Molecular Weight Distributions in Copolymer Systems. I. Living Copolymers[1]

W. H. Ray

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14214. *Received September 14, 1970*

ABSTRACT: An analytical solution to the kinetic equations for living copolymers is presented which allows the easy calculation of the molecular weight distributions (MWD). An example is worked to illustrate the value of the solution.

The kinetics of copolymerization has been discussed extensively in the literature[2,3] and several workers[4,5] have analyzed the molecular weight distribution (MWD) derived from some simple cases. Even though recent contributions[6-8] allow easy calculation of the asymptotic behavior for living copolymerizations, there seems to be a lack of both a general formulation of the problem and a calculation procedure which produces the polymer MWD in an efficient fashion. This lack is possibly due to the formidable nature of the equations as well as the great difficulty in experimentally producing copolymer MWD's. In any case, there seems to be a need for a general approach and computational algorithm for producing copolymer MWD's, both because there has been some recent progress in solving the experimental problem,[9] and because, by simulation of proposed mechanisms, one can see the effect of parameters on the MWD. This simulation would seem to offer a way to easily test kinetic hypotheses.

In this paper we will analyze the copolymer MWD for systems having only initiation and propogation steps (living copolymers). A later paper will treat the case where transfer and termination steps occur.

The equations occurring in the steady state in continuous, well-mixed reactors are all algebraic and straightforward to solve; thus we will be concerned here with the more complicated analysis of batch or plug flow tubular reactors. Let us assume that the initiation step is very much faster than the propogation step so that it is a good approximation to assume that all initiation takes place instantaneously at time zero. Gold[10] has shown that this is often a good assumption for living homopolymerizations.

In this case our mechanism is

$$\begin{aligned} \mathrm{P}_{n,m} + \mathrm{M}_1 &\xrightarrow[k_{11}]{} \mathrm{P}_{n+1,m} \\ \mathrm{P}_{n,m} + \mathrm{M}_2 &\xrightarrow[k_{12}]{} \mathrm{Q}_{n,m+1} \\ \mathrm{Q}_{n,m} + \mathrm{M}_2 &\xrightarrow[k_{22}]{} \mathrm{Q}_{n,m+1} \\ \mathrm{Q}_{n,m} + \mathrm{M}_1 &\xrightarrow[k_{21}]{} \mathrm{P}_{n+1,m} \end{aligned} \tag{1}$$

where $\mathrm{P}_{n,m}$ is a polymer (concentration = $P_{n,m}$) with n units of M_1 and m units of M_2 and terminal M_1, while $\mathrm{Q}_{n,m}$ is a polymer (concentration = $Q_{n,m}$) with n units of M_1 and m units of M_2 and terminal M_2.

In a batch or plug flow tubular reactor our kinetic equations are

$$\frac{\mathrm{d}P_{n,m}}{\mathrm{d}t} = k_{11}M_1(P_{n-1,m} - P_{n,m}) + k_{21}M_1Q_{n-1,m}, - k_{12}M_2P_{n,m} \qquad P_{n,m}(0) = \delta_{n,m}{}^{1,0}P_0 \tag{2}$$

$$\frac{\mathrm{d}Q_{n,m}}{\mathrm{d}t} = k_{22}M_2(Q_{n,m-1} - Q_{n,m}) + k_{12}M_2P_{n,m-1} - k_{21}M_1Q_{n,m} \qquad Q_{n,m}(0) = \delta_{n,m}{}^{0,1}Q_0 \tag{3}$$

where

$$\delta_{n,m}{}^{r,s} = \begin{cases} 1 \text{ if } n = r,\ m = s \\ 0 \text{ otherwise} \end{cases} \tag{4}$$

