Molecular Weight Distributions in Copolymer Systems. II. Free Radical Copolymerization

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ABSTRACT: Explicit algebraic expressions are given for the molecular weight distribution (MWD) surfaces for the growing copolymer chains. For the dead polymer the MWD computation reduces to a simple integration which can be performed very rapidly on a digital computer. An example is worked to illustrate the technique.

In part I of this series,[1] analytical expressions for the molecular weight distribution (MWD) of living copolymerizations in batch or plug flow tubular reactors were presented. In this paper we treat free radical copolymerizations where the quasi-steady-state approximation (QSSA) can be made. We first review the work of Simha and Branson[2] and Stockmayer[3] on the MWD of the growing chains, making explicit the treatment for a wider class of kinetic steps, and then demonstrate a very efficient computational technique for the dead polymer MWD. Finally, the vinyl acetate–methyl methacrylate copolymer MWD is computed to illustrate the results.

I. Kinetic Mechanism. We shall assume that the copolymerization in question can be represented by the following mechanism.[4,5] This mechanism, while not completely general, allows most of the commonly accepted kinetic phenomenon. Extensions to multiple transfer agents, monomer termination, etc., are trivial. Since there are claims that sometimes the termination steps are diffusion controlled,[6,7] it is useful to discuss how this mechanism could be included in our scheme. If the diffusion-controlled termination steps were approximately independent of composition, then this would mean that the ϕ factor would be unity and $K_{c_{aa}} = K_{c_{ab}} = K_{c_{bb}}$, $K_{d_{aa}} = K_{d_{ab}} = K_{d_{bb}}$ would hold. For concentration-dependent termination constants, one could use ones like those of Atherton and North[7] in the equations which follow. Therefore, diffusion-controlled termination offers no particular difficulty in simulation.

Initiation

$$A \longrightarrow P_{10}$$

$$B \longrightarrow Q_{01}$$

Propagation

$$P_{n,m} + A \xrightarrow[K_{p_{aa}}]{} P_{n+1,m}$$

$$P_{n,m} + B \xrightarrow[K_{p_{ab}}]{} Q_{n,m+1}$$

$$Q_{n,m} + A \xrightarrow[K_{p_{ba}}]{} P_{n+1,m}$$

$$Q_{n,m} + B \xrightarrow[K_{p_{bb}}]{} Q_{n,m+1}$$

Combination termination

$$P_{n,m} + P_{r,q} \xrightarrow[K_{c_{aa}}]{} M_{n+r,m+q}$$

$$P_{n,m} + Q_{r,q} \xrightarrow[K_{c_{ab}}]{} M_{n+r,m+q}$$

$$Q_{n,m} + Q_{r,q} \xrightarrow[K_{c_{bb}}]{} M_{n+r,m+q}$$

Disproportionation termination

$$P_{n,m} + P_{r,q} \xrightarrow[K_{d_{aa}}]{} M_{n,m} + M_{r,q}$$

$$P_{n,m} + Q_{r,q} \xrightarrow[K_{d_{ab}}]{} M_{n,m} + M_{r,q}$$

$$Q_{n,m} + Q_{r,q} \xrightarrow[K_{d_{bb}}]{} M_{n,m} + M_{r,q}$$

Chain transfer to monomer

$$P_{n,m} + A \xrightarrow[K_{f_{aa}}]{} M_{n,m} + P_{10}$$

$$P_{n,m} + B \xrightarrow[K_{f_{ab}}]{} M_{n,m} + Q_{01}$$

$$Q_{n,m} + A \xrightarrow[K_{f_{ba}}]{} M_{n,m} + P_{10}$$

$$Q_{n,m} + B \xrightarrow[K_{f_{bb}}]{} M_{n,m} + Q_{01}$$

Chain transfer to agent

$$P_{n,m} + S \xrightarrow[K_{f_{sa}}]{} M_{n,m} + R_1$$

$$Q_{n,m} + S \xrightarrow[K_{f_{sb}}]{} M_{n,m} + R_1$$

Propagation of radicals R_1

$$R_1 + A \xrightarrow[K_{sa}]{} P_{10}$$

$$R_1 + B \xrightarrow[K_{sb}]{} Q_{01}$$

II. MWD for Growing Polymer. The kinetic rate equations resulting from the mechanism above are given in Appendix I; however, they can be greatly simplified by making some common assumptions. Applying the quasi-steady-state-approximation (QSSA) to the live polymer equations gives

$$R_1 = \frac{(K_{f_{sa}}P + K_{f_{sb}}Q)S}{(K_{sa}A + K_{sb}B)} \tag{1}$$

$$P_{n0} = c_1\alpha_a^{\,n} \tag{2}$$

$$Q_{0m} = c_4\alpha_b^{\,m} \tag{3}$$

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(1) W. H. Ray, *Macromolecules*, **4**, 162 (1971).
(2) R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).
(3) W. H. Stockmayer, *ibid.*, **13**, 199 (1945).
(4) H. W. Melville, B. Noble, and W. F. Watson, *J. Polym. Sci.*, **2**, 229 (1947).
(5) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).
(6) A. M. North, *Polymer*, **4**, 134 (1963).
(7) J. N. Atherton and A. M. North, *Trans. Faraday Soc.*, **58**, 2049 (1962).

$$P_{n,m} = \alpha_a P_{n-1,m} + \frac{\gamma\alpha_a}{r_1} Q_{n-1,m} \quad (4)$$

$$Q_{n,m} = \frac{\alpha_b}{\gamma r_2} P_{n,m-1} + \alpha_b Q_{n,m-1} \quad (5)$$

where P, Q, A, B, and S represent concentrations of the corresponding species, and the important parameters are

$$\alpha_a = \frac{K_{p_{aa}}A}{[(K_{p_{aa}} + K_{f_{aa}})A + (K_{p_{ab}} + K_{f_{ab}})B + K_{f_{aa}}S + (K_{c_{aa}} + K_{d_{aa}})P + (K_{c_{ab}} + K_{d_{ab}})Q]} \quad (6)$$

the probability of a P chain adding another A monomer, and

$$\alpha_b = \frac{K_{p_{bb}}B}{[(K_{p_{bb}}) + (K_{f_{bb}})B + (K_{p_{ba}} + K_{f_{ba}})A + K_{f_{ab}}S + (K_{c_{bb}} + K_{d_{bb}})Q + (K_{c_{ab}} + K_{d_{ab}})P]} \quad (7)$$

the probability of a Q chain adding another B monomer. Other important parameters are

$$c_1 = \frac{I_A + (K_{f_{aa}}P + K_{f_{ba}}Q + K_{sa}R_1)A}{K_{p_{aa}}A} \quad (8)$$

$$c_2 = c_4 r_2 \gamma \quad (9)$$

$$c_3 = \frac{c_1 r_1}{\gamma} \quad (10)$$

$$c_4 = \frac{I_B + (K_{f_{bb}}Q + K_{f_{ab}}P + K_{sb}R_1)B}{K_{p_{bb}}B} \quad (11)$$

and

$$r_1 = \frac{K_{p_{aa}}}{K_{p_{ab}}}$$

$$r_2 = \frac{K_{p_{bb}}}{K_{p_{ba}}}$$

$$\gamma = \frac{K_{p_{bb}}}{K_{p_{ab}}} \quad (12)$$

$$x = \frac{1}{r_1 r_2}$$

The total amounts of growing polymer given by

$$P = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} P_{n,m}$$

$$Q = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} Q_{n,m} \quad (13)$$

can be found by applying the long-chain hypothesis (LCH) to eq I.7 and I.8 to yield

$$P = \left\{\frac{I_A + I_B}{(K_{c_{aa}} + K_{d_{aa}}) + 2\beta(K_{c_{ab}} - K_{d_{ab}}) + \beta^2(K_{c_{bb}} + K_{d_{bb}})}\right\}^{1/2} \quad (14)$$

$$Q = \beta P \quad (15)$$

where

$$\beta = \frac{(K_{p_{ab}} + K_{f_{ab}})B}{K_{p_{ba}} + K_{f_{ba}})A} \quad (16)$$

