Cycles frustrating fractal formation in an AB_2 step growth polymerization

Colin Cameron,[a] Allan H. Fawcett,*[b] Cecil R. Hetherington,[b] Richard A. W. Mee[b] and Frederick V. McBride[c]

[a] *Courtaulds Coatings, Stoneygate Lane, Felling, Gateshead, UK NE10 0JY*
[b] *School of Chemistry, The Queen's University of Belfast, UK BT9 5AG*
[c] *Institute of Computer-Based Learning, The Queen's University of Belfast, UK BT9 5AG*

The step growth of a flexible AB_2 monomer, normally considered to produce dendrimers or fractal molecules, as they are themselves self-similar to their branches, is frustrated by the formation of one cycle within each molecule, according to a Monte Carlo lattice study of the evolution of the topological trees that are embedded in three-dimensional space; the number of cycles of m residues is well fitted by the relationship $R_m = K_0 p_a{}^m m^{-e}$, p_a being the extent of reaction of the A groups; at the end of a polymerization of N_0 monomers the total number of cycles, and of molecules, is given by the product of K_0 and the Euler–Riemann function $\xi(e)$ so there is a simple relationship between these quantities and the mean number average degree of polymerization at infinite time: $N_0 = K_0 <x>_{n,\infty} \xi(e)$.

The step growth of an AB_2 monomer, the next more elaborate after the AB system, is usually considered to follow the classical branching pattern of polymerization of Flory,[1,2] the molecules evolving in the forms of Cayley trees,[3] each being rooted upon an A group. At each step the A group of one molecule reacts with a B group of another. A and B groups might form, for example, ester links. The growth has a fractal characteristic, for at each step molecules and branches are self-similar.[4] The assumption that intramolecular reactions do not take place, or the neglect of them in the treatment, means that molecules tend towards an infinitely high molecular mass with one A group each.[1] This common[5] assumption is inherently unrealistic, unless some special stiffness factor applies, such as the presence of *p*-substituted aromatic rings.[6] We envisage intramolecular reactions in molecules that have several flexible bonds between the functional groups, each bond being subject to simple rotational isomeric state considerations,[7] as when developing step-growth chemistry of difunctional monomers did Carothers, who recognised the formation of small rings as competing with linear growth.[8] To tackle such issues in a manner that allows the proper competition in three-dimensional space between fractal growth to yield trees and their cyclisation to yield graphs[3,9] we have embedded them upon a lattice of a type that we have devised to minimise any effect from its particular structure,[10] and explore it with the Monte Carlo method to establish the involved and elusive pattern of behaviour.[11,12] Our three-dimensional lattice model for step growth[10] resembles the two-dimensional fluctuating bond model used for other purposes:[13] components of the structures are linked through bonds that lie on the lattice spacings, l, on the in-plane diagonals, $\sqrt{2}l$, and on the through-space diagonals, $\sqrt{3}l$. (One such bond corresponds to several covalent bonds in a real molecule.[10,13]) Here we represent the monomer on four lattice sites as $A–N(B)_2$, the A group and the two B groups attached directly to the node N. This allows the explicit representation as a three-membered ring of the loop, the pendent structure that forms from an A group and a B group on the same node. 10% of the lattice sites were left vacant to represent free volume to facilitate movement throughout the polymerization.

We show a single monomer and a dimer placed upon the lattice in two dimensions in Fig. 1(*a*) in the form of Cayley trees. In Fig. 1(*b*) is the structure obtained by a B group movement, and the product after that dimer reacts to form a loop. In Fig. 1(*c*) is a hexamer with two possible internal reactions of the A group, and one is performed. Though this is rather confined, it does show that, as the lattice-represented molecule grows in size, the A group may become surrounded by an increasing number of B groups within the same molecule, and the chance of an intramolecular reaction may well increase. A group reactions will take place quite readily for there is always an excess of B groups. A simple consideration will recognise that eventually all the free A groups, located throughout at the root of a tree,[3] if not used in a step growth to enhance the degree of polymerization, will be so consumed, and then growth within the system will cease. This may have happened with a tetrafunctional siloxane alkene system,[14] for it was reported that the molecular mass was not increased by extra time or catalyst.

Initially the molecules were placed in random orientations within layers, and then were moved to randomise their configurations and positions. A,B pairs adjacent upon the lattice were randomly joined by a new bond, and simultaneously units moved upon the lattice by exchanging bead sites within the constraints of the molecular framework to randomise configurations.[15,16] We have tested that movements cause no bond or unit to pass through another: topological requirements are respected.[15] Five attempts at movement were performed each time a reaction was with success rates (> 70%) higher than for a single chain on a simple cubic lattice.[17] The competing processes of chain branching and cycle formation thus take place in a manner that faithfully reflects the considerations of space, topology and configurations, as the A groups react with the excess of B groups present. (This competition is also present in gel formation.[18,19]) For the system of 60^3 lattice sites, we used 5M CHOICE[11] or time cycles, when only 0.003% of the A groups remained.

