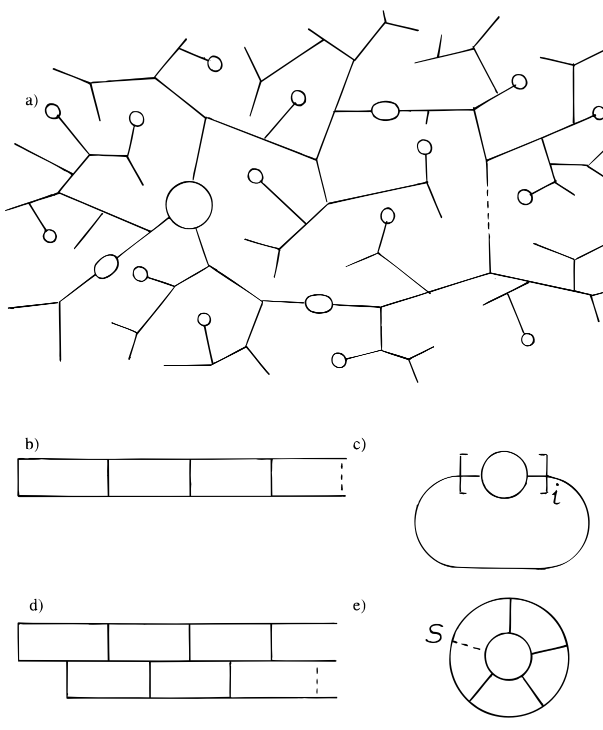
Cycle Rank, Cycle Number, and Some Model or Standard Networks

Micronet molecules with several cycles may be distinguished by their cycle structure. We show in Scheme 2 a series of networks with cycle ranks[12,44,45] c of 1, 2, 3, and 4, where, in each case, the total number of cycles, C, is indicated. When $c = 1$ or 2, the structures are found in both two and three dimensions, but when c is larger there are possibilities for structures in three dimensions not found in two. Also possible in three dimensions is catenation of single cycles[16] and, whenever c is greater than 1, is an entanglement within the molecule: we show only a few such structures, but essentially any two segments may be entangled provided that they do not share a single node (and where the nodes are based on tetravalent carbon atoms this qualification is not valid).

Scheme 2



Scheme 3



We distinguish four types of entanglement, those, E in which two distinct cycles are involved, those E' in which segments on different nodes are entwined, those of E^3—the Borromean type—in which three cycles are bound but which is not true for pairs of the cycles, and those E'' which involve two segments sharing a node which must therefore be chiral.[48] Some have Hamilton cycles (of all the nodes): H. The structures with $c = 3$ are of two types, those with four $f = 3$ nodes, and one with two $f = 4$ nodes. It may be seen that C ranges from 3 to 7 for these four structures. When $c = 4$, we show eight different micronets, with C ranging from 4 to 16, with a mean value of ~ 9. $\langle C \rangle$ rises faster than c (1:1; 2: 2.4, 3: ~ 5.1, 4: ~ 9.4), but the values are illustrative rather than exhaustive, and provoke the questions: how are these quantities related in networks of a standard form, and how they are related in real systems where cycles are formed randomly at all stages?

