(7) Freed, K. F.; Wang, S.; Roovers, J.; Douglas, J. F. *Macromolecules* **1988**, *21*, 2219.
(8) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(9) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(10) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(11) Zimm[9] originally used $h = N^{1/2}f_0/(12\pi^3)^{1/2}\sigma\eta_s$. Later $h^* \equiv h/N^{1/2}$ was introduced by: Thurston, G. B.; Morrison, J. D. *Polymer* **1969**, *10*, 421.
(12) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980; pp 183-198.
(13) Sammler, R. L.; Schrag, J. L.; Lodge, A. S. Rheology Research Center Report No. 82; University of Wisconsin—Madison: Madison, WI, 1982.
(14) Sammler, R. L.; Schrag, J. L. *Macromolecules* **1988**, *21*, 3273.
(15) Johnson, R. M.; Schrag, J. L.; Ferry, J. D. *Polym. J.* **1970**, *1*, 742.
(16) Osaki, K.; Mitsuda, Y.; Johnson, R. M.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *5*, 17.
(17) Warren, T. C.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *6*, 467.
(18) Soli, A. L.; Schrag, J. L. *Macromolecules* **1979**, *12*, 1159.
(19) Lodge, T. P.; Schrag, J. L. *Macromolecules* **1982**, *15*, 1376.
(20) Martel, C. J. T.; Lodge, T. P.; Dibbs, M. G.; Stokich, T. M.; Sammler, R. L.; Carriere, C. J.; Schrag, J. L. *Faraday Symp. Chem. Soc.* **1983**, *18*, 173.
(21) Tschoegl, N. W. *J. Chem. Phys.* **1963**, *39*, 149.
(22) Ptitsyn, O. B.; Eisner, Y. E. *Zh. Fiz. Khim.* **1958**, *32*, 2464.
(23) Tschoegl, N. W. *J. Chem. Phys.* **1964**, *40*, 473.
(24) For example: Fixman, M. *J. Chem. Phys.* **1966**, *45*, 785, 793.
(25) Sammler, R. L.; Schrag, J. L. *Macromolecules* **1989**, *22*, 3435.
(26) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.
(27) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986; pp 108-116.
(28) Equation 13 gives a corrected value for the G'' prefactor in ref 27, p 116, eq 4.167.
(29) Muthukumar, M. *J. Chem. Phys.* **1985**, *83*, 3161.
(30) Seery, T. A. P.; Shorter, J. A.; Amis, E. J. *Polymer* **1989**, *30*, 1197.
(31) Meyerhoff, G.; Appelt, B. *Macromolecules* **1979**, *12*, 968.
(32) Schulz, V. G. V.; Baumann, H. *Makromol. Chem.* **1963**, *60*, 120.
(33) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4551.
(34) Inagaki, H.; Suzuki, H.; Fujii, M.; Matsuo, T. *J. Phys. Chem.* **1966**, *70*, 1718.
(35) Kotera, A.; Matsuda, H.; Konishi, K.; Takemura, K. *J. Polym. Sci. C* **1968**, *23*, 619.
(36) Birnboim, M. H.; Elyash, L. *J. Bull. Am. Phys. Soc.* **1966**, *11*, 165.
(37) Schrag, J. L.; Johnson, R. M. *Rev. Sci. Instrum.* **1971**, *42*, 224.
(38) Amis, E. J.; Hair, D. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 273.
(39) Hair, D. W.; Amis, E. J. *Proc. Am. Chem. Soc., Div. Polym. Mater. Eng.* **1988**, *59*, 1121.
(40) Hair, D. W.; Niertit, F.; Hodgson, D. F.; Amis, E. J. *Rev. Sci. Instrum.* **1989**, *60*, 2780.
(41) Reference 12, p 213.
(42) Mitsuda, Y.; Schrag, L. L.; Ferry, J. D. *Polym. J.* **1973**, *4*, 668.
(43) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(44) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 1122.
(45) Chu, B.; Nose, T. *Macromolecules* **1980**, *13*, 122.
(46) Morris, R. L.; Amelar, S.; Lodge, T. P. *J. Chem. Phys.* **1988**, *89*, 6523.
(47) Schrag, J. L., private communication.
(48) Waldow, D. A.; Johnson, B. S.; Hyde, P. D.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1989**, *22*, 1345.
(49) Bird, R. B.; Curtiss, C. F.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*; John Wiley and Sons: New York, 1987; Vol. 2, pp 76, 162.
(50) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(51) Reference 27, p 93.
(52) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2464.
(53) Pusey, P. N.; Vaughn, J. M.; Williams, G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1969.
(54) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.
(55) Rosser, R. W.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1978**, *11*, 1060.
(56) Sammler, R. L., private communication.
(57) Lodge, T. P.; Miller, J. W.; Schrag, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1409.
(58) Lodge, T. P.; Hermann, K. C.; Landry, M. R. *Macromolecules* **1986**, *19*, 1996.
(59) Wang, S.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 1346.
(60) Shiwa, Y.; Oono, Y., submitted for publication in *J. Chem. Phys.*