By defining the dimensionless quantities

$$\begin{aligned} \tau &= \int_0^t k_{12}M_2\mathrm{d}t & \rho_1 &= \frac{k_{11}M_1}{k_{12}M_2} \\ \rho_2 &= \frac{k_{22}M_2}{k_{21}M_1} & \gamma &= \frac{k_{21}M_1}{k_{12}M_2} \\ y_{n,m} &= \frac{P_{n,m}}{P_0} & z_{n,m} &= \frac{Q_{n,m}}{P_0} \\ \alpha &= \frac{Q_0}{P_0} & x &= \frac{1}{\rho_1\rho_2} \end{aligned} \tag{5}$$

and assuming that γ, ρ_1, ρ_2 are maintained invariant with time (*e.g.*, by adjusting M_1, M_2, or temperature[11]), we get the dimensionless equations

$$\frac{\mathrm{d}y_{n,m}}{\mathrm{d}\tau} = \rho_1 y_{n-1,m} + \gamma z_{n-1,m} - (\rho_1 + 1)y_{n,m} \qquad y_{n,m}(0) = \delta_{n,m}{}^{1,0} \tag{6}$$

$$\frac{\mathrm{d}z_{n,m}}{\mathrm{d}\tau} = \gamma\rho_2 z_{n,m-1} + y_{n,m-1} - \gamma(\rho_2 + 1)z_{n,m} \qquad z_{n,m}(0) = \alpha\delta_{n,m}{}^{0,1} \tag{7}$$

Solution to the Kinetic Equations. Through the use of Laplace transforms and generating functions (*cf.* Appendix), one can get a solution to these equations in the form

---

[1] Part of this work was done at the University of Waterloo, Waterloo, Ontario, Canada.

[2] (a) H. W. Melville, B. Noble, and W. F. Watson, *J. Polym. Sci.*, **2**, 229 (1947); (b) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[3] G. E. Ham, "Copolymerization," Wiley, New York, N. Y., 1964.

[4] R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).

[5] W. H. Stockmayer, *ibid.*, **13**, 199 (1945).

[6] F. Horn and J. Klein, *Ber. Bunsenges. Phys. Chem.*, in press.

[7] F. Horn and J. Klein, *ibid.*, in press.

[8] F. Horn and J. Klein, *ibid.*, in press.

[9] H. Inagaki, H. Matsuda, and F. Kamiyama, *Macromolecules*, **1**, 520 (1968).

[10] Louis Gold, *J. Chem. Phys.*, **28**, 91 (1958).

[11] W. H. Ray and C. E. Gall, *Macromolecules*, **2**, 425 (1969).

$$y_{n,m}(\tau) = \phi(n,m,\tau) \times \left[\frac{1}{\rho_1} f(n-1,m,x) + (\alpha x - 1/\rho_1) f(n-1,m-1,x)\right] \quad n,m \geq 1 \tag{8}$$

$$z_{n,m}(\tau) = \phi(n,m,\tau)\left[\frac{\alpha}{\rho_2\gamma}\frac{m}{n} f(n-1,m,x) + \left\{\frac{x}{\gamma} - \frac{\alpha}{\rho_2\gamma}\left(x\left[1-\frac{m}{n}\right]+\frac{m}{n}\right)\right\} f(n-1,m-1,x)\right] \quad n,m \geq 1 \tag{9}$$

where

$$\phi(n,m,\tau) = \frac{(\rho_1)^n(\gamma\rho_2)^m\tau^{m+n-1}\exp\{-(\rho_1+1)\tau\} \times F_1(m,m+n,[\rho_1+1-\gamma(\rho_2+1)]\tau)}{(m+n-1)!} \tag{10}$$

and

$$f(n,m,x) = \sum_{k=0}^{\min(n,m)} \binom{n}{k}\binom{m}{k} x^k = F(-n,-m,1,x) \tag{11}$$

where $F(a,b,c,x)$ is the Gauss hypergeometric function.[12]

The function

$$F_1(a,c,y) = 1 + \sum_{n=1}^{\infty} \prod_{i=1}^{n} \left\{\frac{a+i-1}{c+i-1}\right\}\frac{y^n}{n!} \tag{12}$$

is a confluent hypergeometric function known as a Kummer function.[12] The homopolymer is given by the Poisson distribution

$$y_{n,0}(\tau) = \frac{\exp\{-(\rho_1+1)\tau\}(\rho_1\tau)^{n-1}}{(n-1)!} \tag{13}$$

$$z_{0,m}(\tau) = \frac{\alpha\exp\{-\gamma(\rho_2+1)\tau\}(\gamma\rho_2\tau)^{m-1}}{\gamma(m-1)!} \tag{14}$$

These solutions are readily calculated on the computer and provide a means of determining explicitly the influence of the parameters α, γ, ρ_1, ρ_2, and τ on the shape of the MWD. To illustrate this, a simple example is worked.

