Number-Average Molecular Weights from Viscosity Measurements during Random Degradation of Polymers

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SUMMARY

Using the theories of random degradation of Montroll and Simha, relationships are derived among limiting viscosity number, degree of degradation, and number-average molecular weight for a polymer undergoing random degradation in a closed system. Relationships among these parameters are derived for initial distributions of the "coupling" and the monodisperse types. Computer programs have been written which rapidly provide reliable values of number-average molecular weights and degrees of degradation from measured viscosity data on polymers with these initial distributions undergoing random degradation.

It is now a well-established fact that many polymers are degraded by heat and other agencies (except mechanical) in an essentially random manner. The rate at which backbone bonds are broken randomly is given by the relationship

$$\frac{1}{DP_t} - \frac{1}{DP_0} = \alpha = kt_d \tag{1}$$

where DP_t and DP_0 are number-average degrees of polymerization at time of degradation t_d and zero time, respectively, and k is the rate constant for bond breaking. α is known as the "degree of degradation." This equation holds provided (1) $\alpha \ll 1$, (2) no loss of low polymer occurs by evaporation or otherwise (i.e., the system is "closed"), (3) depropagation by unzipping to monomer does not occur, and (4) all interunit bonds are equally susceptible to attack.

Equation (1) provides a convenient basis for studying the effects of structural and other changes on polymer stability and on activation energies of bond scission, particularly in the early stages of degradation.

When provisions (1) to (3) are satisfied but a proportion of the interunit bonds (randomly distributed) are labile, the linear relationship indicated by Eq. (1) breaks down and a plot of α versus time may show curvature or an ordinate intercept. In such cases plots of α versus time can provide a sensitive method of detecting structural abnormalities.

Equation (1) has been widely applied in degradation studies, but unfortunately its limitations have not always been fully appreciated. The accuracy and sensitivity of this approach depend upon the accuracy with which number-average molecular weights, $\overline{Mn}$, can be measured. Ideally, $\overline{Mn}$ should be measured by osmometry, but this technique is unreliable when low molecular weight polymer, which can diffuse through the membrane [1], is present, and some low polymer is almost invariably produced during degradation. Modern high-speed membrane osmometers reduce, but do not totally eliminate, this source of inaccuracy.

Limiting viscosity numbers (LVN), $[\eta]$, and bulk viscosities, can be measured quickly with a high degree of precision and have been used to estimate $\overline{Mn}$ [2-4]. However, the Mark-Houwink relationship between the LVN and average molecular weight, $\overline{Mv}$, will only yield a true number-average value if the molecular weight distribution of the sample is identical with the distribution of the calibration samples used to obtain the constants, K and a. When the molecular weight distribution of a degrading sample changes with time of reaction, it is not possible to obtain $\overline{Mn}$ directly from viscosity measurements. Consequently, kinetic parameters based on such measurements become suspect. It is possible, however, to calculate accurate number-average molecular weights from LVN measurements of randomly degraded polymers provided the initial molecular weight distribution is known and can be expressed mathematically. The particular case of an initial logarithmic normal distribution has recently been treated in relation to the degradation of polypropylene [5] and polystyrene [4].

In the present paper this approach is extended and a method is presented for obtaining number-average molecular weights and degrees of degradation from LVN measurements on randomly degraded polymers having initial molecular weight distributions of two

types—the "coupling" distribution and the monodisperse distribution. Along with the "most probable" distribution, these distributions are of wide interest, particularly in relation to synthetic addition polymers.

THEORETICAL TREATMENT AND DISCUSSION

Three basic assumptions are made. These are:

1. The initial molecular weight can be expressed in terms of a distribution function.

2. The accessibility to reaction of a bond in a given chain is independent of its position in the chain and independent of the length of the parent chain.

