Solutions for polymerization kinetics by application of graph theory

Zhou Pu and Sun Zaijian
Department of Organo-Chemical Engineering, Jiangsu Institute of Chemical Technology, Changzhou, Jiangsu, Peoples Republic of China

Liu Qirong
Department of Polymeric Materials, Chengdu University of Science and Technology, Chengdu, Sichuan, Peoples Republic of China
(Received 19 November 1984)

Some polymerization kinetic systems in the non-steady state were treated with a graphic theory. It is shown that this solving process is simpler than the general one. The authors' purpose is to illustrate the utility of graphic theory in polymer science, and to stimulate further interest in this topic.

(Keywords: Coates graph: Laplace transformation; monomer transfer; penultimate effect; stereo-configuration; electron transfer)

INTRODUCTION

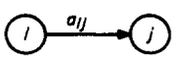
The graphic theory is an important branch of combinatory mathematics[1]. It has undergone extensive development over the past twenty years and still accounts for a major portion of the research effort expended and its applications continue to grow rapidly. Successful applications of the graphic theory in computer science[2], theoretical physics[3] and economics[4] have demonstrated its use in more and more fields. The subject of chemistry was introduced to graphic theory much earlier, however. The idea of a 'Tree' was successfully invoked by Cayley[5] to predict the isomeric forms of alkane in 1857. Later on quantum chemists represented topological matrices as graphs to calculate relevant parameters[6-8]. The graphic theory was also adapted to the study of statistical thermodynamics in the non-equilibrum state[9,10]. In recent years, graphic theory has penetrated into polymer science. Some graphs are used to study random condensation processes by analogy with the *f*-functional group[11,12]. The graphs may also be applied to solve polymerization kinetic systems, especially in non-steady state cases[13,14].

It is well known that it is a complicated task to solve the set of differential equations for such a reaction by the general method. However, this solving process will be simpler and more convenient is we used the Laplace transormation and graphic theory. This paper provides a graphic solution for some polymerization kinetics in non-steady state cases.

The basic concept of the graph and its calculating rule

The graph consists of a vertex and an edge. The graphic theory provides simple techniques for constructing models of systems, and powerful methods for their analysis and optimization.

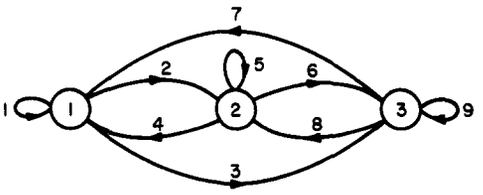
For example, a matrix of order $n \times n$, $A=(a_{ij})_{n\times n}$, may be represented as a graph consisting of n vertices. Each non-zero element a_{ij} in matrix A is an oriented edge which flows from i to j,



Thus, the matrix

$$A=\begin{bmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{bmatrix} \tag{1}$$

can be shown as



These graphs which consist of n vertices corresponding to $n \times n$ matrices are called Coates graphs. We introduce the calculating rule for a Coates graph as follows.

A set of equations having the form

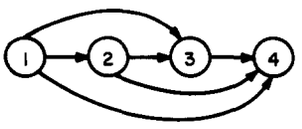
$$\begin{bmatrix} a_{11} & & & \\ a_{12} & a_{22} & & \\ a_{13} & a_{23} & a_{33} & \\ a_{14} & a_{24} & a_{34} & a_{44} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{2}$$

that is 4 linear equations with 4 unknowns X_1, X_2, X_3 and X_4 can be written more briefly as:

$$A \cdot X = B \tag{3}$$

where A, X and B represent the corresponding matrices in equation (2).

Its coefficient matrix A may be shown as:

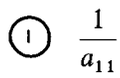


The notations a_{ii} and a_{ij} are denoted to the weight of the vertex i and the edge which flows from i to j, respectively. Thus each unknown X_i in equation (2) can be attained

0032-3861/86/020275-06$03.00

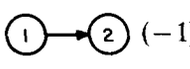
directly. The value of X_i equals the sum of all paths' contributions and the contribution of each path may then be calculated. The weight product of all edges along the path is taken as the numerator and that of the vertices the denominator. Multiplying it by $(-1)^k$, we can obtain the contribution of one path. Where K is the number of edges. We take 1 as the numerator for a source vertex. According to these rules, we can write the unknowns of equation (2) in the following way.

X_1: There is only a source vertex.