Now let us find the concentration of growing polymer by solving eq 4 and 5. The solution, determined by the use of generating functions in Appendix II, is

$$P_{n,m} = \alpha_a{}^n\alpha_b{}^m \left\{\sum_{j=1}^{n}\left[\frac{c_1(n-j)}{j} + c_2\right] \times \binom{n-1}{j-1}\binom{m-1}{j-1} x^j\right\} \quad (17)$$

$$Q_{n,m} = \alpha_a{}^n\alpha_b{}^m \left\{\sum_{j=1}^{n}\left[c_3 + \frac{c_4(m-j)}{j}\right] \times \binom{n-1}{j-1}\binom{m-1}{j-1} x^j\right\} \quad (18)$$

where it can be seen by observing the definitions of c_1, c_2, c_3, and c_4 that the first term in each case is the contribution of chains beginning with P_{10} (either by initiation or chain transfer) and the second term is the contribution of chains beginning with Q_{01}. Results similar to eq 17 and 18 were derived by Simha and Branson[2] just by such physical reasoning. Our result is slightly more general than theirs (allowing explicitly for chain transfer, etc.) and was derived in a more systematic way. A more computationally useful form is given by eq II.21 and II.22 in Appendix II.

The moments of the live polymer distribution have been calculated in Appendix IV from the generating function. For example, the number-average chain length (NACL) of $P_{n,m}$ is

$$\mu_1{}^P = \frac{\lambda_1{}^P}{\lambda_0{}^P} = 1 + \frac{1 - (1-x)\alpha_a\alpha_b}{1 - (\alpha_a + \alpha_b) + (1-x)\alpha_a\alpha_b} - \frac{1}{1 + [(c_2x - c_1)\alpha_b/c_1]} \quad (19)$$

while the number-average molecular weight (NAMW) of $P_{n,m}$ is

$$\hat{\mu}_1{}^P = \frac{\psi_1{}^P}{\psi_0{}^P} = w_a + w_b - \frac{[(w_a + w_b)(1-x)\alpha_a\alpha_b - w_a\alpha_a - w_b\alpha_b]}{1 - (\alpha_a + \alpha_b) + (1-x)\alpha_a\alpha_b} - \frac{w_b}{1 + [(c_2x - c_1)\alpha_b/c_1]} \quad (20)$$

The NACL and NAMW for $Q_{n,m}$ are then

$$\mu_1{}^Q = 1 + \frac{1 - (1-x)\alpha_a\alpha_b}{1 - (\alpha_a + \alpha_b) + (1-x)\alpha_a\alpha_b} - \frac{1}{1 + [(c_3x - c_4)\alpha_a/c_4]} \quad (21)$$

$$\hat{\mu}_1{}^Q = w_a + w_b - \frac{[(w_a + w_b)(1-x)\alpha_a\alpha_b - w_a\alpha_a - w_b\alpha_b]}{1 + (\alpha_a + \alpha_b) + (1-x)\alpha_a\alpha_b} - \frac{w_a}{1 + [(c_3x - c_4)\alpha_a/c_4]} \quad (22)$$

All the higher moments can be calculated in a similar way if necessary.

III. MWD of "Dead" Polymer. Since we are making the QSSA, the MWD for "live" or growing polymer is the same in all reactors and only depends on the local reaction environment. However, to calculate the MWD for "dead" or stable polymer, it is necessary to specify the chemical reactor of interest. In this section, we shall discuss both the batch reactor (BR) and the perfectly mixed continuous

stirred tank reactor (CSTR). By an analysis similar to that in ref 8, it is possible to show that the QSSA applies both to batch and CSTR systems, and thus the live polymer distributions in eq 17 and 18 are valid for both types of reactors.

We must now turn our attention to the dead polymer equations (I.10) and the monomer equations (I.1 and I.2). Applying the LCH to the first and last terms of eq I.1 and I.2 we get

$$r_A = -[(K_{p_{aa}} + K_{f_{aa}})P + (K_{p_{ba}} + K_{f_{ba}})Q]A \quad (23)$$

$$r_B = -[(K_{p_{bb}} + K_{f_{bb}})Q + (K_{p_{ab}} + K_{f_{ab}})P]B \quad (24)$$

where, in some cases, the transfer constants can be negligible. Combining terms in eq I.10, we get

$$r_{M_{n,m}} = {}^1/_2K_{c_{aa}} \sum_{r=0}^{n} \sum_{q=0}^{m} P_{rq}P_{n-r,m-q} +$$

$$K_{c_{ab}} \sum_{r=0}^{n} \sum_{q=0}^{m} P_{rq}Q_{n-r,m-q} + {}^1/_2K_{c_{bb}} \sum_{r=0}^{n} \sum_{q=0}^{m} Q_{rq}Q_{n-r,m-q} +$$

$$[K_{d_{aa}}P + K_{d_{ab}}Q + K_{f_{aa}}A + K_{f_{ab}}B + K_{f_{sa}}S]P_{n,m} +$$

$$[K_{d_{bb}}Q + K_{d_{ab}}P + K_{f_{bb}}B + K_{f_{ba}}A + K_{f_{sb}}S]Q_{n,m} \quad (25)$$

Now it is very straightforward to compute the last two terms of (25) from the live polymer distributions given in eq 17 and 18; however, the direct calculation of the first three terms of (25) requires the computation and summing of all possible combinations of live polymer—a taxing task for even the largest computer. Therefore, through the use of generating functions, we have developed more concise formulas for these double sums. From Appendix III, we see that

$$S_{n,m}{}^{I} \equiv \sum_{r=0}^{n} \sum_{q=0}^{m} P_{rq}P_{n-r,m-q} =$$

$$\alpha_a{}^n\alpha_b{}^m\{\eta_{11}g(n-1, m-2) + \eta_{12}g(n-2, m-2)\} \quad (26)$$

If $n \neq m$

$$S_{n,m}{}^{II} \equiv \sum_{r=0}^{n} \sum_{q=0}^{m} P_{rq}Q_{n-r,m-q} =$$

$$\alpha_a{}^n\alpha_b{}^m\{\eta_{21}g(n-1, m-2) + \eta_{22}g(n-2, m-2)\} \quad (27a)$$