To illustrate the concept of cycle number and the manner in which it characterizes an evolving network structure we provide the following examples in Scheme 3. The first, part a, has cycles of different sizes isolated within a branched chain, and $C = c$ (for simplicity the segments are shown as straight lines). In the second, part b, each cycle fits on the side of the previous one as if rungs were being placed one by one into a ladder. In that case, examination shows that when the cth link between the two strands is formed on the right-hand side, one new cycle is formed of the small ring itself, a second as a fusion with its first neighbor, a third as a fusion with its first and second neighbors, and so on until the cth cycle extends to the first ring of the system. Standard algebra leads to the total number of distinguishable cycles present after completion of the cth ring is $C_c = c(c + 1)/2 \approx c^2/2$. In the third example, we have i small rings in a single larger ring, a cyclized or pearl necklace version. For part c, we find $C_i = 2^i + i$. In part d, a modification of part b in which the third ring is adjacent to the two previous ones, and so on, an enumeration of the first numbers in the series finds successively that C_c is 1, 3, 7, 14, 26, 46, ..., the rule being at large values of c that $C_c \approx 3.064\alpha^c$, where α is $(1 + 5^{1/2})/2 = 1.6180$, the reciprocal of the golden section; the series is thus related to the Fibonacci numbers,[49] but with a different prefactor. An analytical examination of the problem has found exactly that $C_c = F_{c+4} - c - 3$, and that to a good approximation $C_c = (7 + 3 \times 5^{1/2})/2F_c - c - 3 \cong 3.0637\ \alpha^c$, as the empirical examination found (see accompanying material). Thus, the form of C_c is concerned with the manner in which the cycle number depends on the number of elaborated cycles when each elementary cycle is placed in turn beside the last *two* cycles to be drawn, while each Fibonacci number is obtained by adding the *two* previous numbers in the series. In the fifth we have a cyclic version of part b, a structure very similar to that used by Houwink in the question put to Carothers[24] when he noted the avoidance of the issue of multiple as well as single cycles. If s is the number of "spokes" in the wheel, we find that $C_s = 2^s + s(s - 1)$ ($s > 1$; see accompanying material). In this case each spoke, after the first two, is placed at a random point between the inner and outer circles. It is clear from an examination of these standard systems that the number of independent circuits[50] for which we have introduced the term cycle number, C, may be much larger than the Case–Scanlan[44,45] cycle rank, c, and within objects of a finite size might be related to c by a power or by an exponential function.

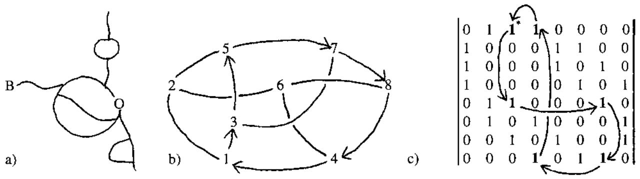
In these examples placed in two-dimensional space, different forms of C_c function are found for the different simple patterns, so these do depend on the topology of the micronets. Within a network system c and C may be huge quantities, and a more tractable quantity might be the number of the number of cycles of finite and accessible sizes that involve a particular node or an "average" node. Cycle number bears a relationship to cycle rank similar to that of $\langle M \rangle_w$ to $\langle M \rangle_n$, and their ratio C/c reflects the cycle topology in a manner that will depend on the size x of the micronet. We consider that a method of forming networks must address such issues at every stage within sol and gel, if that is present. Our model may deal with topologies such as those of Schemes 1–3 and provide statistics to satisfy Houwink's point. When analyzing the evolution of our model, moreover, each cycle must be identified before its size can be determined for inclusion within the R_m counts, where m is the number of nodes in the cycle, and the form of R_m as a function of m will also characterize the topology.

Counting Cycles

During the course of our simulation records are made of the lattice structure, and after the connectivity matrix for the system has been ordered so that nodes are first grouped together and then ordered by priority within the molecule,[30,43] units involved in pendant tails are deleted.

The discovery of loops, or cycles involving only one node, is trivial, for these structures are recorded on the diagonal elements of the **K** matrix as segments linking the same node,[30,43] but for larger cycles a search is executed, the pattern of which we illustrate with the micronet example in Scheme 4b, where the nodes are given an arbitrary priority, for each node in this simple structure has identical values of the first, second, third, ..., priority counts:[30,43] 3, 9, 27, ..., as would happen if the nodes within tails and with only two functionalities

Scheme 4. Two Networks (a) and (b) and a Journey around the Segments of the Second (c) Indicated on Its Kirchhoff Matrix[a]



[a] Journeys around the first network can be planned with the Norwegian Railway timetable. An asterisk in part c indicates that the start and finish are at the same element, and identify a segment, if the number of segments is even, but are on the same row as column number that identifies a node, if the number of segments is odd.