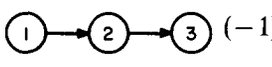
$$X_1=\frac{1}{a_{11}} \tag{4}$$

X_2: One path



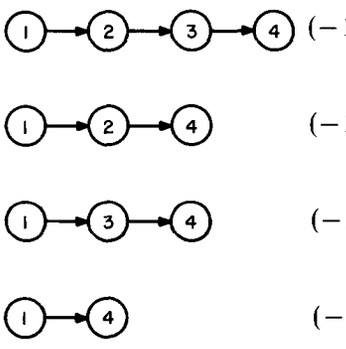
$$X_2=-\frac{a_{12}}{a_{11}a_{22}} \tag{5}$$

X_3: Two paths



$$X_3=-\frac{a_{13}}{a_{11}a_{33}}+\frac{a_{12}a_{23}}{a_{11}a_{22}a_{33}} \tag{6}$$

X_4: Four paths



$$X_4=-\frac{a_{14}}{a_{11}a_{44}}+\frac{a_{13}a_{34}}{a_{11}a_{33}a_{44}}+\frac{a_{12}a_{24}}{a_{11}a_{22}a_{44}}-\frac{a_{12}a_{23}a_{34}}{a_{11}a_{22}a_{33}a_{44}} \tag{7}$$

There are m source vertices, if the constant matrix B contains m non-zero elements and if these elements are not equal to 1, rather $a, b, c \ldots$, then correspondingly we multiply by $a, b, c \ldots$

The graphic method on living polymerization with monomer transfer

In a living polymerization, when monomer transfer is occurring, the kinetic scheme may be written as follows.

The scheme involves three stages:

(1) initiation:

$$\mathrm{I}+\mathrm{M}\xrightarrow{K_\mathrm{i}}\mathrm{N}_1^*$$

(2) propagation:

$$\mathrm{N}_{n-1}^*+\mathrm{M}\xrightarrow{K_\mathrm{p}}\mathrm{N}_2^*(n>1)$$

(3) transfer:

$$\mathrm{N}_n^*+\mathrm{M}\xrightarrow{K_\mathrm{t}}\mathrm{N}_n'+\mathrm{N}_1^*$$

where I, M, N_n^* and N_n' denote the initiator, monomer, active n-mer and dead n-mer, respectively; K_i, K_p and K_t are the rate constants for initiation, propagation and transfer, respectively.

The differential rate equations corresponding to the above kinetic scheme are:

$$\mathrm{dI}/\mathrm{d}t=-K_\mathrm{i}\mathrm{IM} \tag{8}$$

$$\mathrm{dN}_1^*/\mathrm{d}t=K_\mathrm{i}\mathrm{IM}+K_\mathrm{t}\sum_{n\geq 1}\mathrm{N}_n^*\mathrm{M}-K_\mathrm{p}\mathrm{N}_1^*\mathrm{M}-K_\mathrm{t}\mathrm{N}_1^*\mathrm{M} \tag{9}$$

$$\mathrm{dN}_n^*/\mathrm{d}t=K_\mathrm{p}\mathrm{N}_{n-1}^*\mathrm{M}-K_\mathrm{p}\mathrm{N}_n^*\mathrm{M}-K_\mathrm{t}\mathrm{N}_n^*\mathrm{M} \tag{10}$$

$$\mathrm{dN}_n'/\mathrm{d}t=K_\mathrm{t}\mathrm{N}_n^*\mathrm{M} \tag{11}$$

If we denote $X=\int_0^t K_\mathrm{p}\mathrm{M}\mathrm{d}t$, we can obtain $\mathrm{d}X/\mathrm{d}t=K_\mathrm{p}\mathrm{M}$. For convenience, we shall adopt the following shorthand notations:

$$K_\mathrm{i}/K_\mathrm{p}=\alpha \qquad K_\mathrm{t}/K_\mathrm{p}=\beta$$

Substituting these notations into equations (8)–(11) and using the Laplace transformation, we can obtain the following set of linear equations. (Where s is a complex parameter, it is defined as $F(s)=\int_0^{+\infty}f(x)\mathrm{e}^{-sx}\mathrm{d}X$)

$$(s+\alpha)\phi=\mathrm{I}_0 \tag{12}$$

$$(\beta-\alpha)\phi+(s+1+\beta)\mathcal{N}_1^*=-\beta\mathrm{I}_0 \tag{13}$$

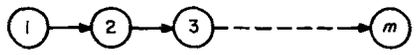
$$(-1)\mathcal{N}_{n-1}^*+(s+1+\beta)\mathcal{N}_n^*=0 \tag{14}$$