3. All chains in the polymer are equally accessible to reaction.

Montroll [6] has derived a theory, based on these assumptions, to show that the totality of t-mers, $N_t(\alpha)$, existing after a degree of degradation α in a system originally consisting of N polymers distributed as Nn_1 monomers, Nn_2 dimers, ..., Nn_p p-mers, is given by

$$
\begin{aligned}
N_t(\alpha) &= \sum_{p+1=t}^{\infty} N_t(p, \alpha) \\
&= Nn_t(1-\alpha)^{t-1} \\
&\quad + N \sum_{p+1=t+1}^{\infty} n_{p+1}\, \alpha(1-\alpha)^{t-1} \left[2 + (p-t)\alpha\right]
\end{aligned}
\tag{2}
$$

where a p-mer comprises p monomeric elements linked by $p-1$ bonds, n_t is the number fraction of t-mers, and n_{p+1} is the number fraction of (p + 1)-mers.

To apply Eq. (2) to practical systems, suitable distribution functions must now be substituted for n_t and n_{p+1}. The first distribution studied is the "coupling" distribution arising from monoradical initiation and termination by combination.

"Coupling" Distribution

In this distribution, the number fraction of t-mers, n_t, is given by [7]

$$
n_t = \frac{4t}{r^2} \exp\left(\frac{-2t}{r}\right)
$$

where $\overline{r}$ is the number-average degree of polymerization. Substituting for n_t and n_{p+1} in Eq. (1) gives

$$N_t(\alpha) = N\frac{4t}{\overline{r}^2} (1 - \alpha)^{t-1} \exp\left(\frac{-2t}{\overline{r}}\right)$$

$$+ N \sum_{p+1 = t+1}^{\infty} \frac{4(p+1)}{\overline{r}^2} \alpha (1 - \alpha)^{t-1} [2 + (p - t)\alpha]$$

$$\exp\left[\frac{-2(p+1)}{\overline{r}}\right] \quad (3)$$

Since p and t are large and the summand is smooth, we may replace summations by integration. Integrating by parts (Appendix 1) results in

$$N_t(\alpha) = \frac{4N}{\overline{r}^2} (1 - \alpha)^{t-1} \exp\left(\frac{-2t}{\overline{r}}\right) \left\{ t + \alpha\,\overline{r}\, \exp\left(\frac{-2}{\overline{r}}\right)\left[t\left(1 + \frac{\alpha\overline{r}}{4}\right)\right.\right.$$

$$\left.\left. + \frac{\alpha\,\overline{r}^2}{4} + \frac{(\alpha+2)\overline{r}}{4} + 1\right]\right\} \quad (4)$$

Equation (4) may be written in the form

$$N_t(\alpha) = K_1(K_2 t + K_3) (1 - \alpha)^{t-1} \exp\left(\frac{-2t}{\overline{r}}\right) \quad (5)$$

where

$$K_1 = \frac{4N}{\overline{r}^2}$$

$$K_2 = 1 + \alpha\,\overline{r}\,\left(1 + \frac{\alpha\,\overline{r}}{4}\right)\, \exp\left(\frac{-2}{\overline{r}}\right)$$

$$K_3 = \alpha\,\overline{r}\,\left[1 + \frac{(\alpha+2)\overline{r}}{4} + \frac{\alpha\overline{r}^2}{4}\right]\, \exp\left(\frac{-2}{\overline{r}}\right)$$

Equation (4) expresses the molecular weight distribution after a degree of degradation α in a polymer with an initial coupling distribution.

As degradation proceeds, the parameter measurable with time is the LVN, $[\eta]$. For any polydisperse polymer, it can be shown that [7]

$$[\eta] = \frac{\sum_t tN_t f(M_0 t)}{\sum_t tN_t} \tag{6}$$

where N_t is the number of each species t present and M_0 is the monomer molecular weight. Suppose $f(M_0 t)$ is of the Mark-Houwink type, since this appears to have a wide applicability. Then