are stripped from the matrix. The procedure generally chooses the node of highest priority (node 1), and then, without returning along the same segment, searches among all the neighbors {(nodes 5, 6, ...)} of the first linked node (node 2) to discover if that is node 1. If a two-node cycle is thus identified, a record of the path is made, as {1, 2, (1)}. The search then proceeds within the remaining neighbors of node 2 for any remaining cycles of size 2 starting from node 1, as would be present were nodes 1 and 2 directly linked by more than two $-\mathbf{A}-\mathbf{A}-$ segments. The next search is performed within the next neighbor of the first node, and so on, until all possibilities of discovering cycles of size 2 involving the first node have been exhausted. The next step is to search for two-node cycles based on node 2, then node 3, ..., i, ..., $x - 1$ within the micronet. The search is then extended to identify three-node cycles involving node 1. In turn the neighbors of its first neighbors are considered: if their neighbors are linked to node 1, such a cycle has been found, and is listed as, e.g., {1, 2, 3 (1)}. The search always proceeds from low-number nodes upward, so that a four- or higher-node cycle identity {1, 3, 2 (1)} or {1, 3, 2, y (1)} would not be considered, for to do so would cause the same cycle to be counted twice, which would not only be an error, but would require more time. The search extends by seeking to discover three-node cycles including node 2 (but not node 1) and then throughout the rest of the system until the $(x - 2)$th node is reached. Success would occur at {3,5,7(3)} and {4,6,8(4)} in the present example. Four-node cycles are then sought, and so on.

One example of a micronet is shown in Scheme 4a, with a c of 4 and a C of 5 (it is based on the Norwegian rail network), and another of eight nodes and $c = 5$ is shown besides that together with its connectivity matrix. The list of $C = 22$ cycles obtained by an analysis of the second of these is given in order of discovery and ascending size: {3,5,7},[51] {4,6,8}, {1,2,5,3}, {1,2,6,4}, {1,2,5,7,3}, {1,2,6,8,4}, {1,3,7,8,4}, {2,5,7,8,6}, {1,2,5,7,8,4}, {1,2,6,8,7,3}, **{1,3,5,7,8,4}**, {1,3,7,8,6,4}, {2,5,3,7,8,6}, {1,2,5,3,7,8,4}, {1,2,5,7,8,6,4}, {1,2,6,4,8,7,3}, {1,3,5,7,8,6,4}, {1,3,7,5,2,6,4}, {2,5,3,7,8,4,6}, *{1,2,5,3,7,8,6,4}*, *{1,2,6,4,8,7,5,3}*, *{1,3,7,5,2,6,8,4}*. One cycle **{1,3,5,7,8,4}** is shown in the Kirchhoff matrix[52] of Scheme 4; note that returning from node 8 to node 1 might also be made via node 6 and node 2, but that route will be found later when the seven-node cycle {1, 2, 6, 8, 7, 5, 3} is discovered, and so routes back to node 1 through only nodes greater than 3 will be sought in the final search. The three Hamilton cycles of the present example are *italicized*, but up to 16 might be present (and then $C = 20$).[53] Should any entry in $\mathbf{K}[i,j]$ be greater than 1, there are that many extra cycles for each time that link is found, and should there be a second or third nonunit entry, the number of such cycles rises by the product of the sets of mutiple links. We may note also that in the micronet of Scheme 4b there are the following topological entanglements: {3,5,7}E{4,6,8}; {3,5,7}E{1,2,6,8,4}; {1,2,5,7,3}E{4,6,8}, but there are no knots in the Hamilton cycles. At the other extreme, from the eight $f = 3$ nodes one might construct a molecule with $c = C = 5$, and no H, all the cycles being loops pendant to or terminating a single chain. Clearly for a particular size of molecule, x, the number of cycles of sizes up to x nodes characterizes the topology. Such an analysis may be obtained from the connectivity matrices that our analytical procedure provides within a finite sized micronet. Within a finite sized sample obtained within periodic boundaries of a gelled system the procedure provides the number of cycles with an ever increasing m count at an ever-increasing cost in search time, as a travelling salesman would appreciate.