$$(-\beta)\mathcal{N}_n^*+(s)\mathcal{N}_n'=0 \tag{15}$$

Here $\mathcal{N}$ and ϕ are the images of the unknowns in equations (8)–(11), and I_0 is the initial value of initiator. Its matrix form is as follows:

$$\begin{bmatrix} a_{11} & & & & & \\ a_{12} & a_{22} & & & & \\ & a_{23} & a_{33} & & & \\ & & a_{34} & a_{44} & & \\ & & & & \cdots & \\ & & & & a_{m-1,m} & a_{mm} \end{bmatrix}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ \vdots \\ X_m \end{bmatrix}=\begin{bmatrix} A \\ B \\ 0 \\ \vdots \\ 0 \end{bmatrix} \tag{16}$$

where $m=n+2$. The subscript i indicates the unknown ordinal and j that of the equation. This corresponds to a weighted digraph consisting of two source vertices and $(m-1)$ edges. The graph is as follows:



We can obtain each solution in equations (8)–(11) as follows:

$$X_1=\frac{A}{a_{11}} \tag{17}$$

$$X_2=-\frac{Aa_{12}}{a_{11}a_{22}}+\frac{B}{a_{22}} \tag{18}$$

$$X_3=\frac{Aa_{12}a_{23}}{a_{11}a_{22}a_{33}}-\frac{Ba_{23}}{a_{22}a_{33}} \tag{19}$$

$$X_m=(-1)^{m-1}\frac{Aa_{12}a_{23}\cdots a_{m-1,m}}{a_{11}a_{22}a_{33}\cdots a_{mm}}+(-1)^{m-2}\frac{Ba_{23}a_{34}\cdots a_{m-1,m}}{a_{22}a_{33}a_{44}\cdots a_{mm}} \tag{20}$$

Using the Heaviside expansion or the table of Laplace transforms, we can obtain:

$$\mathrm{I}=\mathrm{I}_0\mathrm{e}^{-\alpha x} \tag{21}$$

$$\mathrm{N}_1^*=\mathrm{I}_0\left\{\frac{\beta}{1+\beta}(1-\mathrm{e}^{-(1+\beta)x})+\frac{(\alpha-\beta)}{1+\beta-\alpha}\mathrm{e}^{-\alpha x}(1-\mathrm{e}^{-(1+\beta-\alpha)x})\right\} \tag{22}$$

$$\mathrm{N}_n^*=\frac{\mathrm{I}_0\beta}{(1+\beta)^n}\Gamma_{(1+\beta)x(n)}+\frac{\mathrm{I}_0(\alpha-\beta)}{(1+\beta-\alpha)^n}\mathrm{e}^{-\alpha x}\Gamma_{(1+\beta-\alpha)x(n)} \tag{23}$$

$$\mathrm{N}_n'=\mathrm{I}_0\beta\left\{\left[\beta\left(X-\frac{n}{1+\beta}\right)+1-\frac{\beta}{\alpha}\right](1+\beta)^{-n}\Gamma_{(1+\beta)x(n)}-\frac{(\alpha-\beta)}{\alpha(1+\beta-\alpha)^n}\mathrm{e}^{-\alpha x}\Gamma_{(1+\beta-\alpha)x(n)}+\frac{n\beta x^n}{(1+\beta)n!}\mathrm{e}^{-(1+\beta)x}\right\} \tag{24}$$

Evidently the graphic method is more convenient than the general method. Where $\Gamma_{(1+\beta)x(n)}$ and $\Gamma_{(1+\beta-\alpha)x(n)}$ are incomplete gamma functions. Its definition is:

$$\Gamma_{(1+\beta)x(n)}=\frac{1}{(n-1)!}\int_0^x[(1+\beta)x]^{n-1}\mathrm{e}^{-(1+\beta)x}\mathrm{d}[(1+\beta)x]$$

OTHER EXAMPES OF GRAPHIC SOLUTION

The influence of penultimate chain element on the monomer transfer in living polymerization