Monte Carlo Study of Ring Formation during Step-Growth Polymerization in Two Dimensions

Allan H. Fawcett,*[†] Frederick V. McBride,[‡] and Jeffrey Rutherford[§]

Departments of Pure and Applied Chemistry, Computer Science, and Chemical Engineering, The Queen's University of Belfast, Northern Ireland, U.K.

Received February 4, 1989; Revised Manuscript Received April 24, 1989

ABSTRACT: The formation of ring and chain molecules during an irreversible step-growth polymerization has been modeled on a two-dimensional eight-choice lattice and examined by the Monte Carlo method. No movement was allowed in the system in this study; consequently, 5.5% of the reactive groups initially present became isolated and remained unreacted, 14.1% of the monomers entered into ring molecules, and the rest became part of chain molecules. 34% of the molecules finally present were ring molecules. Mean numbers of residues in the rings and chains were obtained. The distribution function for the number of ring molecules of size m had the form $R_m = A_0 m^{-\gamma}$, with γ falling from an initial value of more than 9 to a final value of 2.7 as the degree of polymerization rose from 0.2 to 0.945.

Introduction

The natural consequence of the nonreversible step-growth polymerization of a bifunctional monomer, if sufficient time elapses and if the monomers are in a fluid phase, is for all the material to form ring molecules. On a molecular level, at each growth stage the end group of monomer, oligomer, or polymer either reacts with an end group of a second such molecule, to form a longer chain, or reacts with the other end of the same molecule to form a ring. Rings can form provided that the simple geometrical requirement is satisfied that the two end groups of a linear molecule are adjacent to each other, but once a ring molecule has formed it cannot grow any larger (unless a bond-breaking reaction was first to open the ring and recreate end groups). Rings accumulate in number from chain molecules of the same size, but chain molecules grow in size progressively. In consequence, only small rings may form during the initial stages of the step-growth process,

---

[†] Department of Pure and Applied Chemistry.
[‡] Department of Computer Science.
[§] Department of Chemical Engineering.

0024-9297/89/2222-4536$01.50/0 © 1989 American Chemical Society

but larger rings may be expected to form toward the end. These considerations also apply to a system of monomers in the solid state, but then there is the extra factor, created by the immobility of the units, that the reaction cannot proceed to completion.

The initial treatments of step growth (in solution in three dimensions) described and analyzed the kinetics in terms of second-order reactions of end groups and neglected ring formation.[1-2] Jacobson and Stockmayer have examined the equilibrium that may be obtained in a system of macromolecules produced by a step-growth reaction when a small fraction of end groups remains as a result of a minor proportion of the reverse reaction;[3] from the chain configuration statistics an expression has been produced for the number distribution of rings.[3,4] In this, our initial exploration of these ideas, we use a computer model of step growth in two dimensions to explore the incidence of rings as a fraction of the total quantity of material present and to obtain ring size distributions during the formation of macromolecules, when their formation is governed by chain configuration, excluded volume, and reaction kinetic considerations. The bifunctional residues here are fixed on their initial lattice positions: no movement is allowed, so the simulation corresponds to a reaction in a solid crystalline monolayer. The model has been explored by the Monte Carlo method.