Example. The system styrene–butadiene has the following anionic rate constants at 29° in benzene with Li^+ counterion:[13] $k_{11} = 0.06$, $k_{12} = 1.2$, $k_{21} = 0.006$, $k_{22} = 0.018$. It perhaps is a suitable system for calculation of the copolymer MWD.

Equations 8, 9, 13, and 14 were calculated for a grid of chain lengths n and m for various times in the life of the copolymer. The dimensionless concentrations of both types of growing chains are shown in Figures 1–6 under the assumption that equal numbers of the two types of growing chains were initiated at $t = 0$ (*i.e.*, $\alpha = 1$) and the monomer concentrations are maintained equal (*i.e.*, $M_1/M_2 = 1$).

From the figures it can be seen that the very sharp peak in the MWD surface moves in the direction of increasing n and m with time, and more and more of the growing chains have butadiene as the terminal group (due to the very small value of γ).

Summary

An analytical expression for the MWD of living copolymers in batch or plug flow tubular reactors has been presented. The result is straightforward to use (contact the author for

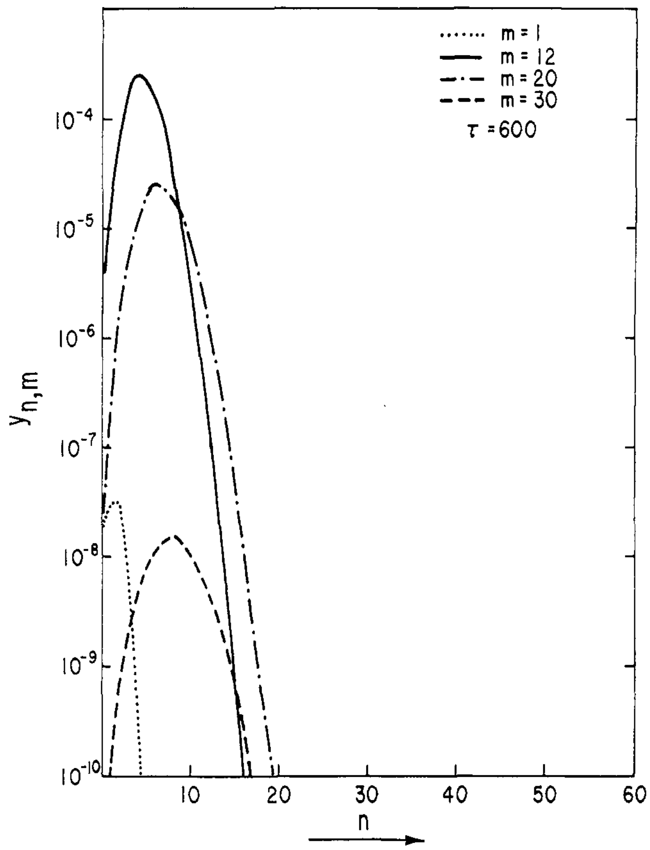

Figure 1. Distribution of growing chains with terminal styrene, $\tau = 600$.