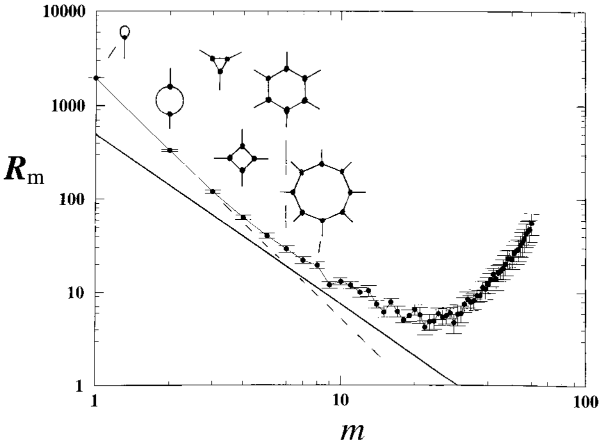


Figure 1. Plot of R_m, the number of cycles of m nodes, against m at the extent of reaction between molecules that corresponds to the gel point, $p_e = 0.8660$, for extra-molecular reaction in the $\mathbf{A}_2 + N\mathbf{B}_3$ system. The dashed line continues the initial trend, with slope $= -2.5$; the full line is the critical slope of -2.00, which if continued to $m = \infty$ causes $\sum mR_m$ itself to become infinity. The data were obtained from eight replicas of a 60^3 lattice system which was randomized before the reaction took place.

Cycle Distributions at the Gel Point

In Figure 1 we show R_m, the number of cycles of size m, plotted against m on double logarithmic scales, as for other studies of cycles formed in step growths.[28,30] The points from the whole system have been used when the extent of reaction of the **A** groups, p_a, was 0.9489 after 3.125M CHOICE cycles or time units on the 60^3 lattice.[54] We have chosen these data for discussion for it transpired that it corresponded to an intramolecular extent of reaction, p_e, of 0.8660; it is just this value for $p_a = (r(f_a - 1)(f_b - 1))^{-0.5} = (3/4)^{0.5}$, which classical theory suggests might be the gel point in the absence of cyclizations, that is, when classical theory has $p_a = p_e^4$ [$r = N_A/N_B = {}^2/_3$, the present ratio of the number of functional groups of each type, $f_a = 2$ and $f_b = 3$ are the functionalities]. This leaves a 0.0829 portion, 8.7% of p_a, to complete cycles—a proportion comparable with some experiments,[15,26,27,55,56] which emerges from the model without any adjustable parameter. A recent theoretical paper has partitioned the bonds that form into those that extend the molecular weight and those that close cycles, c, as we here practice.[57] The data of

Figure 1 was obtained from a study that allowed bonds to form in a random manner between pairs of **A** and **B** groups in molecules which had been randomized in orientation and location on the lattice but which did not move during the reaction. (Assuming that the intermolecular reactions will have led to $\langle M\rangle_w$ reaching infinity, $\langle M\rangle_n$ at that point is only 7.5 residues, and so the average number of nodes per *c*-cycle is also only 7.5.[38])

Above certain points in Figure 1, we have drawn some elementary cycles whose count is there indicated. Of the small cycles shown there, the most frequent are the loops, those of size $m = 1$, and whenever found, whether in *sol* or *gel*, these cannot be part of any elastically active network, for at best they are pendant, if they are not in single node monomers (we allow micronet molecules to be elastically active, as experiments with molecular tweezers might show). All the other cycles may so be active. The extra valencies we show, for example, for the octameric cycle might be linked through $-\mathbf{A}-\mathbf{A}-$ segments to others of that cycle, to form more elementary rings, or be linked to other cycles that share one segment of the cycle shown as well as possibly bearing pendant trees. However, all these with $m > 1$ are candidates for the elastically active systems. Whether this is the case depends on whether their segments are part of or shared with cycles that extend throughout the whole molecule, an idea different from the Scanlan–Case criterion that a segment is elastically active if the two terminating nodes are linked in three ways to the gel network, for that gel might merely be hyperbranched.[27] Our criterion is more strict, for we require a large cycle at "infinity"[12] or at least at the "surface",[27] and expect many before that. Our criterion may be formulated in terms of the relationship between the radius of gyration of the large cycle and the volume of the object: $\langle S^2\rangle_c \sim V^{2/3}$ (and, of course, there would in general be many more than one such cycle).