If $n = m$

$$S_{n,m}{}^{II} \equiv \sum_{r=0}^{n} \sum_{q=0}^{m} P_{rq}Q_{n-r,m-q} =$$

$$\alpha_a{}^n\alpha_b{}^m\{\bar{\eta}_{21}g(n-1, m-2) + \bar{\eta}_{22}g(n-2, m-2) + \bar{\eta}_{23}g(n-1, m-1)\} \quad (27b)$$

$$S_{n,m}{}^{III} \equiv \sum_{r=0}^{n} \sum_{q=0}^{m} Q_{rq}Q_{n-r,m-q} =$$

$$\alpha_a{}^n\alpha_b{}^m\{\eta_{31}g(n-1, m-2) + \eta_{32}g(n-2, m-2)\} \quad (28)$$

where the functions $g(a, b)$ and the η_{ij}'s are defined in Appendix III. The moments of the dead polymer MWD (see Appendix IV) lead to averages such as the NACL

$$\mu_1{}^M = \frac{\lambda_1{}^M}{\lambda_0{}^M} = \frac{\sum_n \sum_m (n+m)M_{n,m}}{\sum_n \sum_m M_{n,m}} \quad (29)$$

and NAMW

$$\hat{\mu}_1{}^M = \frac{\psi_1{}^M}{\psi_0{}^M} = \frac{\sum_n \sum_m (nw_a + mw_b)M_{n,m}}{\sum_n \sum_m M_{n,m}} \quad (30)$$

(8) W. H. Ray, *Can. J. Chem. Eng.*, 47, 503 (1969).

where, to a very good approximation, $\lambda_1{}^M$ = the total concentration of monomer chains in the dead polymer, $\psi_1{}^M$ = the weight volume of dead polymer, and $\lambda_0{}^M$, $\psi_0{}^M$ have the rate expressions

$$r_{\psi_0}{}^M = r_{\psi_0}{}^M = {}^1/_2K_{c_{aa}}P^2 + K_{c_{ab}}PQ +$$

$${}^1/_2K_{c_{bb}}Q^2 + [K_{d_{aa}} + K_{d_{ab}}Q +$$

$$K_{f_{aa}}A + K_{f_{ab}}B + K_{f_{sa}}S]P + [K_{d_{bb}}Q +$$

$$K_{d_{ab}}P + K_{f_{bb}}B + K_{f_{ba}}A + K_{f_{sb}}S]Q \quad (31)$$

where all higher moments can be determined in a similar manner.

IV. The Batch Reactor. Let us now analyze the equations for the batch reactor to produce a MWD. The equations to be solved numerically are

$$dA/dt = r_A \qquad A(0) = A_0 \quad (32)$$

$$dB/dt = r_B \qquad B(0) = B_0 \quad (33)$$

$$dM_{n,m}/dt = r_{M_{n,m}} \qquad n,m \geq 1 \qquad M_{n,m}(0) = N_{n,m} \quad (34)$$

$$d\lambda_0{}^M/dt = r_{\lambda_0{}^M} \qquad \lambda_0{}^M(0) = \sum_n \sum_m N_{n,m} \quad (35)$$

$$\lambda_1{}^M = A_0 + B_0 - (A + B) + \sum_n \sum_m (n+m)N_{n,m} \quad (36)$$

$$\psi_1{}^M = w_A(A_0 - A) + w_b(B_0 - B) + \sum_n \sum_m (nw_a + mw_b)N_{n,m} \quad (37)$$

$$\psi_0{}^M = \lambda_0{}^M \quad (38)$$

where the live polymer quantities are given in section III. An example worked later illustrates the results that can be obtained for batch systems.

V. The CSTR. The kinetic equations for a well-mixed CSTR are very similar to the batch equations for transient operation, and very much simpler for steady state. For transient operation, we must solve

$$dA/dt = [(A_f - A)/\theta] + r_a \qquad A(0) = A_0 \quad (39)$$

$$dB/dt = [(B_f - B)/\theta] + r_B \qquad B(0) = B_0 \quad (40)$$

$$\frac{dM_{n,m}}{dt} = \frac{M_{n,m}{}^f - M_{n,m}}{\theta} + r_{M_{n,m}} \qquad M_{n,m}(0) = N_{n,m} \quad (41)$$

$$\frac{d\lambda_0{}^M}{dt} = \frac{\lambda_{0f}{}^M - \lambda_0{}^M}{\theta} + r_{\lambda_0{}^M} \qquad \lambda_0{}^M(0) = \sum_n \sum_m N_{n,m} \quad (42)$$

$$\frac{d\lambda_1{}^M}{dt} = \frac{\lambda_{1f}{}^M - \lambda_1{}^M}{\theta} - (r_A + r_B)$$

$$\lambda_1{}^M(0) = \sum_n \sum_m (n+m)N_{n,m} \quad (43)$$

$$\frac{d\psi_1{}^M}{dt} = \frac{\psi_{1f}{}^M - \psi_1{}^M}{\theta} - (w_a r_A + w_b r_B)$$

$$\psi_1{}^M(0) = \sum_n \sum_m (nw_a + mw_b)N_{n,m} \quad (44)$$

where the live polymer quantities are again taken from section III. In the reactor steady state the left-hand sides of (39–44) vanish and the equations become algebraic ones which can be solved quite easily. The CSTR transient behavior can be found by an analysis similar to that used for the batch reactor. However, we shall not pursue that further here.

VI. An Example. To illustrate the information which can be obtained from this type of analysis, the MWD surfaces for the methyl methacrylate–vinyl acetate system at 60°

TABLE I
PARAMETERS USED IN SIMULATION OF MMA–VA AT 60° [a,b]

$K_{paa} = 705.00$	$K_d = 10^{-5}$
$K_{pbb} = 3600.00$	$[I]_0 = 0.06$
$K_{pab} = 35.25$	$K_{caa} = K_{cab} = K_{cbb} = 10^7$
$K_{pba} = 2.4 \times 10^5$	

[a] Reference 11. [b] All other kinetic constants zero.

in a batch reactor were generated. The parameters used for the simulation were picked from the literature[9] as representative values. For a detailed study of the MMA–VA system, care would be needed to separate the disproportionation and combination effects in the termination rate constants, a better estimate of $K_{t_{ab}}$ would be needed, and chain-transfer constants would have to be determined. The authors have developed a general purpose computer program capable of handling all these mechanisms in any system where the QSSA and LCH are valid. However, for the example, the parameters (listed in Table I) neglect chain transfer and assume that all termination is through combination.

The concentration distribution of growing chains after 2.5 min of reaction is given in Figures 1 and 2, while the weight fractions are shown in Figures 3 and 4. The distributions for dead polymer are given in Figures 5 and 6. It was found that the monomer composition changed so slowly that the live polymer distributions over a long period of reaction time were essentially those shown in Figures 1–4. The dead polymer distribution was also calculated for 2.5 min of reaction time, but it too changed very little in character from Figures 5 and 6 as the reaction progressed. The distribution would slowly change at longer reaction times as the monomer composition changes, and the equations developed in this paper could be used to make this calculation.