The penultimate chain element will influence the chain propagation in a living polymerization. If we consider this effect, the kinetic mechanism may be represented as follows:

initiation:

$$\mathrm{I}+\mathrm{M}\xrightarrow{K_\mathrm{i}}\mathrm{N}_1^*$$

propagation:

$$\mathrm{N}_1^*+\mathrm{M}\xrightarrow{K_\mathrm{p}'}\mathrm{N}_2^*$$

$$\mathrm{N}_1\ddagger+\mathrm{M}\xrightarrow{K_\mathrm{p}''}\mathrm{N}_2^*$$

$$\mathrm{N}_{n-1}^*+\mathrm{M}\xrightarrow{K_\mathrm{p}}\mathrm{N}_n^*\quad(n\geqslant 3)$$

transfer:

$$\mathrm{N}_n^*+\mathrm{M}\xrightarrow{K_\mathrm{t}}\mathrm{N}_n'+\mathrm{N}_1\ddagger$$

where $\mathrm{N}_1\ddagger$ is the active monomer due to transfer, which is different from that due to initiation N_1^*.

The kinetic equations are:

$$\mathrm{dI}/\mathrm{d}t=-K_\mathrm{i}\mathrm{IM} \tag{25}$$

$$\mathrm{dN}_1^*/\mathrm{d}t=K_\mathrm{i}\mathrm{IM}-K_\mathrm{p}'\mathrm{N}_1^*\mathrm{M}-K_\mathrm{t}\mathrm{N}_1^*\mathrm{M} \tag{26}$$

$$\mathrm{dN}_1\ddagger/\mathrm{d}t=K_\mathrm{t}\sum_{n\geqslant 1}\mathrm{N}_n^*\mathrm{M}-K_\mathrm{p}''\mathrm{N}_1\ddagger\mathrm{M} \tag{27}$$

$$\mathrm{dN}_2^*/\mathrm{d}t=K_\mathrm{p}'\mathrm{N}_1^*\mathrm{M}+K_\mathrm{p}''\mathrm{N}_1\ddagger\mathrm{M}-K_\mathrm{p}\mathrm{N}_2^*\mathrm{M}-K_\mathrm{t}\mathrm{N}_2^*\mathrm{M} \tag{28}$$

$$\mathrm{dN}_n^*/\mathrm{d}t=K_\mathrm{p}\mathrm{N}_{n-1}^*\mathrm{M}-K_\mathrm{p}\mathrm{N}_n^*\mathrm{M}-K_\mathrm{t}\mathrm{N}_n^*\mathrm{M} \tag{29}$$

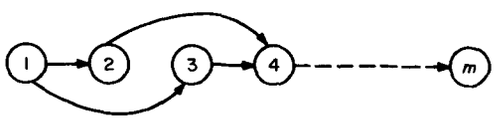
$$\mathrm{dN}_n'/\mathrm{d}t=K_\mathrm{t}\mathrm{N}_n^*\mathrm{M} \tag{30}$$

As mentioned earlier, the matrix form is:

$$\begin{bmatrix} a_{11} & & & & & & \\ a_{12} & a_{22} & & & & & \\ a_{13} & & a_{33} & & & & \\ & a_{24} & a_{34} & a_{44} & & & \\ & & & a_{45} & a_{55} & & \\ & & & & & \cdots & \\ & & & & & a_{m-1,m} & a_{mm} \end{bmatrix}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ \vdots \\ \vdots \\ X_m \end{bmatrix}=\begin{bmatrix} A \\ 0 \\ B \\ 0 \\ \vdots \\ \vdots \\ 0 \end{bmatrix} \tag{31}$$

where $m=n+3$.

The graph corresponding to the above matrix consists of two source vertices and m edges. It is as follows



The respective solutions in equation (31) are as follows:

$$X_1=\frac{A}{a_{11}} \tag{32}$$

$$X_2=-\frac{Aa_{12}}{a_{11}a_{22}} \tag{33}$$

$$X_3=-\frac{Aa_{13}}{a_{11}a_3}+\frac{B}{a_{33}} \tag{34}$$

$$X_m=(-1)^{m-2}\frac{Aa_{12}a_{24}\cdots a_{m-1,m}}{a_{11}a_{22}a_{44}\cdots a_{mm}}+(-1)^{m-2}\frac{Aa_{13}a_{34}\cdots a_{m-1,m}}{a_{11}a_{33}a_{44}\cdots a_{mm}}+(-1)^{m-3}\frac{Ba_{34}a_{45}\cdots a_{m-1,m}}{a_{33}a_{44}a_{55}\cdots a_{mm}} \quad (35)$$

Replacing the transforms by the originals in equations (32)–(35), we obtain the formula for the molecular weight distribution function.