Lattice Model

The monomers were placed on a lattice in two dimensions. Each monomer could form bonds with two of its eight immediate neighbors. For linking residues above, below, and to each side of the central residue, bonds of unit length were required, but bonds of length $\sqrt{2}$ were required between residues that are directed diagonally to the corners of the square. The eight-choice lattice was chosen to enhance the number of configurations available to a molecule of a particular size, in an atttempt to minimize any effect that might be associated with the structure of the lattice. Periodic boundary conditions were applied, so that units at an edge had the capacity to form a bond with units on the opposite edge of the system and so they suffered no diminution in their capacity to react on account of their location. Molecules that grew out of one side thus entered again on the other.

Each step growth was started by the selection of a lattice site at random, an event which was counted as one unit of time, T. If the site so selected had not reacted twice, one of its eight neighbors was selected at random, and a bond was formed with a probability, P_b, which was the product of the two probability factors, P_r, of the units that were concerned. After a bond had formed, the information in the vector for each residue of the newly formed molecule was revised to record the size of the molecule, whether it was a ring or a chain, and the addresses of the neighbors to which the residues were directly linked by a bond. For this study of the polymerization, the value of P_r for a unit at the middle of a chain was 0, for an end group it was 0.5, and for a monomer it was 1. This choice of values for end groups and monomers maintains the simple ratio of their number of functional groups.[5] A further factor governing bond formation arose from spatial considerations: a diagonal bond was not allowed to form between two residues if another bond had previously formed across the same space in the opposite diagonal direction.

When growth took place, chains and rings formed randomly during a reaction as a consequence of the steady accumulation of individual step growths in the system. The number of rings and chains of each size was recorded separately at previously chosen intervals of time during a simulation, together with the number of bonds that had formed—the measure of the extent of the reaction. Within each run, simulations were repeated a number of times, N_{rep}, before the accumulated totals of ring and chain numbers and other factors were placed in a file in the computer system.

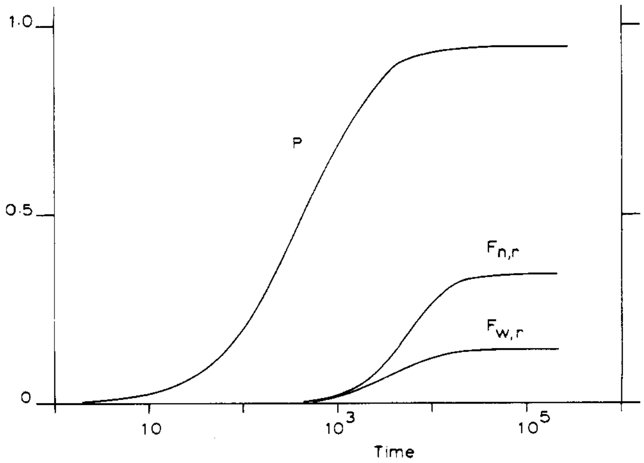

Figure 1. Plots of the extent of reaction, p, the number fraction of ring molecules, $F_{n,r}$, and the fraction of the mass that is rings, $F_{w,r}$, as a function of time of reaction, T, on a logarithmic scale.

The PASCAL language was used for programming the model on an ICL Series 39 Level 80 main-frame computer.[6] The set concept of the language enabled reactions between neighbors to be readily expressed. A pseudo random number sequence was obtained from the NAG routine G05CAF that was seeded in a random manner with procedure G05CCF when each reaction was repeated. The smallest rings that could form contained three units, and others formed once chain tetramers, pentamers, hexamers, and so on had grown, and even a ring as large as 63 units was found. In the standard simulation we used a square lattice of $L_s = 20$ units, with a number, N_{rep}, of 50 repetitions, but for some simulations with short reaction times, 5000 repetitions were performed to generate a satisfactory number of rings for statistical analysis. At each T there were obtained at least 16 and generally more than 22 different simulations. Means and standard deviations were obtained from a set of simulations for factors such as the number of bonds formed, the number of molecules, and the number and weight of ring molecules.