We wish to discuss several features of this plot concerning cycles both in sol and gel that center on the initial slope, and the fact that the steepness of the slope diminishes as m rises, which reflects how cycles are placed with respect to each other. The initial slope of Figure 1 is $-2.50(\pm 0.02)$, and coincides with the Jacobsen-Stockmayer equilibrium theory for cyclization by difunctional residues,[58] a value supported by experiments.[39] For the first two values of m, R_1 is the number of loops in looped monomers and in loops attached to larger structures, and R_2 is not inflated by any dimers of $C = 3$, for, as we have seen in Scheme 1b, even when movements take place the dimers of this type do not form. The initial slope is not influenced by the possibility that a segment might be shared by more than one cycle but this does become possible once m rises and the objects within which the cycles occur are larger sol molecules and the gel itself.

The -2.5 value of the slope is similar to but a little less steep at that value of p_a than the slopes we have found over large ranges of m for cycle formation on a static lattice from difunctional monomers (-2.9)[28] and to the value of -2.8 we found for the polymerization of an $\mathbf{A}-X-X-N(-\mathbf{B})_2$ system (the monomer of which was obtained from the present $\mathbf{A}_2$ and $N\mathbf{B}_3$ monomers).[30] As in other studies of cycles produced kinetically, the value of the slope is large and negative to begin with, for the oligomers initially present may form only the smallest of cycles, but the plots become less steep as p_a rises and the precursors to larger have formed and so such cycles become possible.[46] At any instance in p_a space the number of cycles that may be about to form is determined by the framework of the molecules that are already present. At much lower values of p_a, in this case,[46] as in others we have examined,[28,30] the counts for the higher cycles are zero, as their immediate precursors do not exist, and the plots in the form of Figure 1 show a downward curvature.

It is interesting to examine the consequences of the slopes on this plot. If the number of rings of size m nodes varies according to $R_m = Km^{-2.5}$ (K being a constant $< N_o$), then the weight varies with $R_{w,m} = Km^{-1.5}$ (as $W_m = mR_m = R_{w,m}$), and the total weight of material in cycles is $W_c = K\sum m^{-1.5}$, which is obtained as a finite number ($K\zeta(1.5) = 2.641K$), for the (real) exponent is less than -1.00.[49,58–60] The initial points establish a trend that satisfies this condition. We have placed on the Figure 1 a line of slope -2.00, which corresponds to a previously unrecognized criticality in the context of cycle distributions, for total weight of material in cycles is then $W_c = K'\sum m^{-1.00}$, an infinite number ($K'\zeta(1.00)$) from that argument of the ζ function, if the positive integers m may rise to infinity.[49,58–60] That, if this trend develops W_c is much larger than the size of the system and N_o, is simply a consequence of the fact that each elastically active segment in the sample of gel within the simulation may participate in a huge number of cycles.

For the data we show the points curve upward above the initial line of slope -2.50. This effect is progressive and is outside the bounds of error once m rises as far as 6 to 8, and indeed by the time we reach m about 10 to 12, a tangent to the curve has the critical slope of -2.0. The model finds 58% more cycles when $m = 8$ than predicted by the line of slope -2.50, and more than twice as many when $m = 10$. Further on, at about $m = 22$ to 25, the points reach a minimum, and then they start to rise. First, we consider whether these are real effects or are artifacts deriving from the fact that our ring recognition procedure has counted as cycles structures that link up by re-entering through the periodic boundaries.[28] This would be possible only once m reached 12, for a line of 12 $N\mathbf{B}_3$ molecules linked by 12 $\mathbf{A}_2$ molecules would achieve such as thing. We are thus certain that the initial trend is not maintained, and that by the time $m \sim 8$ the slope is as small as -2.00 at the gel point, a result which suggests that then progressively cycles within the network begin to share segments as m rises, so greatly magnifying the count of $R_{w,m}$; the value of $\sum R_{w,m}$ would only be limited by the size of the molecule itself, might well be a number very much greater than the total weight of main chain atoms, and if the number of residues in the gel might approach infinity, then $\sum R_{w,m}$ would certainly do so faster. What we may do is to establish such behavior by drawing inferences from within the bounds of finite sized samples of the system which we examine. The sharing of segments is not indicated for the small cycles at the start of the R_m plot, but clearly develops as m rises. Just before the gel point, m is limited by $x_{\max}$, the degree of polymerization of the largest micronet, but after it $m_{\max}$ may rise toward the total number of $N\mathbf{B}_3$ residues in the system: it is the fact that $m \to x_{\max} \to \infty$ that causes $\sum R_{w,m} \to \infty$, rather than the exact form of the curve, as long as the slope is greater than -2.00. Furthermore, a simulation of this growth on a 120^3 lattice found, at values of p_a just before and just after the gel point, R_m data that, after normalizing to the size of the present system, were not significantly different from those of this study up to $m = 60$ at the same values of p_a.[46] Up to $m = 23$ the present data are thus supported. While we are not certain of the exact form of R_m once m rises further beyond $m = 25$, that is whether it is a power law or an exponential, we found no significant difference between the data from the two models at any value of $m < 60$,[46] when the cycle counts of the two systems will be very differently liable to the effect of the boundary size. We can be certain that there is a very substantial rise in R_m as m rises during the latter part of the figure.