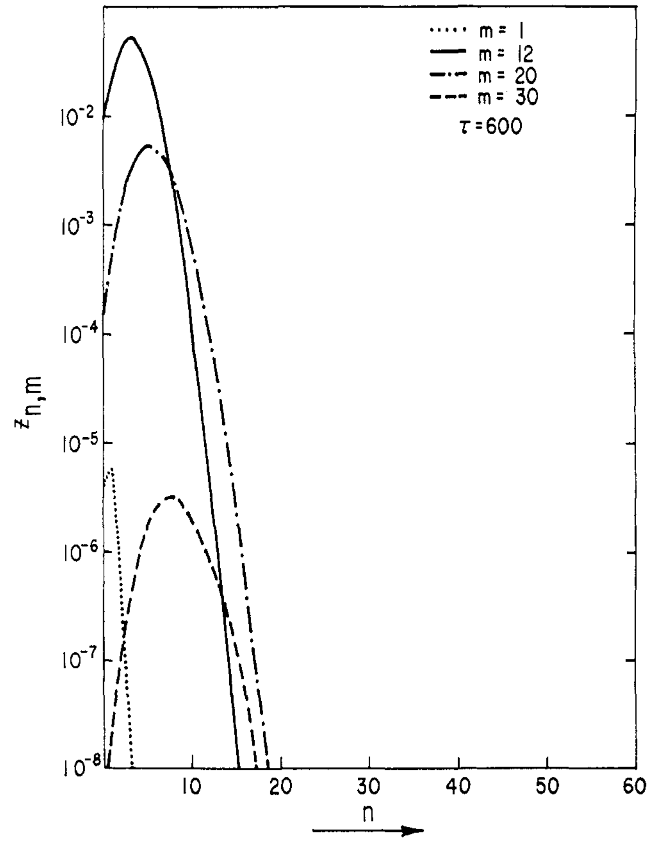

Figure 2. Distribution of growing chains with terminal butadiene, $\tau = 600$.

---

(12) A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, "Higher Transcendental Functions," McGraw-Hill, New York, N. Y., 1955.

(13) M. Szwarc and J. Smid, *Progr. React. Kinet.*, 2, 218 (1964).

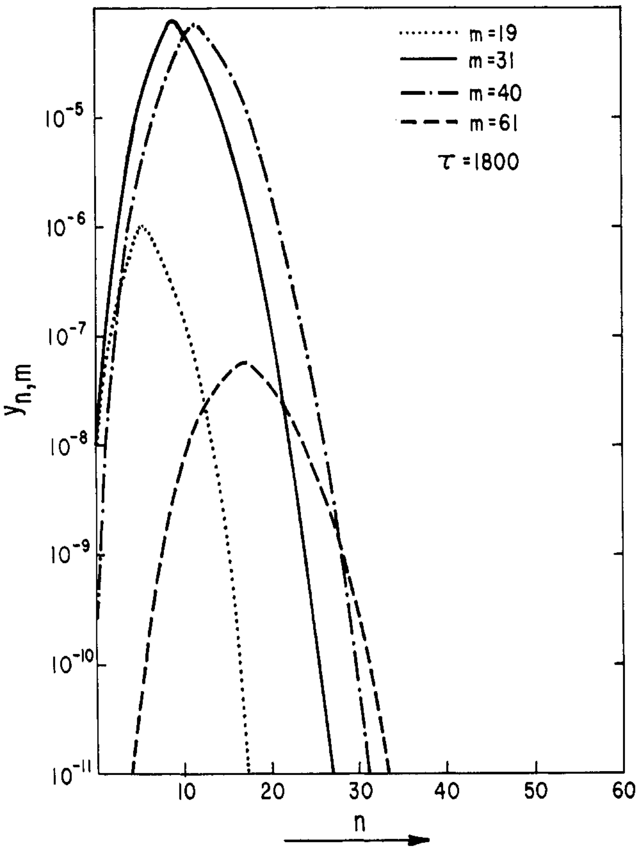

Figure 3. Distribution of growing chains with terminal styrene, $\tau = 1800$.