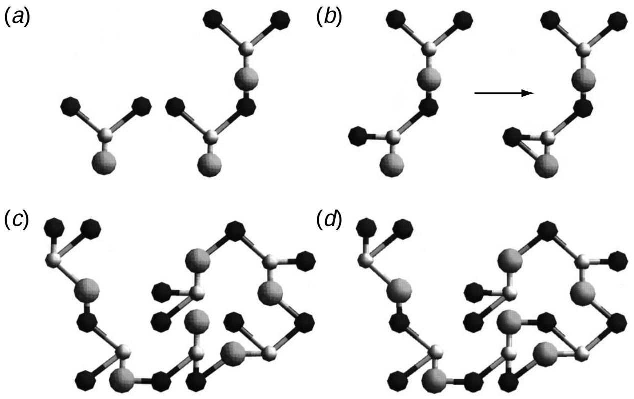

Fig. 1 (*a*) AB_2 monomer and dimer displayed as trees, (*b*) dimer after a B group movement that facilitates the reaction whose product is shown, (*c*) a representative hexamer: note how the A end group is adjacent to two B groups on the same molecule, (*d*) the structure formed by an intramolecular reaction: a two-residue ($m = 2$) cycle with two two-residue tails. The products in (*b*) and (*d*) lack A groups. These illustrations are drawn in two dimensions; the simulations were performed in three dimensions.

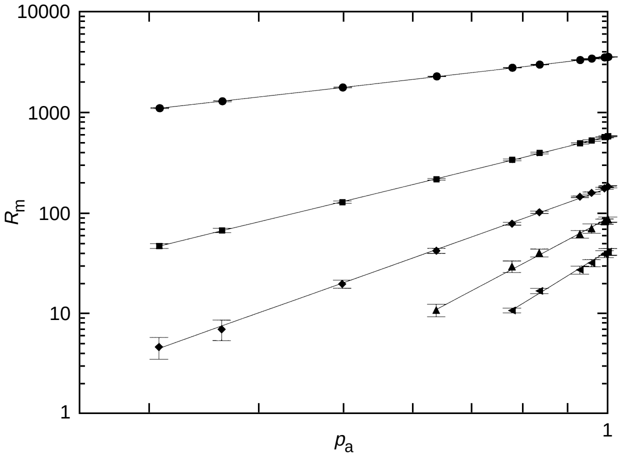

Fig. 2 Logarithmic plots of R_m, the number of rings of size m found in the system, against the extent of reaction, p_a. The lines fall in the order $m = 1,2,..5$, and have integer slopes.

We obtained from the records R_m, the number of cycles involving m residues, at several values of p_a. From nine simulations we plot the mean data for loops ($m = 1$) and cycles up to $m = 5$ on the log R_m–log p_a plots of Fig. 2, where it may be seen that the points fall onto good straight lines: the slopes of these lines are well given by the integers, m, within a standard error or so [*e.g.* for the cycles with $m = 5$ the exponent obtained by non-linear least-squares fitting[20] is 5.13 (±0.14)]. Thus $R_m = C_m p_a{}^m$. It is not difficult to envisage such integer power relationships as a limiting behaviour at low p_a and when m is small, for example the formation of a loop ($m = 1$) will have a finite probability at the very start, and once a dimer has formed with a chance proportional to p_a its cyclization will have the same proportionality to p_a. But this clearly persists to the end of the reaction and at higher m, where it expresses the structural results of a complex set of serial and parallel chemical reactions within a variety of configurations and structural isomers of an increasingly large range of oligomers.

If we examine the data as a function of m, we find that at each value of p_a they are well fitted by $R_m = A_p m^\gamma$, the values of γ falling linearly with p_a as usual during the reaction.[10] It appears that γ at the end of the polymerization is 2.714 (±0.0005), which is not significantly different from e. These two power relationships may be combined to yield:

$$R_m = K_0 p_a{}^m m^{-\mathrm{e}} \qquad (1)$$

the incidence of rings of size m within the system at any p_a, when growth is kinetically controlled ($K_0 = A_1 = C_1$).