Part a of Scheme 3 has one-, two- and three-node cycles in the approximate proportion of $m^{-2.5}$, as our simulation found. The possibility of composite cycles such as part c is indicated with a dashed line, and the completion of such composite cycles would allow for the rise in R_m above the initial slope. The question remains as to whether beyond $m = 30$, as m rises further, do the composite cycles of type c lie isolated within much larger fractals of form a, or do collections of cycles as in parts b or d or more elaborate forms in three dimensions exist beyond the regions we have sampled at present. The answer may be found in two ways, first by obtaining the form of R_m on m as m rises further and by obtaining $C(c)$ as x rises to infinity, for comparison with standard networks. Alternatively, but perhaps more severely, we may approach the issue by discovering whether there are large cycles with a radius of gyration $\langle S^2\rangle_c \sim \langle S^2\rangle_{x_m}$, the latter being the radius of gyration of the largest micronet of x_m nodes within the system as the gel point is approached.

Our initial value of slope of -2.50 contrasts with that of -1.5 used by some in finding the distribution of cycles at the gel point as an extension of a statistical branching process.[15,27,60] When we use the latter slope to calculate $W_c = K\sum m^{-0.5}$, we obtain an infinite number, as the series diverges.[49,59,60] This is paradoxical, for while the total weight of material in cycles is infinite, and we may explain this as by having cycles share segments, yet this is not thought to be the case, for the calculation intends to find the probabilities of different sizes of cycles forming within merely a hyperbranched molecule,[15,27] and does not allow for the formation of any cycles previous to reaching the gel point. A constant value of $k = 1.5$ in the distribution function $R_m = Km^{-k}$ for the accumulated R_1 and R_2 in the distribution function is impossible, as we have seen, for when $m = 1$ the loop's segment cannot be shared with a larger cycle and when $m = 2$ the statistics do not produce dimers of type D_e, the only molecules in which two-node cycles may share segments. As has been observed,[62] when the gel point is reached by a kinetically controlled route, it may be a serious error to ignore the integrity of previously formed structures. Elsewhere it has been stated that "attempts to include cyclizations" in mean field theories "are very crude or just not realistic",[8] which does rather seem to be the case. Thus, while the statistics provided by our model are mathematically consistent initially with the molecules at the gel point containing a finite and rapidly diminishing number and weight of small rings as their size increases which then turns to another type of behavior at larger values of m as cycles come to share segments, any theory with $R_m \sim m^{-1.5}$ throughout is inconsistent in this respect.

Conclusions

In our 26-choice lattice-bound Monte Carlo approach to modeling network formation we map each residue onto more than one lattice site. A bond forms irrespective of whether it causes a step growth or completes one, two, or indeed any number of cycles—a possibility present if segments are shared. In doing this it does build upon previously formed structures. We show that 78% of the two-node molecules lack cycles at the end of one simulation, and that a proportion of them have two cycles, so that there are 28 $-\mathbf{A}-\mathbf{A}-$ segments per 100 dimer molecules. To compensate for the general lack of cycles in the smaller oligomers, the larger molecules, including any gel molecule, must contain more than one cycle, for $c = N_\infty$, the final number of molecules present.