$$f(M_0 t) = K(M_0 t)^a$$

where K and a have the usual significance. Equation (6) becomes

$$[\eta] = \frac{\sum_t tN_t K(M_0)^a t^a}{\sum_t tN_t} \tag{7}$$

$$[\eta] = \frac{KM_0^a \sum_t t^{1+a} N_t}{\sum_t tN_t} \tag{8}$$

For high molecular weight polymers t is very large. The summation is virtually continuous, and is commonly replaced by an integral. Substitution of the value of $N_t(\alpha)$ in Eq. (5) for N_t in Eq. (8), and integration by parts (Appendix 2) gives

$$[\eta] = \frac{KM_0^a \, \Gamma(a+2) \left\{ K_2(a+2) + K_3[2/\overline{r} - \ln(1-\alpha)] \right\}}{[2/\overline{r} - \ln(1-\alpha)]^a \left\{ 2K_2 + K_3[2/\overline{r} - \ln(1-\alpha)] \right\}} \tag{9}$$

where $\Gamma(x)$ is the well-known "gamma" function of x. The validity of Eq. (9) can be readily checked by setting $\alpha = 0$, whereupon $K_2 = 1$ and $K_3 = 0$. Thus Eq. (9) simplifies to the form

$$[\eta] = \frac{KM_0^a \, \Gamma(a+2)(a+2)}{2(2/\overline{r})^a}$$

$$= \frac{K(M_0 \overline{r})^a \, \Gamma(a+3)}{2^{a+1}}$$

which is the correct relationship between $[\eta]$ and $\bar{r}$ for a polymer with a "coupling" distribution [7].

The insertion of known values of $\bar{r}, M_0, K,$ and a into Eq. (9) permits the calculation of the LVN, $[\eta]$, for any degree of degradation, α, in the initial coupling distribution; conversely α can be evaluated from Eq. (8) from any value of LVN. As an illustrative example, the values of K (1.12×10^{-4}) and a (0.73) for polystyrene in benzene at 25°C [8] are used here.

Number-average molecular weights may be obtained from α by the equation relating α and $\overline{Mn}$ for random scission in a closed system,

$$\frac{1}{\overline{Mn}_t} - \frac{1}{\overline{Mn}_0} = \frac{\alpha}{M_0} \quad \alpha \ll 1 \tag{10}$$

where $\overline{Mn}_0$ is the initial $\overline{Mn}$ and $\overline{Mn}_t$ is the $\overline{Mn}$ after degree of degradation α, i.e., after time of degradation t_d. Equation (10) rearranges to give

$$\frac{1}{\overline{Mn}_t} = \frac{\alpha \bar{r}_0 + 1}{M_0 \bar{r}_0} \tag{11}$$

where $\bar{r}_0$ is the initial number-average DP. Combining Eq. (11) with the Mark-Houwink equation, $[\eta] = K\overline{Mv}^a$, gives

$$\frac{\overline{Mv}_t}{\overline{Mn}_t} = \frac{[\eta]^{1/a}}{K} \times \frac{1 + \alpha \, \bar{r}_0}{M_0 \bar{r}_0} \tag{12}$$

Therefore, for any value of the LVN, the degree of depolymerization, α, can be obtained from Eq. (9), the number-average molecular weight can be calculated from Eq. (11), and the ratio $\overline{Mv}/\overline{Mn}$ can be had from Eq. (12). These three equations were combined, and a computer program was written to express the LVN and the ratio $\overline{Mv}_t/\overline{Mn}_t$ as functions of α for the random scission of polymers with a series of arbitrary initial number-average DP's and an initial coupling distribution. Figures 1 and 2 show plots of LVN and $\overline{Mv}_t/\overline{Mn}_t$, respectively, as function of α. Three important features are immediately apparent from these diagrams:

1. The LVN's all tend to the same value at high values of α.

2. There is an upper limiting value of the ratio $\overline{Mv}_t/\overline{Mn}_t$ which is attained more rapidly as the initial DP of the polymer increases but which is not attained, within the range of α studied, by polymers of low initial DP.
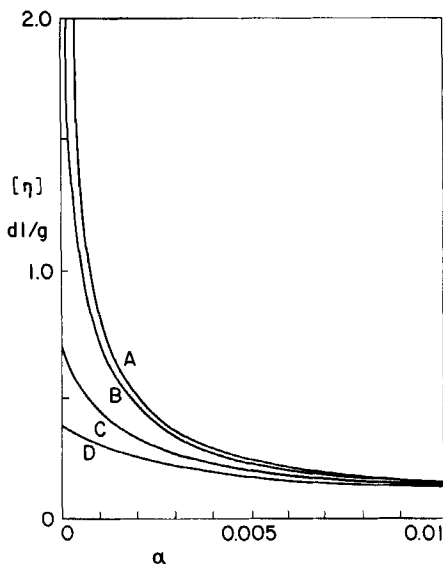
Fig. 1. Limiting viscosity number, $[\eta]$, as a function of degree of random degradation, α, for a polymer having an initial "coupling" distribution. Initial number-average DP: A, 100, 000; B, 5000; C, 1000; D, 500. Mark-Houwink constants: $K = 1.12 \times 10^{-4}$; $a = 0.73$.

3. The limiting value of $\overline{M}v_t/\overline{M}n_t$ lies within 1% of 1.88, which is the required figure for a polymer with a "most probable" distribution of molecular weights and a Mark-Houwink constant, a, 0.73. (Boyd and Tung-Po Lin [9] and others have shown, from theory, that all polymers tend to this distribution on random degradation.)

A computer program was also constructed in which the summations in Eq. (3) were not replaced by integrals. The computed values of $[\eta]$ and $\overline{M}v_t/\overline{M}n_t$ as functions of α were identical with those obtained when the summations were replaced by integrals, but whereas the complete program using integrals took 12 min to run, the program employing summations required 30 min for each individual computation of $[\eta]$ and $\overline{M}v_t/\overline{M}n_t$ from α. Consequently, the programs using integrals can be employed with no loss in accuracy and considerable saving in time.

The close correspondence between the limiting value of the ratio $\overline{M}v_t/\overline{M}n_t$ obtained by this method and the required theoretical value (1.88) supports the validity of the above treatment.
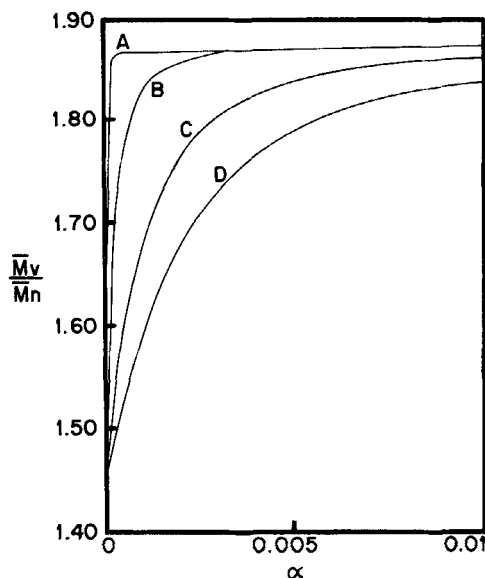
Fig. 2. Ratio of viscosity-average to number-average molecular weight, $\overline{Mv}/\overline{Mn}$, as a function of α, for a polymer having an initial "coupling" distribution. Initial number-average DP : A, 100, 000; B, 5000; C, 1000; D, 500. Mark-Houwink constants: $K = 1.12 \times 10^{-4}$; $a = 0.73$.

Monodisperse System

After a degree of degradation α in a system originally comprising N $(p + 1)$-mers, the total number of $(p + 1)$-mers uncut is given by [10]

$$N_{p+1}(p, \alpha) = N(1 - \alpha)p \tag{13}$$

and the totality of t-mers generated by scission of $(p + 1)$-mers is

$$N_t(\alpha) = N \sum_0^{p+1} n_{p+1} \alpha (1 - \alpha)^{t-1} [2 + (p - t)\alpha] \tag{14}$$