The stereo-configurational sequences in vinyl polymers

Generally, the theoretical treatment of the configurational sequence distribution has been made using a statistical method. We can solve the kinetic equations of the living copolymerization in Bernoulli processes with the aid of a linear differential technique, also.

Assuming there are l and d optical isomers in each structure unit, we have an isotactic placement m consisting of ll or dd pairs, and a syndiotactic placement r consisting of ld or dl pairs, respectively. Let m_n^* and r_n^* represent the active isotactic and syndiotactic sequences, respectively, with degree of polymerization n, while m_n' and r_n' have no activity.

We can write the kinetic mechanism generating these stereoconfigurational sequences as follows:

$$I+M\xrightarrow{K_i}N_1^*$$

$$N_1^*+M\xrightarrow{K_m}m_1^*$$

$$N_1^*+M\xrightarrow{K_r}r_1^*$$

$$m_n^*+M\xrightarrow{K_m}m_{n+1}^*$$

$$m_n^*+M\xrightarrow{K_r}m_n'+r_1^*$$

$$r_n^*+M\xrightarrow{K_r}r_{n+1}^*$$

$$r_n^*+M\xrightarrow{K_m}r_n'+m_1^*$$

The differential rate equations corresponding to the above scheme are:

$$dI/dt=-K_iIM \quad (36)$$

$$dN_1^*/dt=K_iIM-(K_m+K_r)N_1^*M \quad (37)$$

$$d(\Sigma m_n^*)/dt=K_mN_1^*M+K_m(\Sigma r_n^*)M-K_r(\Sigma m_n^*)M \quad (38)$$

$$dm_1^*/dt=K_m(N_1^*+\Sigma r_n^*)M-(K_m+K_r)m_1^*M \quad (39)$$

$$dm_n^*/dt=K_mm_{n-1}^*M-(K_m+K_r)m_n^*M \quad (40)$$

with $X=\int_0^t(K_m+K_r)M\,dt$, $\alpha=K_i/(K_i+K_m)$

and $\beta=K_m/(K_m+K_r)$.

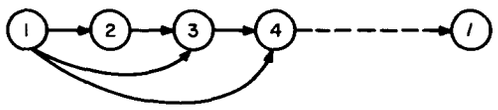
Substituting these notations into the equations (36)–(40), we use Laplace transforms to replace the unknown functions in the above equations.

Clearly, the matrix form is as follows:

$$\begin{bmatrix} a_{11} & & & & & & & \\ a_{12} & a_{22} & & & & & & \\ a_{13} & a_{23} & a_{33} & & & & & \\ a_{14} & & a_{34} & a_{44} & & & & \\ & & & a_{45} & a_{55} & & & \\ & & & & & \cdots & & \\ & & & & & & a_{l-1,l} & a_{ll} \end{bmatrix}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ \vdots \\ X_l \end{bmatrix}=\begin{bmatrix} A \\ 0 \\ B \\ B \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad (41)$$

where $l=n+3$.

As the formulae for r_n^*, r_n' are symmetrically disposed to m_n^*, m_n', we can obtain the distribution functions of the formula only by interchanging β and $(1-\beta)$. The coefficient matrix (41) corresponds to a graph consisting of three source vertices and $(l+1)$ edges, shown as follows:



We can obtain every solution in equation (41) quite conveniently as follows:

$$X_1=\frac{A}{a_{11}} \quad (42)$$

$$X_2=-\frac{Aa_{12}}{a_{11}a_{22}} \quad (43)$$

$$X_3=-\frac{Aa_{13}}{a_{11}a_{33}}+\frac{Aa_{12}a_{23}}{a_{11}a_{22}a_{33}}+\frac{B}{a_{33}} \quad (44)$$

$$X_l=(-1)^{l-1}\frac{Aa_{12}a_{23}\cdots a_{l-1,l}}{a_{11}a_{22}a_{33}\cdots a_{ll}}+(-1)^{l-2}\frac{Aa_{13}a_{34}\cdots a_{l-1,l}}{a_{11}a_{33}a_{44}\cdots a_{ll}}+(-1)^{l-3}\frac{Aa_{14}a_{34}\cdots a_{l-1,l}}{a_{11}a_{44}a_{55}\cdots a_{ll}}+(-1)^{l-3}\frac{Ba_{34}a_{45}\cdots a_{l-1,l}}{a_{33}a_{44}a_{55}\cdots a_{ll}}+(-1)^{l-4}\frac{Ba_{45}a_{56}\cdots a_{l-1,l}}{a_{44}a_{55}a_{66}\cdots a_{ll}} \quad (45)$$

As a next step, we again use the formulae from the Laplace transform table to replace the transforms with the originals.