When $p_a = 1$, the total number of rings is the product of K_0 and the Euler–Riemann ξ function,[21] $K_0\ \xi(\mathrm{e}) = K_0\ (1 + 2^{-\mathrm{e}} + 3^{-\mathrm{e}} + \ldots)$, a finite number as $\mathrm{e} > 1$. Since the number of rings and the number of molecules is then identical, for each molecule contains one cycle, we have the relationship between the initial number of molecules, N_0 the number average degree of polymerization finally achieved, $<x>_{n,\infty}$:

$$N_0 = K_0 <x>_{n,\infty} \xi(\mathrm{e}) \qquad (2)$$

Taking our value of $C_1 = 3564 \pm 3 = K_0$, we find $<x>_{n,\infty}$ to be 10.75 ± 0.01 model residues, a number which compares well with the ratio of the number of molecules present at the start to that at the end, 10.78 ± 0.07. A real AB_2 molecule may have a different propensity to form loops from the 78.2% predicted in this calculation, depending upon the configurations it might adopt and the possibilities of ring strain,[7] so cycle numbers may deviate from eqn. (1). (There might be too few bonds to allow a reaction between the A and B functional groups to form loops: then rings of size $m = 2$ might assume the main role for limiting the formation of high molecular mass material.[16]) We note a second study using a different lattice representation of the flexible AB_2 monomer found essentially the same behaviour:[22] the forms of eqns. (1) and (2) are not dependent upon the monomer representation. As well as first utilising e,[23] Euler also introduced the ξ-function with real arguments when developing number theory.[21] Here e appears unusually as an exponent of the integers m in this account of the formation of single cycle graphs from Cayley trees when both are embedded and growing from AB_2 monomers within three-dimensional space.

This AB_2 step growth follows a complicated pattern of two competing processes, the development of highly branched structures resplendent with functional groups and simultaneous cyclizations to give a range of ring sizes. Though cyclization consumes only a small proportion of the A functional groups, the proportion being 1 in $<x>_{n,\infty}$, it does eventually terminate the polymerization. Fractal formation by a flexible AB_2 monomer is frustrated by the formation of cycles.

C. R. H. thanks DENI for a CAST Studentship, supported by Courtaulds Coatings and R. A. W. M. thanks the EPSRC for a Fellowship.

References

1 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, ch. 9.
2 P. J. Flory, *J. Phys. Chem.*, 1942, **42**, 132.
3 R. J. Wilson, *Introduction to Graph Theory*, Longman, Harlow, 4th edn., 1996.
4 B. B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, Oxford, 1982.
5 E. Malmstrom and A. Hult, *Macromolecules*, 1996, **29**, 1222.
6 R. H. Jin and Y. Andou, *Macromolecules*, 1996, **29**, 8010.
7 P. J. Flory, *Statistical Mechanics of Chain Molecules*, Interscience, New York, 1969.
8 *Collected Papers of Wallace H. Carothers on Polymerization*, ed. H. Mark and C. S. Whitby, Interscience, New York, 1940.
9 K. Dusek, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 507.
10 A. H. Fawcett, R. A. W. Mee and F. V. McBride, *Macromolecules*, 1995, **28**, 481.
11 *Monte Carlo Methods in Statistical Physics*, ed. K. Binder, Springer Verlag, Berlin, 1979.
12 A. H. Fawcett, in *Macromolecular Chemistry, Specialist Periodical Reports*, ed. A. D. Jenkins and J. F. Kennedy, Royal Society of Chemistry, 1984, vol. 3.
13 I. Carmesin and K. Kremer, *Macromolecules*, 1988, **21**, 2819.
14 L. J. Mathias, T. W. Carothers and R. Bozen, *ACS Polym. Prep.*, 1991, **32**, 82.
15 A. H. Fawcett, R. A. W. Mee and F. V. McBride, *J. Chem. Phys.*, 1996, **104**, 1743.
16 A. H. Fawcett, F. V. McBride, D. McKay and R. A. W. Mee, work in progress.
17 P. Romiszowski and W. H. Stockmayer, *J. Chem. Phys.*, 1984, **80**, 485.
18 M. Gordon and S. B. Ross-Murphy, *Pure Appl. Chem.*, 1975, **43**, 1.
19 C. R. Hetherington, PhD Thesis, Queen's University of Belfast.
20 J. J. Volberg, *Prediction Analysis*, Van Nostrand, London, 1967.
21 *Encyclopedia of Mathematics*, ed. I. M. Kinogradov, Reidel, Lancaster, 1988, vol. 1A–B.
22 C. Cameron, A. H. Fawcett, C. R. Hetherington, R. A. W. Mee and F. V. McBride, submitted.
23 C. B. Boyer and U. C. Merzbach, *A History of Mathematics*, Wiley, Chichester, 2nd edn., 1989.

Received in Cambridge, UK, 22nd May 1997; 7/03567E