The number fraction of $(p + 1)$-mers initially is unity. Replacing the summation in Eq. (14) by an integral gives

$$N_t(\alpha) = N \int_0^{p+1} \alpha (1 - \alpha)^{t-1} [2 + (p - t)\alpha] \, dt \tag{15}$$

Thus the total number of molecules in the system after degree of degradation α in a monodisperse polymer comprising initially N $(p + 1)$-mers is

$$N_{total}(\alpha) = N(1 - \alpha)^p + N \int_0^{p+1} \alpha (1 - \alpha)^{t-1}[2 + (p - t)\alpha]\,dt \tag{16}$$

The LVN, $[\eta]$, of a polydisperse system with an upper size limit of of $p + 1$ is given by [7]

$$[\eta] = \frac{KM_0^a \int_0^{p+1} t^{1+a}N_t\,dt}{\int_0^{p+1} tN_t\,dt} \tag{17}$$

$$= \frac{KM_0^a}{p+1} \left\{ (p + 1)^{1+a}(1 - \alpha)^p \right.$$

$$\left. + \int_0^{p+1} t^{1+a}\,\alpha\,(1 - \alpha)^{t-1}\,[2 + (p - t)\alpha]\,dt \right\} \tag{18}$$

Evaluation of the integral (Appendix 3) in Eq. (18) gives

$$[\eta] = \frac{KM_0^a}{p+1} \left\{ (p + 1)^{1+a}(1 - \alpha)^p + \frac{\alpha}{(1 - \alpha)[\ln(1/1 - \alpha)]^{3+a}} \right.$$

$$\left. (2 + p\alpha) \ln\frac{1}{1 - \alpha}\,\gamma\,[a + 2, \theta] - \gamma\,[a + 3, \theta] \right\} \tag{19}$$

where $\theta = (p + 1)\ln(1/1 - \alpha)$. The integrals $\gamma[\beta, \theta]$ are incomplete "gamma" functions. As a check of Eq. (19) set $\alpha = 0$. In this special case Eq. (19) becomes

$$[\eta] = \frac{KM_0^a\,(p + 1)^{a+1}}{p+1}$$

$$= KM_0^a\,(p + 1)^a$$

which is the correct relationship for a monodisperse polymer of $p + 1$ monomeric elements.

From Eq. (19), α can be calculated for any measured value of $[\eta]$, and $\overline{Mn}_t$ and $\overline{Mv}_t/\overline{Mn}_t$ as functions of α may be obtained from Eqs. (11) and (12), respectively. All three equations were combined

as before, and a computer program was written to yield $[\eta]$ and $\overline{Mv}_t/\overline{Mn}_t$ as functions of α. Figures 3 and 4 show $[\eta]$ and $\overline{Mv}_t/\overline{Mn}_t$ as functions of α and are qualitatively similar to Figs. 1 and 2, respectively, for the "coupling" distribution; i.e., the LVN's tend to the same value as α increases and the ratio $\overline{Mv}_t/\overline{Mn}_t$ for polymers of high initial DP reaches a limiting value which is in good agreement with the required figure, 1.88.

As would be expected, polymers with the "coupling" distribution attain a wider distribution (i.e., a higher $\overline{Mv}_t/\overline{Mn}_t$ ratio) than the monodisperse polymers of the same initial DP at a given value of α. This is particularly noticeable for samples of lower initial DP.

In the case of the monodisperse system the replacement of summations by integrals is fundamentally less correct except at values of α sufficiently large to render the summand smooth. This condition appears to obtain in the present treatment, since computed
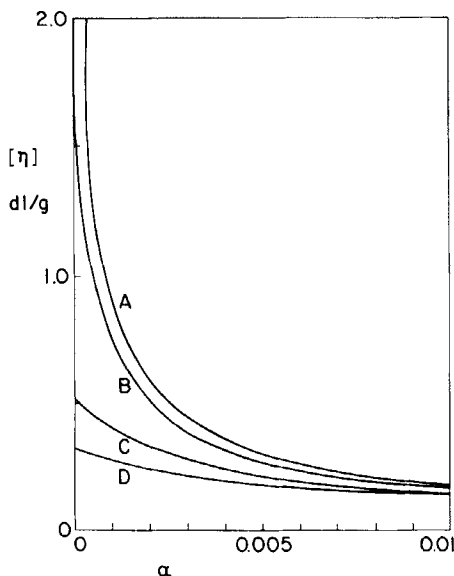