The computational algorithm used can be summarized

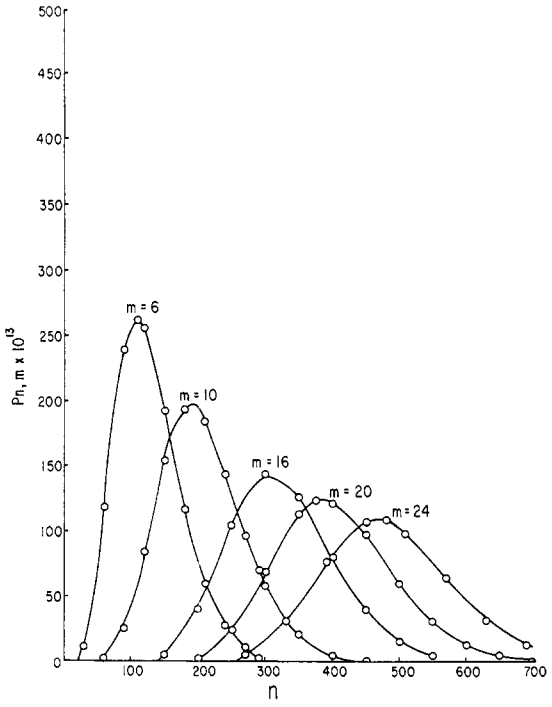

Figure 1. Concentration of live polymer P.

(9) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Interscience, New York, N. Y., 1966.

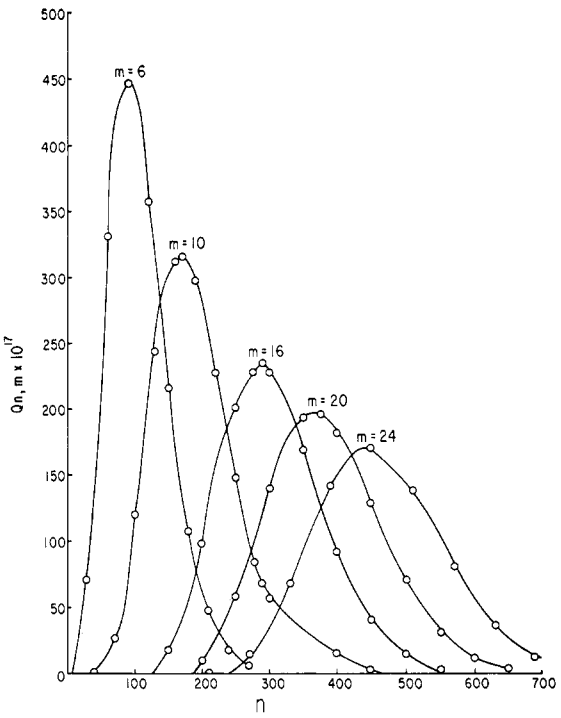

Figure 2. Concentration of live polymer Q.

briefly as follows. (1) Read in the data, as well as the maximum chain lengths and grid size (since the algorithm does not require the precursors calculated for each chain length, the grid spacing should be as sparse as possible to minimize computing effort). (2) Compute and store the values of $f(n, m, x)$, $g(n, m)$ required for all n and m of interest. (3) Specify time interval of interest and compute monomer concentrations and total polymer concentrations. (4) Compute the live polymer MWD and MWD moments. (5) Compute the dead polymer MWD and MWD moments. (6) Go back to (3) and continue until the desired reaction time is covered.

This scheme seems to work very efficiently, even though

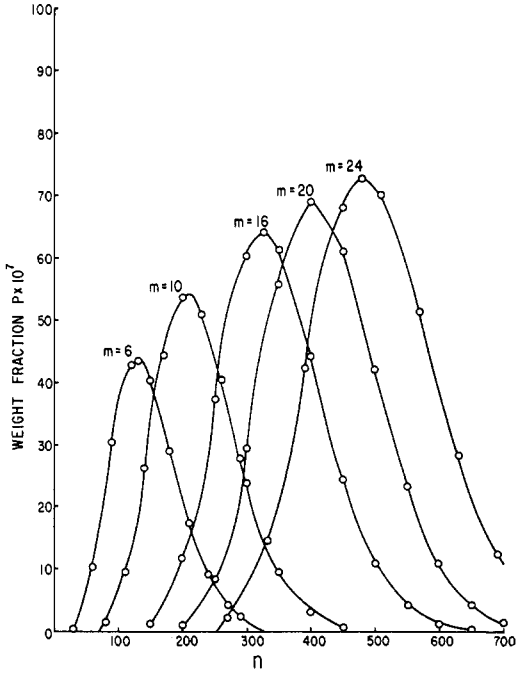

Figure 3. Weight fraction of live polymer P.

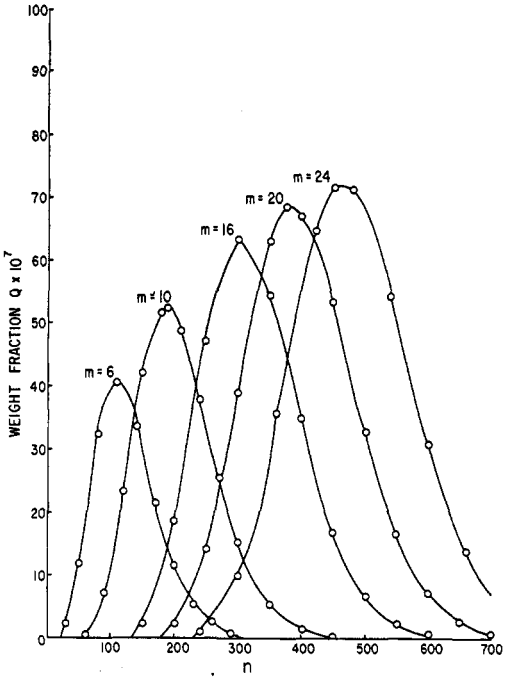

Figure 4. Weight fraction of live polymer Q.

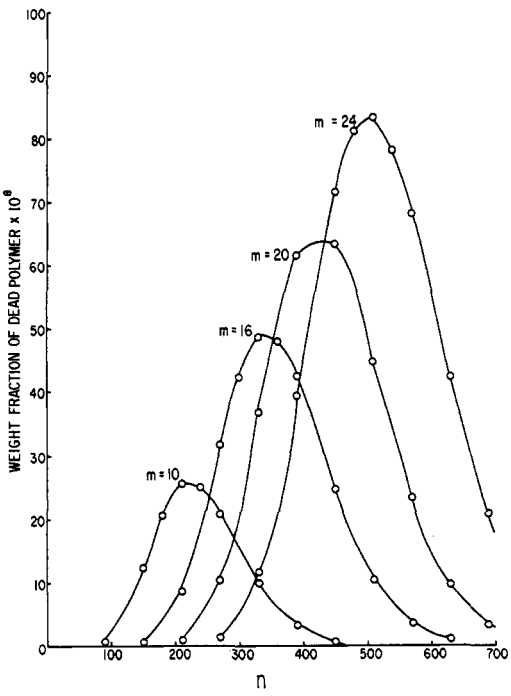

Figure 5. Weight fraction of dead polymer.

there were no special pains taken in programming. The computing time required to produce the live polymer distribution is only a few seconds, while the effort required to carry our complete example to 2.5 min of reaction time using an integration step of 5 sec was approximately 1 min on an IBM 360/75.

Summary

In this paper we have demonstrated a very efficient computational algorithm for determining the MWD surfaces for free-radical copolymerization, and have a computer program capable of treating all the mechanisms discussed above. The equations developed here should be quite useful in determining explicitly the effect of reaction conditions on the MWD of free-radical copolymerizations. In addition, these results should allow one to check for each problem some commonly made assumptions (like the uniform composition of chains assumption) in deriving composition distributions, because these results allow the prediction of kinetic randomness as well as composition variations due to changing reaction conditions.