Anionic polymerization initiated by electron transfer

Chain initiation might conceivably be brought about by electron transfer in an anionic polymerization. An example is the case where vinyl mesitylene polymerization is initiated by sodium-naphthalene in tetrahydrofuran. This kinetic mechanism has the following form:

$$dI/dt=-K_iIM \quad (46)$$

$$dN_1^*/dt=K_t(2\Sigma N_n^{**}+\Sigma N_n^*)M-(K_p+K_t)N_1^*M \quad (47)$$

$$dN_2^*/dt=2K_tN_2^*M+K_pN_1^*M-(K_p+K_t)N_2^*M \quad (48)$$

$$dN_2^{**}/dt=\tfrac{1}{2}K_iIM-2(K_p+K_t)N_2^{**}M \quad (49)$$

$$dN_n^*/dt=2K_tN_n^*M+K_pN_{n-1}^*M-(K_p+K_t)N_n^*M \quad (50)$$

$$dN_n^{**}/dt=2K_pN_{n-1}^*M-2(K_p+K_t)N_n^{**}M \quad (51)$$

$$dN_n'/dt=K_tN_n^*M \quad (52)$$

where N_n^{**} denotes the n-mer with double anions and N_n^* that with the single anion. Similarly, we can write their matrix form:

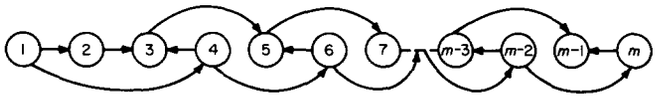
$$\begin{bmatrix} a_{11} & & & & & & & & & & & \\ a_{12} & a_{22} & & & & & & & & & & \\ & a_{23} & a_{33} & a_{43} & & & & & & & & \\ a_{14} & & & a_{44} & & & & & & & & \\ & & a_{35} & & a_{55} & a_{65} & & & & & & \\ & & & a_{46} & & a_{66} & & & & & & \\ & & & & a_{57} & & a_{77} & a_{87} & & & & \\ & & & & & a_{68} & & a_{88} & & & & \\ & & & & & & \cdots & & & & & \\ & & & & & & & a_{m-3,m-1} & & a_{m-1,m-1} & a_{m,m-1} \\ & & & & & & & & a_{m-2,m} & & a_{mm} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ X_m \end{bmatrix} = \begin{bmatrix} A \\ B \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{bmatrix} \quad (53)$$

where $m=2n+1$.

Its oriented graph has two source vertices and

$$\begin{cases} (3m-4)/2 & (m \text{ is even}) \\ (3m-5)/2 & (m \text{ is odd}) \end{cases}$$

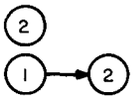
edges. The graph is as follows:



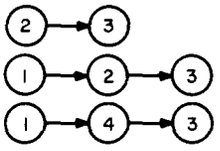
This graph seems much more complicated than others, yet it can be solved easily in accordance with the above rule. To find the regularity, we may write more terms.

X_1: There is only a source vertex.

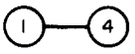
X_2: There is a source vertex and one path.



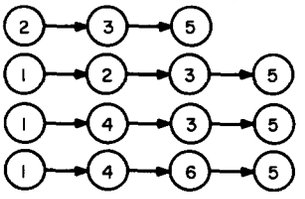
X_3: There are three paths.



X_4: There is one path.

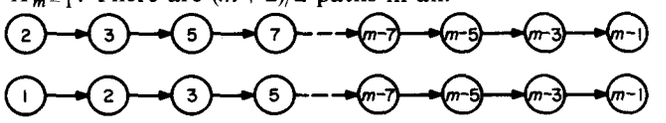


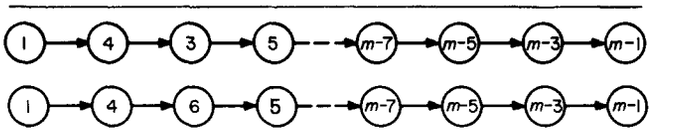
X_5: There are four paths.