After considering a small number of standard micronetworks drawn in two dimensions, we show that the Case–Scanlon cycle rank, c, must be supplemented by a new measure, cycle number, C, to count cycles when segments may be shared by more than one cycle, a possibility which is inherent in our model but which has been rejected outright by all previous network theorists, except for a remark by Houwink. The topology of the micronets determines the form of $C(c)$ and the ratio C/c (a sort of cycle polydispersity), but it remains to be established for a randomly grown micronet. We suggest that only if segments are shared by more than one cycle can they be candidates for an elastically active network. For discovering the different cycles present in micronets and representative portions of a gel we have described a procedure which starts with small cycles and proceeds systematically to larger ones. A network, like a micronet, may be characterized by the form of R_m, the number of cycles of m nodes; we have obtained this function by examining the structure of cycles in the system at an extent of reaction between molecules, p_e, that corresponds to the gel point for low values of m. Other characteristics of cycle topology have been suggested.

A consideration of the relationship between R_m and m has identified a critical point, as that at which when m is rising to infinity, as it may within the gel, the value of k in $R_m = Km^{-k}$ becomes less than 2.00, for then the total weight of materials in cycles, W_c, becomes infinite (since $\sum R_{w,m} = \sum mKm^{-k} = K\zeta(k - 1)$, and $\zeta(1.00)$ is unbounded). In contrast to some statistics, which chose a constant value of $k = 1.5$ at the gel point, and which are therefore less consistent in their description of the distribution of the sizes of isolated cycles, at the gel point as identified by the extent of intermolecular reactions, our model finds that k falls from an initial value of 2.50 for a region ($m = 1, 2, 3$) in which segments are not shared to the critical value of 2.00 by the time m reaches 8 or 10, and k becomes zero at $m \sim 24$. (This last effect is real, and not an artifact of our cycle recognition procedure being unable at present to discriminate against cycles that are creatures of the periodic boundaries, for a simulation on a larger lattice found trends at reaction times just before and after the gel point not different, within a standard deviation, from the results shown here, even up to $m = 60$.) The fall in k that our model has detected is caused by certain network segments being shared by many cycles, and k need not fall further below 2.00 before its value implies an explosion in cycle number. Such an explosion is indicated strongly by our results, which furthermore find a real rise in R_m with m once that passes about 24, but the form of R_m is not yet established for comparison with standard networks.

Our lattice-based fluctuating bond polymerization model, which succeeded in predicted the important role of single cycles in $\mathbf{AB}_2$ polymerizations, predicts that in polymerizations leading to gels there is a significant sharing of a segment by a number of cycles. At the gel point itself, large numbers of large cycles eventually form, as they may within the huge gel molecules. This is in contrast to the $\mathbf{AB}_2$ cases,[29,30,34] where we recognized that large cycles cannot be present, for the molecular weight was limited by cycle formation, as experiments have found. It appears, contrary to earlier and widely adopted assumptions based upon a mean field approach that a gel is already a resilient gel at the gel point, before any more intramolecular reactions take place.

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Supporting Information Available: Text giving empirical and analytical results on the number of cycles present in the topological objects of Scheme 3, parts d and e, as the cycle rank rises. This material is available free of charge via the Internet at http://pubs.acs.org.

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(51) In these lists we imply the final return to the staring point, as used explicitly in the previous paragraph.
(52) To save storage space, the information in the Kirchhoff matrix was stored and examined in a vector,[46] but we present this account in terms of the matrix form of the information.
(53) There may be more than one Hamilton cycle: their number is, however, limited by the number of ways of finding directions away from a node. At most when $f = 3$ and all the nodes are in a necklace of cycles as in Scheme 3c, there may be $H = 2^i$, where $i = x/2$ is the number of nodes at which divergence occurs, so that for an eight-node system $H_8 = 16$, but C would then be just 20.
(54) The 60^3 lattice system was 90% filled with an equal number of $\mathbf{A}_2$ molecules and $N\mathbf{B}_3$ molecules distributed on the lattice randomly and then randomised by 2.6 M movements, which corresponded to five correlation times of an orientation correlation function.[46] Periodic boundary conditions applied. The methodology was similar to that reported in the study

of the $\mathbf{A}-X-X-N(-\mathbf{B})_2$ system,[30] whose monomer was obtained from a pair of the present monomers. The reactions of the **A** and **B** groups were performed randomly whenever two such pairs were found by the CHOICE routine.[30] The mean and standard deviations we report were obtained from 8 replications.

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