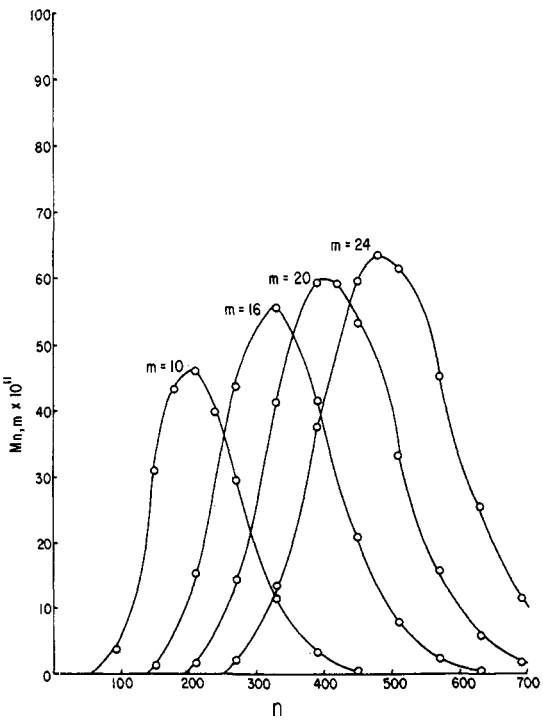

Figure 5. Concentration of dead polymer.

If one were interested in the total chain length distribution, T_l

$$T_l = \sum_{n=0}^{l} M_{n,l-n} \tag{45}$$

or the composition distribution (including the composition variations due to the kinetic randomness), X_y

$$X_y = \frac{\sum_{l=1}^{\infty} M_{yl,(1-y)l}}{\sum_{n}\sum_{m} M_{n,m}} \tag{46}$$

of the dead polymer (the growing polymer distributions were treated in detail by Stockmayer[3]), these could be found by computing a sparse grid of $M_{n,m}$ and using interpolation to get the intermediate values. Our experience with this approach has been very good.

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Appendix I. Kinetic Rate Expressions

The kinetic rate expressions resulting from the mechanisms given in section II above are as follows. For monomer A and B

$$r_A = -I_A - [(K_{p_{aa}} + K_{f_{aa}})P + (K_{p_{ba}} + K_{f_{ba}})Q]A - K_{sa}R_1A \tag{I.1}$$

$$r_B = -I_B - [(K_{p_{bb}} + K_{f_{bb}})Q + (K_{p_{ab}} + K_{f_{ab}})P]B - K_{sb}R_1B \tag{I.2}$$

For "live" or growing polymer

$$r_{P_{10}} = I_A + (K_{t_{aa}}P + K_{t_{ba}}Q)A + K_{s_a}AR_1 - [(K_{p_{aa}} + K_{t_{aa}})A + (K_{p_{ab}} + K_{t_{ab}})B + K_{t_{sa}}S + (K_{c_{aa}} + K_{d_{aa}})P + (K_{c_{ab}} + K_{d_{ab}})Q]P_{10} \quad (I.3)$$

$$r_{Q_{01}} = I_B + (K_{t_{bb}}Q + K_{t_{ab}}P)B + K_{s_b}BR_1 - [(K_{p_{bb}} + K_{t_{bb}})B + (K_{p_{ba}} + K_{t_{ba}})A + K_{t_{sb}}S + (K_{c_{bb}} + K_{d_{bb}})Q + (K_{c_{ab}} + K_{d_{ab}})P]Q_{01} \quad (I.4)$$

$$r_{P_{n,m}} = (K_{p_{aa}}P_{n-1,m} + K_{p_{ba}}Q_{n-1,m})A - [(K_{p_{aa}} + K_{t_{aa}})A + (K_{p_{ab}} + K_{t_{ab}})B + K_{t_{sa}}S + (K_{c_{aa}} + K_{d_{aa}})P + (K_{c_{ab}} + K_{d_{ab}})Q]P_{n,m} \quad (I.5)$$

$$r_{Q_{n,m}} = (K_{p_{bb}}Q_{n,m-1} + K_{p_{ab}}P_{n,m-1})B - [(K_{p_{bb}} + K_{t_{bb}})B + (K_{p_{ba}} + K_{t_{ba}})A + K_{t_{sb}}S + (K_{c_{bb}} + K_{d_{bb}})Q + (K_{c_{ab}} + K_{d_{ab}})P]Q_{n,m} \quad (I.6)$$

$$r_P = I_A + (K_{p_{ba}} + K_{t_{ba}})QA - (K_{p_{ab}} + K_{t_{ab}})PB + K_{s_a}AR_1 - K_{t_{sa}}SP + (K_{c_{aa}} + K_{d_{aa}})P^2 + (K_{c_{ab}} + K_{d_{ab}})PQ \quad (I.7)$$

$$r_Q = I_B + (K_{p_{ab}} + K_{t_{ab}})PB - (K_{p_{ba}} + K_{t_{ba}})QA + K_{s_b}BR_1 - K_{t_{sb}}SQ + (K_{c_{bb}} + K_{d_{bb}})Q^2 + (K_{c_{ab}} + K_{d_{ab}})PQ \quad (I.8)$$

For activated agent such as solvent

$$r_{R_1} = K_{t_{sa}}SP + K_{t_{sb}}SQ - (K_{s_a}A + K_{s_b}B)R_1 \quad (I.9)$$

For "dead" or stable polymer

$$r_{M_{n,m}} = {}^1/_2K_{c_{aa}}\sum_{r=0}^{n}\sum_{q=0}^{m}P_{rq}P_{n-r,m-q} + K_{c_{ab}}\sum_{r=0}^{n}\sum_{q=0}^{m}P_{rq}Q_{n-r,m-q} + {}^1/_2K_{c_{bb}}\sum_{r=0}^{n}\sum_{q=0}^{m}Q_{rq}Q_{n-r,m-q} + K_{d_{aa}}P_{n,m}P + K_{d_{ab}}(P_{n,m}Q + Q_{n,m}P) + K_{d_{bb}}Q_{n,m}Q + [K_{t_{aa}}A + K_{t_{ab}}B + K_{t_{sa}}S]P_{n,m} + [K_{t_{bb}}B + K_{t_{ba}}A + K_{t_{sb}}S]Q_{n,m} \quad (I.10)$$

Appendix II. Derivation of the Growing Polymer Distribution

To produce a solution to eq 4 and 5, we shall use the generating functions

$$G = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}u_1^n u_2^m P_{n,m} \quad (II.1)$$

$$\Phi = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}u_1^n u_2^m Q_{n,m} \quad (II.2)$$

By multiplying eq 4 and 5 by $u_1^n u_2^m$ and summing, we get

$$G = [G + (\gamma/r_1)\Phi + c_1]\alpha_a u_1 \quad (II.3)$$

$$\Phi = [\Phi + (1/\gamma r_2)G + c_4]\alpha_b u_2 \quad (II.4)$$

These linear algebraic equations can be solved to yield

$$G = [c_1 y_a + (c_2 x - c_1)y_a y_b]/D \quad (II.5)$$

$$\Phi = \frac{c_4 y_b + (c_3 x - c_4)y_a y_b}{D} \quad (II.6)$$

where

$$D = 1 - \{y_b + y_a[1 + (x-1)y_b]\} \quad (II.7)$$

and

$$y_a = \alpha_a u_1 \qquad y_b = \alpha_b u_2 \quad (II.8)$$

Now to invert (II.5) and (II.6) to produce $P_{n,m}$, $Q_{n,m}$, we must expand D^{-1} in a double power series in y_a, y_b and collect coefficients.