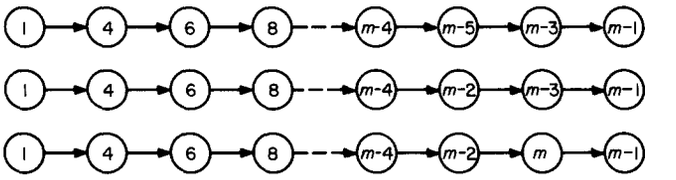


when m is even.

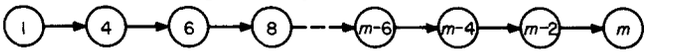
X_{m-1}: There are $(m+2)/2$ paths in all.





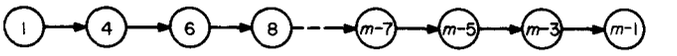


X_m: There is one path only.

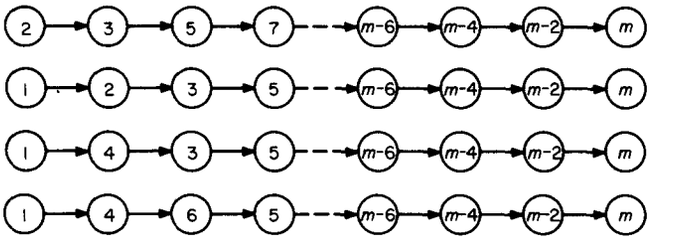


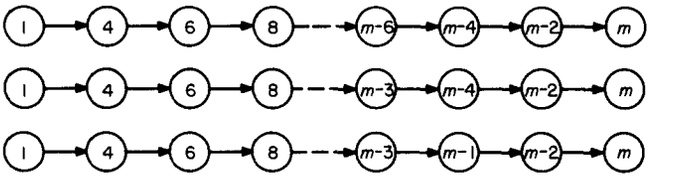
when m is odd.

X_{m-1}: There is only one path.



X_m: There are $(m+1)/2$ paths in all.





To obtain each solution for the unknowns in equation (53), we have only to sum up the contributions of each path, respectively. By use of the expressions given in the Laplace transform table, the images may be replaced by the respective originals.

CONCLUSIONS

We have provided a simple account of the basic results and techniques of graphic theory, with particular emphasis on its application in solving polymerization kinetics problems. A detailed analysis of the living polymerization monomer transfer is presented and some other examples of similar systems are used in highlighting of the kinetic mechanism. It has been unequivocally shown, that the graphic theory is a powerful method for analysing and calculating these complicated systems. We have tried to describe the graphic method in such a way, that for polymer scientists familar with construction of kinetic models, the principle of the solving procedure would be clearly visible. In conclusion, we believe that the graphic theory can be a useful technique for researching polymerization kinetic problems, and we intend to apply it in further investigations.

REFERENCES

1 Harary, F. Graph Theory, Reading, Addison–Wesley Publishing Company, 1969
2 Bowie, W. S. *Int. J. Comp. Info. Soc.* 1976, **5**, 9
3 Lee, T. D. and Yang, C. N. *Phys. Rev.* 1959, **113**, 1165
4 Oraga, K. K., Tani and Chan, S. P. Conference Proceedings, 14th Asilomar Conference on Circuits, Systems and Computers, Pacific Grove, California, p. 168, 1980
5 Cayley, A. *Phil. Mag.* 1857, **13**, 19
6 Gouarnes *Thesis*, University of Paris, 1956
7 Schmidtke, H. H. *J. Chem. Phys.* 1966, **45**, 3920
8 Halford, J. O. *J. Am. Chem. Soc.* 1967, **89**, 5338
9 Mayer, J. E. and Mayer, M. G. 'Statistical Mechanics', 1940
10 Reichl, L. E. *Physica.* 1973, **64**, 433
11 Butler, D. S., Gordon, M. and Malcolm, G. N. *Proc. Roy. Soc. Lond. A* 1966, **295**, 29
12 Gordon, M. and Parker, T. G. *Proc. Roy. Soc. Lond. A* 1970, **69**, 181
13 Deyue, Y., Guoyong, L. and Yuanshen, J. *Scientia Sinica* 1981, **24**, 46
14 Zhou, P., Deyue, Y. and Weifung, T. *Makromol. Chem.* 1985, **186**, 159