Results and Discussion

The extent of reaction, p, was related to the number of bonds that form, N_b, and the number of molecules initially present in the system, N_o, by

$$p = N_b/N_o \tag{1}$$

We plot p in Figure 1 against the time, T, on a logarithmic scale. At the start inspection showed that the value of p rose linearly with T, but as sites became occupied by dimers and by other oligomers, the chance that a randomly chosen pair of residues could react fell from the initial value of unity, and the rate of the reaction was correspondingly reduced. Had the initial rate applied throughout, for the 20 × 20 system, half the reactive groups would have reacted after 200 units of time. For the model, the extent of reaction was 0.50 at approximately 420 units of time, was 0.75 at approximately 1410 units of time, but did not reach unity even after a lapse of time of 500 000 units. In fact, the extent of reaction approached a limiting value as T rose, being effectively constant once T passed 50 000 units: from the 23 reactions with time of 500 000 units, the value of p was 0.9451 (±0.0011), but a slightly

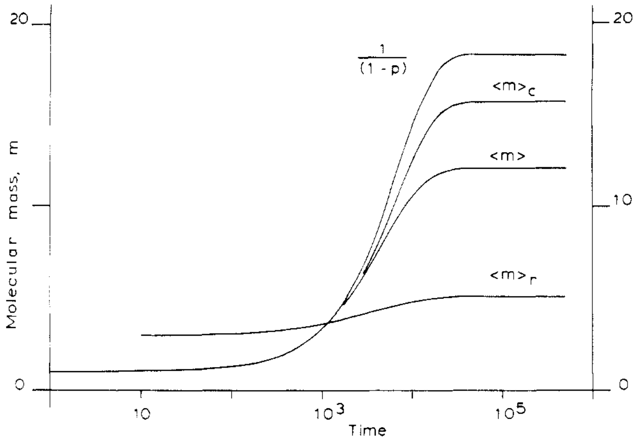

Figure 2. Plots of mean ring size, $\langle m \rangle_r$, mean chain size, $\langle m \rangle_c$, and mean molecule size, $\langle m \rangle$, obtained from the Monte Carlo simulation and of the Carothers function (eq 3) against the logarithm of the time, T. The function differs from the Monte Carlo result for $\langle m \rangle$, because ring formation increases p but does not alter $\langle m \rangle$.

larger mean for p of 0.9452 (±0.0010) was obtained for the 33 or more reactions we performed for times of 100 000 and 200 000 units (the errors are standard deviations). The limiting value is a property of the lattice model we have adopted and was determined by the number of monomers and of oligomer end groups that had become isolated, and so were unable to react, as a consequence of their eight neighbors becoming linked to each other and to other residues.

In the absence of ring formation, at time T the number of bonds that form plus the number of molecules, N_t, would be constant, at the value of the initial number of monomers, N_0. When a ring forms, the number of molecules remains unaltered, but the number of bonds rises by one. There is thus the simple relationship between the value of N_t, the number of bonds that have formed, N_b, and the number of rings that have formed, N_r:

$$N_b + N_t = N_0 + N_r \tag{2}$$

Ring formation may be measured directly in three ways: by N_r itself (or N_r/N_0), by the weight of material that enters into rings, as a fraction of the total number of residues in the system, $F_{w,r}$, and by the number fraction of molecules that are rings, $F_{n,r} = N_r/N_t$. The latter factors are plotted in Figure 1. It may be seen that neither measure of ring formation grows much until p has passed 0.50 but that before the reaction has ceased significant quantities of rings have formed. The limiting values of $F_{n,r}$ and of $F_{w,r}$, taken from the 23 results obtained at T = 500 000, were 0.337 (±0.017) and 0.1412 (±0.0069), respectively: one-third of the molecules that formed were rings, but only 14% of the residues initially present entered into rings.