Thus

$$D^{-1} = \sum_{p=0}^{\infty}\{y_b + y_a[1 + (x-1)y_b]\}^p \quad (II.9)$$

$$= \sum_{p=0}^{\infty}\sum_{n=0}^{p}\binom{p}{n}y_a^n y_b^{p-n}[1 + (x-1)y_b]^n$$

by application of the binomial expansion. Making the substitution $l = p - n$ and applying the binomial expansion again produces

$$D^{-1} = \sum_{l=0}^{\infty}\sum_{n=0}^{\infty}\sum_{k=0}^{n}\binom{l+n}{n}\binom{n}{k}y_a^n y_b^{l+k}(x-1)^k \quad (II.10)$$

Finally, if we let $m = l + k$, we get

$$G = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\left\{c_1\sum_{k=0}^{n-1}\binom{m+n-k-1}{n-1}\times\binom{n-1}{k}(x-1)^k + (c_2x - c_1)\sum_{k=0}^{n-1}\binom{m+n-k-2}{n-1}\times\binom{n-1}{k}(x-1)^k\right\}y_a^n y_b^m \quad (II.11)$$

$$\Phi = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\left\{c_4\sum_{k=0}^{m-1}\binom{m+n-k-1}{n}\binom{n}{k}(x-1)^k + (c_3x - c_4)\sum_{k=0}^{m-1}\binom{m+n-k-2}{n-1}\times\binom{n-1}{k}(x-1)^k\right\}y_a^n y_b^m \quad (II.12)$$

where it is useful to remember the property of the binomial coefficient

$$\binom{b}{a} = 0 \text{ for } a > b \text{ or } a < 0 \quad (II.13)$$

Thus by comparing (II.11) and (II.12) with (II.1) and (II.2) we get

$$P_{n,m} = \alpha_a^n\alpha_b^m\left\{c_1\sum_{k=0}^{n-1}\binom{m+n-k-1}{n-1}\times\binom{n-1}{k}(x-1)^k + (c_2x - c_1)\sum_{k=0}^{n-1}\binom{m+n-k-2}{n-1}\times\binom{n-1}{k}(x-1)^k\right\} \quad (II.14)$$

$$Q_{n,m} = \alpha_a^n\alpha_b^m\left\{c_4\sum_{k=0}^{m-1}\binom{m+n-k-1}{n-1}\times\binom{n}{k}(x-1)^k + (c_3x - c_4)\sum_{k=0}^{m-1}\binom{m+n-k-2}{n-1}\times\binom{n-1}{k}(x-1)^k\right\} \quad (II.15)$$

In order to put this result in a more useful form and in the same format as the previous results of Simha and Branson,[2] we make use of the identity

$$F(-a, -b, 1, x) \equiv \sum_{k=0}^{a} \binom{a+b-k}{a}\binom{a}{k}(x-1)^k \tag{II.16}$$

where $F(a_1, a_2, a_3, x)$ is the hypergeometric function[10] defined

$$F(a_1, a_2, a_3, x) \equiv 1 + \sum_{n=1}^{\infty}\prod_{i=0}^{n-1}\frac{(a_1+i)(a_2+i)}{(a_3+i)}\frac{x^n}{n!} \tag{II.17}$$

A further useful identity

$$F(-a, -b, 1, x) \equiv \sum_{k=0}^{a}\binom{a}{k}\binom{b}{k}x^k \tag{II.18}$$

allows us to put the solution in the following form

$$P_{n,m} = \alpha_a{}^n\alpha_b{}^m\{c_1F(1-n, -m, 1, x) + (c_2x - c_1)F(1-n, 1-m, 1, x)\}$$
$$= \alpha_a{}^n\alpha_b{}^m\left\{\sum_{j=1}^{n}\left[\frac{c_1(n-j)}{j} + c_2\right]\binom{n-1}{j-1}\times\binom{m-1}{j-1}x^j\right\} \tag{II.19}$$

$$Q_{n,m} = \alpha_a{}^n\alpha_b{}^m\{c_4F(-n, 1-m, 1, x) + (c_3x - c_4)F(1-n, 1-m, 1, x)\}$$
$$= \alpha_a{}^n\alpha_b{}^m\left\{\sum_{j=1}^{n}\left[c_3 + c_4\frac{(m-j)}{j}\right]\times\binom{n-1}{j-1}\binom{m-1}{j-1}x^j\right\} \tag{II.20}$$

$$f(n, m, x) \equiv F(-n, -m, 1, x) \tag{II.21}$$

and making use of the Gauss identities[10] for the hypergeometric function, we get

$$P_{n,m} = \alpha_a{}^n\alpha_b{}^m\left\{\frac{c_1n}{m}f(n, m, -1, x) + \left[\left(c_2 + \frac{(n-m)}{m}c_1\right)x - \frac{n}{m}c_1\right]f(n-1, m-1, x)\right\} \tag{II.22}$$

$$Q_{n,m} = \alpha_a{}^n\alpha_b{}^m\{c_4f(n, m-1, x) + (c_3x - c_4)f(n-1, m-1, x)\} \tag{II.23}$$

which is computationally the most convenient form because it requires the calculation of only two hypergeometric series.

Appendix III. Evaluation of Double Sums

The first three terms of eq 25 can be evaluated by means of generating functions so that if we let

$$H^{\mathrm{I}}(u_1, u_2) = \sum_n\sum_m u_1{}^nu_2{}^mS_{n,m}{}^{\mathrm{I}} \tag{III.1}$$

$$H^{\mathrm{II}}(u_1, u_2) = \sum_n\sum_m u_1{}^uu_2{}^mS_{n,m}{}^{\mathrm{II}} \tag{III.2}$$

$$H^{\mathrm{III}}(u_1, u_2) = \sum_n\sum_m u_1{}^nu_2{}^mS_{n,m}{}^{\mathrm{III}} \tag{III.3}$$

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

where $S_{n,m}{}^{\mathrm{I}}$, $S_{n,m}{}^{\mathrm{II}}$, and $S_{n,m}{}^{\mathrm{III}}$ are the double sums defined by eq 26–28. By the convolution theorem for generating functions,[10] we see that

$$H^{\mathrm{I}} = G(u_1, u_2)^2 \tag{III.4}$$

$$H^{\mathrm{II}} = G(u_1, u_2)\Phi(u_1, u_2) \tag{III.5}$$

$$H^{\mathrm{III}} = \Phi(u_1, u_2)^2 \tag{III.6}$$

where $G(u_1, u_2)$ and $\Phi(u_1, u_2)$ are given by eq II.5 and II.6. Substituting, we get

$$H^{\mathrm{I}} = \{[c_1y_a + (c_2x - c_1)y_ay_b]^2\}/D^2 \tag{III.7}$$

$$H^{\mathrm{II}} = \{[c_1y_a + (c_2x - c_1)y_ay_b][c_4y_b + (c_3x - c_4)y_ay_b]\}/D^2 \tag{III.8}$$

$$H^{\mathrm{III}} = \{[c_4y_b + (c_3x - c_4)y_ay_b]^2\}/D^2 \tag{III.9}$$

where D, y_a, and y_b are defined in eq II.7 and II.8. The expressions III.7–III.9 must be expanded into a double power series in y_ay_b and this requires the expansion of D^{-2}. Thus

$$D^{-2} = \sum_{p=0}^{\infty}(p+1)\{y_b + y_a[1 + (x-1)y_b]\}^p \tag{III.10}$$

or by repeated expansion in binomial series, we get

$$D^{-2} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\sum_{k=0}^{n}\binom{m+n-k}{n}\times\binom{n}{k}(x-1)^k(m+n-k+1)y_a{}^ny_b{}^m \tag{III.11}$$