Fig. 3. Limiting viscosity number, $[\eta]$, as a function of α, for an initially monodisperse polymer. Initial number-average DP: A, 100, 000; B, 5000; C, 1000; D, 500. Mark-Houwink constants: $K = 1.12 \times 10^{-4}$; $a = 0.73$. (Note: Because of the large numbers involved, the computer could not provide solutions of $[\eta]$ as a function of α, $\alpha > 0.0022$, for curve A. Since $\overline{Mv}_t/\overline{Mn}_t$ reached the steady limiting value at $\alpha \ll 0.0022$ in Fig. 4, values of α and $[\eta]$ for Fig. 3 were calculated by assuming that $\overline{Mv}_t/\overline{Mn}_t$ remained constant up to $\alpha = 0.01$.)
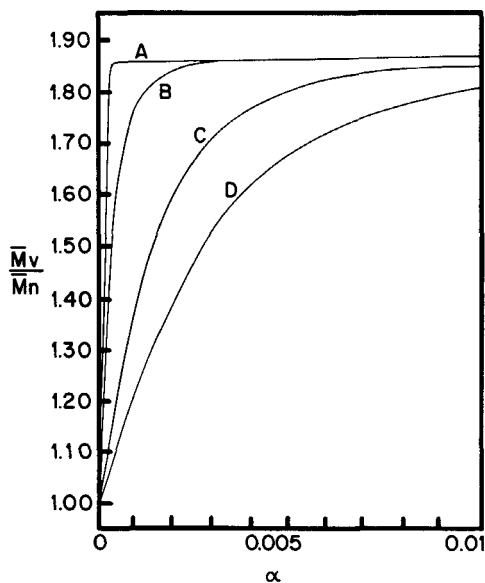
Fig. 4. Ratio of viscosity-average to number-average molecular weight, $\overline{Mv}/\overline{Mn}$, as a function of α for an initially monodisperse polymer. Initial number-average DP: A, 100, 000; B, 5000; C, 1000; D, 500. Mark-Houwink constants: $K = 1.12 \times 10^{-4}; a = 0.73$. (See note with Fig. 3.)

values of $[\eta]$ and $\overline{Mv}_t/\overline{Mn}_t$ by both summations and integration were virtually identical. As before, the program involving integrals was very much faster and can be employed with no perceptible loss in accuracy.

"Most Probable" Distribution

The third commonly encountered distribution is the "most probable" distribution, which results, for example, from free radically prepared polymers when initiation is monoradical and termination is by disproportionation. During a closed random degradation this distribution remains invariant [9]. Consequently, the ratio $\overline{Mv}/\overline{Mn}$ is constant throughout degradation and $\overline{Mn}$ may be calculated directly from viscosity measurements using the appropriate Mark-Houwink constants, since $\overline{Mv}/\overline{Mn} = \{\Gamma(a + 2)\}^{1/a}$. For the particular case of polystyrene in benzene at 25°C, this relationship gives $\overline{Mv}/\overline{Mn}$ = 1.88.

COMPUTER PROGRAMS

The computer programs were written in Fortran II-D and run on an IBM 1620 computer. Copies of the programs are available on request.

CONCLUSIONS

A method has been derived to permit the determination from viscosity data of number-average molecular weights of polymers which have undergone random degradation in a closed system. The method combines the advantages of the experimental accuracy of viscometry techniques with the exact theoretical significance of number-average molecular weights. The treatment is valid for values of $\alpha \ll 1$, and in the present study an upper limit of 0.01 was chosen. This is not a serious deficiency, however, as the experimentally useful range of α generally lies below this limit.