As the formation of rings is accompanied by a rise in N_b and p, but not by a rise in N_t, the mean degree of polymerization of the molecules that had formed, $\langle m \rangle = N_0/N_t$, is less than the value provided by the Carothers equation[1]

$$\overline{\mathrm{DP}_n} = 1/(1 - p) \tag{3}$$

as we show in the plot given in Figure 2. The two curves, for $\langle m \rangle$ and 1/(1 − p), begin to deviate from each other once rings form in significant quantities. Even for the chain fraction alone the Carothers expression provides an overestimation of the mean molecular size. By combining eq 1 and eq 2, we obtain

$$1/(1 - p) = N_0/(N_t - N_r) \tag{4}$$

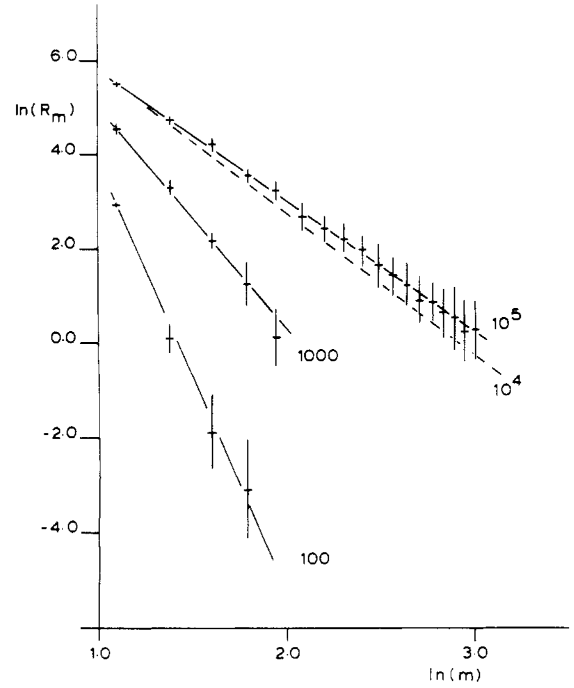

Figure 3. Plots of R_m, the number of rings of size m, vs m on a double-logarithmic scale for the times T that are indicated at the end of each line. The error bars shown are standard deviations. The data was obtained from at least 16 simulations of the process, each simulation consisting of 50 reactions on the 20 × 20 residue square lattice. Only the fitted line has been drawn for T = 10 000. For T = 100 the points have been raised by an arbitrary amount (2.60), to place them on the plot. To obtain a satisfactory number of rings at T = 100 (and 200), N_{rep} was 5000, but the data have been adjusted to a value of 50.

The denominator of the right-hand side of this equation is simply the number of chain molecules, N_c, but the numerator includes those monomers that became residues in rings. When rings first formed (and none were found until T = 10), their mean size, $\langle m \rangle_r$, was 3.00, but the value slowly rose to a limiting value of 5.06 (±0.34) as is shown in Figure 2. Limiting values of the mean molar mass of chains, $\langle m \rangle_c$, of the mean molar mass of all the molecules, $\langle m \rangle$, and of the function $1/(1 - p)$ were found to be 15.65 (±0.58), 12.08 (±0.22), and 18.21 (±0.36), respectively. Rings are thus much smaller than the chains, in terms of their average size and in their proportion of the mass of the system, when movements on the lattice do not take place.

To allow a study of the ring size distributions at each reaction time greater or equal to 100 units, the mean number of each ring size and its standard deviation was computed. The results invariably showed that the number of ring molecules diminished as ring size increased, particularly at the start of the process, when few rings had formed. Some of the ring distributions are plotted on Figure 3 using a double-logarithmic scale, as suggested by the form of eq 5 that was found to be suitable for describing ring number distributions under equilibrium conditions.[3,4] This equation does appear to be suitable for the data. Using the NAG routine EO4FBA,[7] the ring distributions were fitted with eq 5:

$$R_m = A_0 m^{-\gamma} \tag{5}$$

In the fitting, the square of each residual (the difference between the actual and the predicted values of R_m) was weighted according to the square of the reciprocal of the standard deviation of the value for R_m.[8] We used only those values of R_m that were greater than ≃1: 21 values