Thus by substitution into (III.7–III.9) we get, by collecting coefficients of $u_1{}^nu_2{}^m$

$$S_{n,m}{}^{\mathrm{I}} = \alpha_a{}^n\alpha_b{}^m\{c_1{}^2g(n-2, m) + 2c_1(c_2x - c_1)\times g(n-2, m-1) + (c_2x - c_1)^2g(n-2, m-2)\} \tag{III.12}$$

$$S_{n,m}{}^{\mathrm{II}} = \alpha_a{}^n\alpha_b{}^m\{c_1c_4g(n-1, m-1) + c_1(c_3x - c_4)g(n-2, m-1) + c_4(c_2x - c_1)\times g(n-1, m-2) + (c_2x - c_1)(c_3x - c_4)g(n-2, m-2)\} \tag{III.13}$$

$$S_{n,m}{}^{\mathrm{III}} = \alpha_a{}^n\alpha_b{}^m\{c_4{}^2g(n, m-2) + 2c_4(c_3x - c_4)g(n-1, m-2) + (c_3x - c_4)^2g(n-2, m-2)\} \tag{III.14}$$

where

$$g(n, m) \equiv \sum_{k=0}^{n}(m+n-k+1)\binom{m+n-k}{n}\times\binom{n}{k}(x-1)^k$$
$$= \sum_{k=0}^{n}(n+1)\binom{m+n-k+1}{n+1}\times\binom{n}{k}(x-1)^k \tag{III.15}$$

and it can be shown that

$$g(n, m) \equiv g(m, n) \equiv (m+1)(n+1)F(-n, -m, 2, x) \tag{III.16}$$

where $F(a_1, a_2, a_3, x)$ is the hypergeometric function defined in eq II.17. Using the Gauss identities[10] for the hypergeometric function, we get the useful relations

$$g(n, m+1) = \frac{[2(1+m)+(n-m)x]}{(1+m)} g(n, m) + (x-1)g(n, m-1) \quad \text{(III.17)}$$

$$g(n+1, m) = \frac{[2(1+n)+(m-n)x]}{(1+n)} g(n, m) + (x-1)g(n-1, m) \quad \text{(III.18)}$$

$$g(n-1, m) = \frac{(1+m)}{(1+n)} g(n, m-1) - \frac{(m-n)}{(1+n)} g(n, m) \quad \text{(III.19)}$$

$$g(n, m-1) = \frac{(1+n)}{(1+m)} g(n-1, m) - \frac{(n-m)}{(1+m)} g(n, m) \quad \text{(III.20)}$$

$$g(n, m+1) = \frac{(1+n)}{(1+m)} g(n+1, m) - \frac{(n-m)}{(1+m)} g(n, m)(1-x) \quad \text{(III.21)}$$

which allow us to reduce eq III.12–III.14 to

$$S_{n,m}{}^{\mathrm{I}} = \alpha_a{}^n \alpha_b{}^m \{\eta_{11} g(n-1, m-2) + \eta_{12} g(n-2, m-2)\} \quad \text{(III.22)}$$

If $n \neq m$

$$S_{n,n}{}^{\mathrm{II}} = \alpha_a{}^n \alpha_b{}^m \{\eta_{21} g(n-1, m-2) + \eta_{22} g(n-2, m-2)\} \quad \text{(III.23a)}$$

If $n = m$

$$S_{n,m}{}^{\mathrm{II}} = \alpha_a{}^n \alpha_b{}^m \{\bar{\eta}_{21} g(n-1, m-2) + \bar{\eta}_{22} g(n-2, m-2) + \bar{\eta}_{23} g(n-1, m-1)\} \quad \text{(III.23b)}$$

$$S_{n,m}{}^{\mathrm{III}} = \alpha_a{}^n \alpha_b{}^m \{\eta_{31} g(n-1, m-2) + \eta_{32} g(n-2, m-2)\} \quad \text{(III.24)}$$

where

$$\eta_{11} = \frac{(n-1)}{(m-1)} \left\{\frac{c_1{}^2}{m} [2m + (n-m-1)x] + 2c_1 [c_2 x - c_1]\right\} \quad \text{(III.25)}$$

$$\eta_{12} = c_1{}^2(x-1) + (c_2 x - c_1)^2 - \frac{(1-x)(n-m)}{(n-1)} \eta_{11} \quad \text{(III.26)}$$

$$\eta_{21} = \frac{c_1 c_4 m}{m-n} + c_3(c_2 x - c_1) + \frac{(n-1)}{(m-1)} \left[c_1(c_3 x - c_4) - \frac{c_1 c_4 n}{m-n}\right] \quad \text{(III.27)}$$

$$\eta_{22} = (c_2 x - c_1)(c_3 x - c_4) - \frac{(1-x)(n-m)}{(m-1)} \times \left[c_1(c_3 x - c_4) - \frac{c_1 c_4 n}{m-n}\right] \quad \text{(III.28)}$$

$$\bar{\eta}_{21} = c_1(c_3 x - c_4) + c_4(c_2 x - c_1) \quad \text{(III.29)}$$

$$\bar{\eta}_{22} = (c_2 x - c_1)(c_3 x - c_4) \quad \text{(III.30)}$$

$$\bar{\eta}_{23} = c_1 c_4 \quad \text{(III.31)}$$

$$\bar{\eta}_{31} = [(c_4)^2/n][2n + (m-n-1)x] + 2c_4(c_3 x - c_4) \quad \text{(III.32)}$$

$$\eta_{32} = (c_4)^2(x-1) + (c_3 x - c_4)^2 \quad \text{(III.33)}$$

where, during computation under isothermal conditions, the $g(n-1, m-2)$, $g(n-2, m-2)$ terms can be precomputed and stored for all values of n and m of interest and only the η_{ij} values need be recalculated as the reaction progresses. Even more convenient is the fact that we can make use of the Gauss identities[10] to get the double sums in terms of $f(n, m-1, x)$, $f(n-1, m-1, x)$, the hypergeometric series required for calculation of the live polymer. This results in

$$g(n-1, m-2) = (n/x)[f(n, m-1, x) - f(n-1, m-1, x)] \quad \text{(III.34)}$$

$$g(n-2, m-2) = \frac{1}{x(x-1)} \{[(m-1)x + n] \times f(n-1, m-1, x) - nf(n, m-1, x)\} \quad \text{(III.35)}$$

$$g(n-1, m-1) = (n/x)[f(n, m-1, x) - (1-x)f(n-1, m-1, x)] \quad \text{(III.36)}$$

Thus, by using these equations, we can effect enormous computational efficiencies in calculating the MWD for the dead polymer.