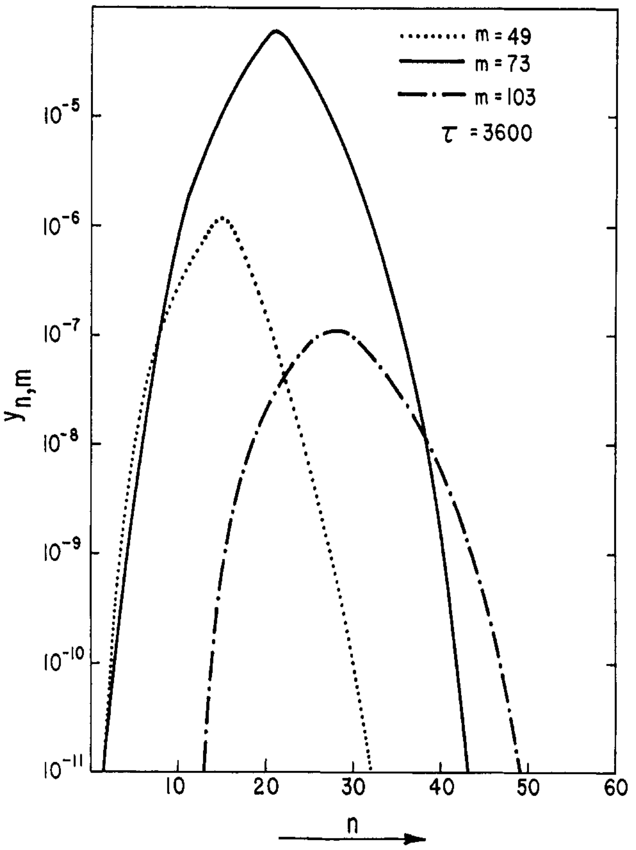

Figure 5. Distribution of growing chains with terminal styrene, $\tau = 3600$.

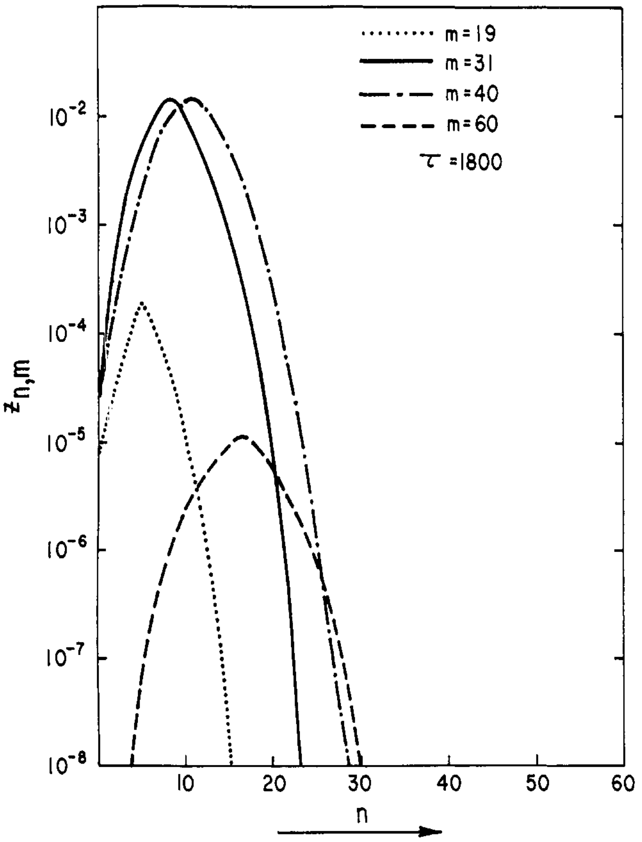

Figure 4. Distribution of growing chains with terminal butadiene, $\tau = 1800$.

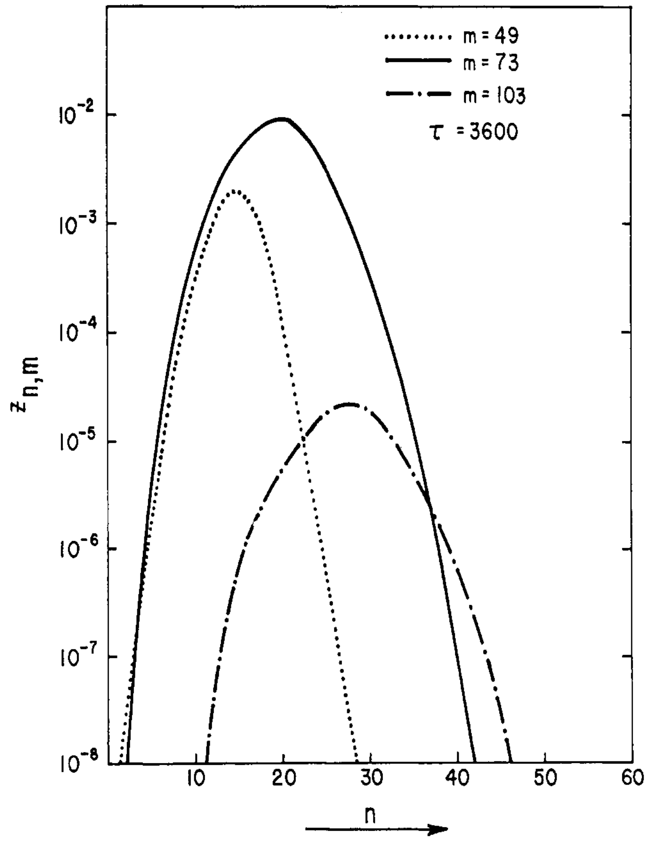

Figure 6. Distribution of growing chains with terminal butadiene, $\tau = 3600$.