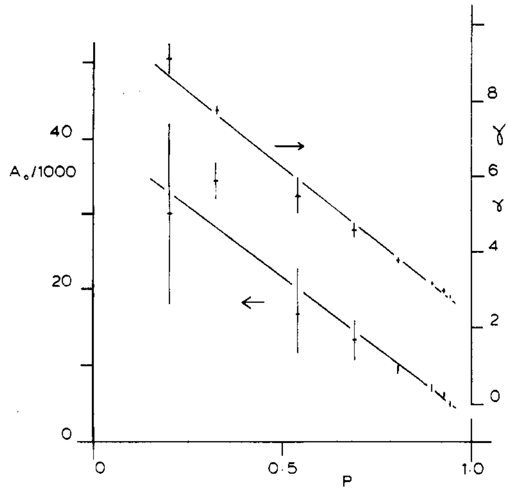

Figure 4. Plots of the γ and A_0 parameters, obtained by fitting eq 5 to simulation data at different reaction times, against the extent of reaction, p. The parameters are nearly linearly related to p. (As for Figure 3, the A_0 values correspond to the 20 × 20 system, with $N_{\text{rep}} = 50$.)

were used for $T = 100\,000$, but only 6 values, for $T < 1000$. There is little indication of any systematic deviation of the first few points from or of oscillations about the line, as might occur if the eight-choice lattice structure was influencing the data. The equation appeared to give an adequate account of the distribution over the whole range: for example, for the most extensive set of data (30 repeats) that were obtained when T was 100 000 and that is shown at the top of Figure 3, the value we found for γ was little altered by using 19 values of R_m ($\gamma = 2.728 \pm 0.017$) or by using merely the first 10 values ($\gamma = 2.673 \pm 0.019$). The values of γ fell progressively during the reaction, as larger rings were able to form from the larger chain molecules that had then developed.

We plot the values of γ and of A_0 against p in Figure 4, which shows that there is an approximately linear relationship between p and each of these factors. (The lines shown in Figure 4 have the following forms: $A_0 = 40\,400–37\,250p$ and $\gamma = 10.25–7.85p$.) The mean of the three values we found for γ at the longest times used was 2.73 (±0.02), when p was 0.945 and the first 20 values of R_{m} were fitted. The values found for γ, even at high p, are greater than the value of 2.00 for the exponent of m that would be expected for the equilibrium distribution function, if the treatment[3] were extended to the present two-dimensional case.

In conclusion, we record that both ring and chain molecules have been formed by an elementary model of the kinetics of the step-growth process on an eight-choice two-dimensional lattice. In this study in the absence of movement the simulation corresponds to a reaction in a crystalline state, the maximum extent of reaction achievable was just below 95%, one-third of the molecules so produced were rings, and within the class of ring molecules, the large rings diminish in proportion with ring size significantly faster than would an equilibrium distribution.

Acknowledgment. We thank The Queen's University of Belfast for access to the ICL computer and Dr. G. W. Cran for a helpful discussion.

References and Notes

(1) Flory, P. J. *Introduction to Polymer Chemistry*; Cornell: Ithaca, NY, 1953.
(2) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(3) Jacobson, H.; Stockmayer, W. S. *J. Chem. Phys.* **1950**, *18*, 1600.
(4) Flory, P. J. In *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; Appendix D.
(5) In this respect, the system resembles case I of ref 3, where the reaction is the formation of a Si–O–Si link from two Si–O–H groups.
(6) The PASCAL program was developed as part of a microcomputer-based teaching package by F. E. Crowe (MS Thesis, The Queen's University of Belfast, 1984) and Dr. R. Cromie (MS Thesis, The Queen's University of Belfast, 1987) and was converted to run on the ICL machine by J.R.
(7) Procedure EO4FBA, from NAG library Mk. 4.5, incorporates the Powel Routine, M.J.D. Powell, Harwell Report, AERE-R5947, Her Majesties Stationary Office, U.K., 1968.
(8) Wolberg, J. R. *Prediction Analysis*; Van Nostrand: London, 1967.