Appendix IV. Calculation of MWD Moments

It is quite simple to calculate the moments of the MWD from the generating functions by making use of the substitution $u_1 = su^{w_a}$

$$G(s, u) = \sum_n \sum_m s^{n+m} u^{nw_a + mw_b} P_{n,m} \quad \text{(IV.1)}$$

$$\Phi(s, u) = \sum_n \sum_m s^{n+m} u^{nw_a + mw_b} Q_{n,m} \quad \text{(IV.2)}$$

and the dead polymer generating function is

$$\textcircled{H}(s, u) = \sum_n \sum_m s^{n+m} u^{nw_a + mw_b} M_{n,m} \quad \text{(IV.3)}$$

and all the CLD and MWD moments for $P_{n,m}$ are defined by

$$\lambda_k{}^{\mathrm{P}} \equiv \sum_n \sum_m (n+m)^k P_{n,m} = \sum_{i=0}^{k} a_{ki} \left[\frac{\partial^i G}{\partial s^i}\right]_{s=u=1} \quad k = 0, 1, 2, \ldots \quad \text{(IV.4)}$$

$$\hat{\lambda}_k{}^{\mathrm{P}} = \sum_n \sum_m (nw_a + mw_b)(n+m)^k P_{n,m} = \sum_{i=0}^{k} a_{ki} \left[\frac{\partial^{i+1} G}{\partial s^i \partial u}\right]_{s=u=1} \quad k = 0, 1, 2, \ldots \quad \text{(IV.5)}$$

$$\psi_k{}^{\mathrm{P}} \equiv \sum_n \sum_m (nw_a + mw_b)^k P_{n,m} = \sum_{i=0}^{k} a_{ki} \left[\frac{\partial^i G}{\partial u^i}\right]_{s=u=1} \quad k = 0, 1, 2, \ldots \quad \text{(IV.6)}$$

$$\psi_k{}^{\mathrm{P}} \equiv \sum_n \sum_m (nw_a + mw_b)^{k+1} P_{n,m} = \sum_{i=0}^{k+1} a_{k+1,i} \left[\frac{\partial^i G}{\partial u^i}\right]_{s=u=1} \quad k = 0, 1, 2, \ldots \quad \text{(IV.7)}$$

where the coefficients a_{ki} are given by

$$a_{ki} = 1 \quad \text{if } i = k \quad \text{(IV.8a)}$$

$$a_{ki} = -S_{k-i}{}^{(k)} \quad \text{if } i \neq k \quad \text{(IV.8b)}$$

where $S_q^{(p)}$'s are Stirling numbers of the first kind.[11] For most applications, only the first few coefficients are needed and these are given by the matrix

$$\{a_{kl}\} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 3 & 1 & 0 \\ 0 & -11 & 7 & 6 & 1 \\ . & . & . & . & . \\ . & . & . & . & . \end{bmatrix} \quad \text{(IV.9)}$$

(11) G. A. Korn and T. M. Korn, "Mathematical Handbook for Scientists and Engineers," McGraw-Hill, New York, N. Y., 1968.

The moments for $Q_{n,m}$ and $M_{n,m}$ are given by similar expressions. Thus all the live polymer moments can be obtained by performing the indicated differentiation on (II.5) and (II.6).

The dead polymer moments must be found by making use of eq 29 to give the rate of production of $\textcircled{H}(s, u)$

$$r_{\textcircled{H}} = \sum_n \sum_m s^{n+m} u^{nw_a+mw_b} r_{Mn,m} \quad \text{(IV.10)}$$

Then by performing the differentiation with respect to s and u on eq IV.10 we get rates of formation of all the moments. For example

$$r_{\lambda_k M} = \sum_{i=0}^{k} a_{ki} \left[\frac{\partial^i r_{\textcircled{H}}}{\partial s^i}\right]_{s=u=1} \quad k = 0, 1, 2, \ldots \quad \text{(IV.11)}$$

and the other moments are obtained by similar expressions.

Photooxidation of Polypropylene Films. IV. Surface Changes Studied by Attenuated Total Reflection Spectroscopy[1,2]

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ABSTRACT: The photooxidation of unstabilized polypropylene films was found to occur primarily in thin surface layers of the samples. The formation of –OH and >C=O oxidation products was monitored by transmission and attenuated total reflection (ATR) spectroscopy in the infrared. By selecting appropriate reflection conditions, the ATR spectra of surface layers corresponding to four different depths of penetration of the ir beam were recorded with each sample. The phenomenon of surface oxidation was found to occur with all of the commercial film samples and uv sources employed, and is believed to result in the brittle failure of the degraded films at very low overall degrees of oxidation. Surface product concentrations and concentration–depth distributions are derived from the spectroscopic data at various irradiation times.

The photooxidative deterioration of polypropylene films and fibers at relatively long ultraviolet (uv) wavelengths (>3000 Å) has been found to involve several competing or consecutive radical and molecular reactions.[3] These reactions result in a buildup in oxidation products, together with various associated physical changes, such as a drop in molecular weight and an increase in the brittleness of the polymer sample. Polymer photodeterioration has frequently been studied by such techniques as chemical analysis, transmission spectroscopy (in the infrared (ir) or uv regions), solution viscometry, and stress–strain analysis. For many purposes, these methods can provide adequate experimental information. However, all of these techniques usually give results which sum or average changes which have occurred across the total thickness of the sample, and give no information on the exact location of the onset of deterioration. This shortcoming can be expected to be of great importance in the study of polymer–gas reactions, owing to the possibilities of nonuniform product distributions in such systems. For example, during the photooxidation of polyolefins diffusion effects[4] and variations in polymer reactivity may cause preferential reaction in certain regions.

Attenuated total reflection (ATR) ir spectroscopy provides a means of observing surface changes in a given sample, and hence, when used in conjunction with transmission ir spectroscopy, provides a means of studying reaction uniformity in solids. The technique of ATR spectroscopy involves the measurement of the ir spectrum of the surface of a sample which has been placed in intimate contact with a suitable reflection element.[5] With the correct choice of reflection element and angle of incidence, it is possible to record the ir spectra corresponding to various depths of penetration (usually from 0.1 to 4.0 μ) of the ir beam into the surface of a given sample. By the use of this technique, one can build up a partial "concentration profile" across the thickness of the sample. The scope of this ATR procedure and the normalization procedure which is required in order to make meaningful quantitative comparisons between ATR spectra have been discussed previously.[6] In this paper, we discuss the use of the ATR technique to study the extent of photooxidation of polypropylene films as a function of distance into the sample from the film surface.

Experimental Section

Polypropylene Films.[7] Six films (designated A–F) were obtained

(1) Issued as NRCC Report No. 11864.
(2) Previous paper in this series: D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 597 (1969).
(3) (a) Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, **13**, 1447 (1969); (b) J. H. Adams, *J. Polym. Sci., Part A-1*, **8**, 1269, 1279 (1970).
(4) J. E. Wilson, *J. Chem. Phys.*, **22**, 334 (1954).
(5) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, New York, N. Y., 1967.
(6) D. J. Carlsson and D. M. Wiles, *Can. J. Chem.*, **48**, 2397 (1970).
(7) The results obtained with the commercial films used in this work should not be considered to endorse or discredit the products of any manufacturer. Many of the samples were experimental grades, or subjected to unusual treatments.