information about the computer program) and allows very detailed information about the MWD surface of the copolymer. The requirement that the parameters ρ_1, ρ_2, and γ be invariant with time means that the results are best applicable to systems where M_1/M_2 is maintained nearly constant either through addition of monomer or by operation at nearly azeotropic conditions. If one wished to compute total chain length distributions or composition distributions from these detailed surfaces, it would be very straightforward to compute a small grid of $y_{n,m}$, $z_{n,m}$ (enough to define the surface) and use interpolation and summation to produce the other distributions of interest. Our experience with this approach has been very favorable.

Acknowledgments. The author is indebted to Mr. B. S. Jung for carrying out the numerical calculations and to the National Research Council of Canada for research support. Very helpful discussions with Dr. F. Horn and Dr. J. Klein are gratefully acknowledged.

Appendix

We shall here derive the solution to eq 6 and 7. Let us first take the Laplace transform to yield

$$\bar{\mathbf{x}}_{n,m}(s) = \mathbf{A}\mathbf{x}_{n,m}(0) + \mathbf{B}_1\bar{\mathbf{x}}_{n-1,m}(s) + \mathbf{B}_2\bar{\mathbf{x}}_{n,m-1} \quad \text{(A-1)}$$

where

$$\mathbf{x}_{n,m} = \begin{bmatrix} y_{n,m} \\ z_{n,m} \end{bmatrix}$$

$$\mathbf{A} = \begin{bmatrix} a_{11} & 0 \\ 0 & a_{22} \end{bmatrix} = \begin{bmatrix} (s + \rho_1 + 1)^{-1} & 0 \\ 0 & [s + \gamma(\rho_2 + 1)]^{-1} \end{bmatrix}$$

$$\mathbf{B}_1 = \begin{bmatrix} b_{11} & b_{12} \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} \dfrac{\rho_1}{s + \rho_1 + 1} & \dfrac{\gamma}{s + \rho_1 + 1} \\ 0 & 0 \end{bmatrix}$$

$$\mathbf{B}_2 = \begin{bmatrix} 0 & 0 \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ \dfrac{1}{s + \gamma(\rho_2 + 1)} & \dfrac{\gamma\rho_2}{s + \gamma(\rho_2 + 1)} \end{bmatrix} \quad \text{(A-2)}$$

and the overbar denotes a transformed variable. Now let us define the generating function

$$\mathbf{G}(u_1,u_2,\tau) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} u_1^n u_2^m \mathbf{x}_{n,m}(\tau) \quad \text{(A-3)}$$

and transform (A-1) to

$$\bar{\mathbf{G}}(u_1,u_2,s) = \mathbf{A}\mathbf{G}(u_1u_2,0) + u_1\mathbf{B}_1\bar{\mathbf{G}} + u_2\mathbf{B}_2\bar{\mathbf{G}} \quad \text{(A-4)}$$

so that

$$\bar{\mathbf{G}} = [\mathbf{I} - (\mathbf{B}_1u_1 + \mathbf{B}_2u_2)]^{-1}\mathbf{A}\mathbf{G}(u_1u_2,0) \quad \text{(A-5)}$$

Now remembering that

$$\mathbf{G}(u_1,u_2,0) = \begin{bmatrix} u_1 \\ \alpha u_2 \end{bmatrix} \quad \text{(A-6)}$$

we get

$$\bar{\mathbf{G}} = D^{-1}\begin{bmatrix} a_{11}u_1 + (\alpha b_{12}a_{22} - a_{11}b_{22})u_1u_2 \\ \alpha a_{22}u_2 + (b_{21}a_{11} - \alpha a_{22}b_{11})u_1u_2 \end{bmatrix} \quad \text{(A-7)}$$

where

$$D = 1 - \{b_{11}u_1 + b_{22}u_2 + (b_{12}b_{21} - b_{11}b_{22})u_1u_2\} \quad \text{(A-8)}$$

Now letting

$$c = b_{12}b_{21} - b_{11}b_{22} \quad \text{(A-9)}$$

and expanding D^{-1} in a power series in u_1 and u_2 we get

$$D^{-1} = \sum_{p=0}^{\infty} \{b_{22}u_2 + u_1[b_{11} + cu_2]\}^p \quad \text{(A-10)}$$

Now making use of the binomial expansion we get

$$D^{-1} = \sum_{p=0}^{\infty} \sum_{n=0}^{p} \binom{p}{n} (b_{22}u_2)^{p-n} u_1^n [b_{11} + cu_2]^n \quad \text{(A-11)}$$

Then letting $l = p - n$ and using another binomial expansion results

$$D^{-1} = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \sum_{k=0}^{n} \binom{l+n}{n} \binom{n}{k} u_1^n b_{22}^l b_{11}^{n-k} c^k u_2^{l+k} \quad \text{(A-12)}$$

Finally, letting $m = l + k$ gives

$$D^{-1} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{k=0}^{n} \binom{m+n-k}{n} \times \binom{n}{k} b_{11}^n b_{22}^m \left(\frac{c}{b_{11}b_{22}}\right)^k u_1^n u_2^m \quad \text{(A-13)}$$

By collecting coefficients of $u_1^n u_2^m$ and noting that $c/b_{11}b_{22} = x - 1$

$$\bar{y}_{n,m} = a_{11} \sum_{k\geq 0} \binom{m+n-k-1}{n-1} \binom{n-1}{k} \times (b_{11})^{n-1} b_{22}^m (x-1)^k + (b_{12}\alpha a_{22} + a_{11}b_{22}) \times \sum_{k\geq 0} \binom{m+n-k-2}{n-1} \binom{n-1}{k} (b_{11})^{n-1} (b_{22})^{m-1} (x-1)^k \quad \text{(A-14)}$$

$$\bar{z}_{n,m} = \alpha a_{22} \sum_{k\geq 0} \binom{m+n-k-1}{n} \binom{n}{k} \times (b_{11})^n (b_{22})^{m-1} (x-1)^k + (b_{21}a_{11} - \alpha a_{22}b_{11}) \times \sum_{k\geq 0} \binom{m+n-k-2}{n-1} \binom{n-1}{k} (b_{11})^{n-1} (b_{22})^{m-1} (x-1)^k \quad \text{(A-15)}$$

By making use of the identities

$$F(-a,-b,1,x) \equiv \sum_{k\geq 0} \binom{a+b-k}{a} \binom{a}{k} (x-1)^k = \sum_{k\geq 0} \binom{a}{k} \binom{b}{k} x^k \quad \text{(A-16)}$$

where F is the Gauss hypergeometric function,[12] and defining

$$f(a,b,x) \equiv F(-a,\ -b,1,x) \quad \text{(A-17)}$$

we get

$$\bar{y}_{n,m} = \phi(n,m,s)\left[\frac{1}{\rho_1} f(n-1,m,x) + \left[\alpha x - \frac{1}{\rho_1}\right] f(n-1,m-1,x)\right] \quad \text{(A-18)}$$

$$\bar{z}_{n,m} = \phi(n,m,s)\left[\frac{\alpha}{\gamma\rho_2} f(n,m-1,x) + \left[\frac{1}{\gamma\rho_1\rho_2} - \frac{\alpha}{\rho_2\gamma}\right] f(n-1,m-1,x)\right] \quad \text{(A-19)}$$

where

$$\phi(n,m,s) = \left(\frac{\rho_1}{s + \rho_1 + 1}\right)^n \left(\frac{\gamma\rho_2}{s + \gamma(\rho_2 + 1)}\right)^m \quad \text{(A-20)}$$

Now inverting the Laplace transform and making use of the identity

$$f(n,m-1,x) = \frac{m}{n} f(n-1,m,x) + \left(1 - \frac{m}{n}\right) \times (1-x) f(n-1,m-1,x) \quad \text{(A-21)}$$

we get the solution given in eq 8–10.