ACKNOWLEDGMENT

APPENDIX I

This appendix evaluates the integral in

$$N_t(\alpha) = \frac{4Nt}{\overline{r}^2}(1-\alpha)^{t-1}\exp\left(\frac{-2t}{\overline{r}}\right)$$

$$+\frac{4\alpha}{\overline{r}^2}(1-\alpha)^{t-1}N\int_{p=t}^{\infty}[2+(p-t)\alpha](p+1)$$

$$\exp\left(\frac{-2(p+1)}{\overline{r}}\right)dp$$

$$\int u\,dv = uv - v\,du$$

Let

$$v = -\frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right)$$

$$\therefore \exp\left(\frac{-2p}{\bar{r}}\right) dp = dv$$

$$\text{Integral } I_{(q)} = \int_t^\infty p^q \exp\left(\frac{-2p}{\bar{r}}\right) dp$$

$$= \left[p^q - \frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right)\right]_t^\infty$$

$$- \int_t^\infty -\frac{\bar{r}}{2} \exp\left(\frac{-2p}{\bar{r}}\right) qp^{q-1} dp$$

$$= \frac{\bar{r}}{2} t^q \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{\bar{r}}{2} I_{(q-1)}$$

$$I_{(0)} = \int_t^\infty \exp\left(\frac{-2p}{\bar{r}}\right) dp = \left[-\frac{\bar{r}}{2} \exp\frac{-2p}{\bar{r}}\right]_t^\infty$$

$$= \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right)$$

Thus we obtain

$$I_{(1)} = \frac{\bar{r}}{2} t \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{\bar{r}}{2} I_{(0)}$$

$$= \frac{\bar{r}}{2} t \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{\bar{r}}{2} \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right)$$

$$= \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left[t + \frac{\bar{r}}{2}\right]$$

$$I_{(2)} = \frac{\bar{r}}{2} \, t^2 \exp\left(\frac{-2t}{\bar{r}}\right) + \frac{\bar{r}}{2} \, 2I_{(1)}$$

$$= \frac{\bar{r}}{2} \, t^2 \exp\left(\frac{-2t}{\bar{r}}\right) + \bar{r} \, \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left[t + \frac{\bar{r}}{2}\right]$$

$$= \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left[t^2 + \bar{r}t + \tfrac{1}{2}\bar{r}^2\right]$$

Now,

$$N_t(\alpha) = \frac{4Nt}{\bar{r}^2} \, (1 - \alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right)$$

$$+ \frac{4N\alpha}{\bar{r}^2} \, (1 - \alpha)^{t-1} \exp\left(\frac{-2}{\bar{r}}\right) \int_t^\infty (p + 1) \, [2 + (p - t)\alpha]$$

$$\exp\left(\frac{-2p}{\bar{r}}\right) dp$$

Let

$$\int_t^\infty (p + 1) \, [2 + (p - t)\alpha] \exp\left(\frac{-2p}{\bar{r}}\right) dp = G$$

$$\therefore \quad G = \int_t^\infty (p + 1) \, (2 + \alpha p - \alpha t) \exp\left(\frac{-2p}{\bar{r}}\right) dp$$

$$G = \int \exp\left(\frac{-2p}{\bar{r}}\right) [2p + \alpha p^2 - \alpha pt + 2 + \alpha p - \alpha t] \, dp$$

$$= \int \exp\left(\frac{-2p}{\bar{r}}\right) [\alpha p^2 + p(2 + \alpha - \alpha t) + (2 - \alpha t)] \, dp$$

$$\therefore \quad G = \alpha I_{(2)} + [2 + \alpha(1 - t)]I_{(1)} + (2 - \alpha t)I_{(0)}$$

$$= \frac{\alpha \bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) (t^2 + \bar{r}t + \tfrac{1}{2}\bar{r}^2)$$

$$+ [2 + \alpha(1 - t)] \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left(t + \frac{\bar{r}}{2}\right) + (2 - \alpha t) \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right)$$

$$= \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left\{ \alpha\,(t^2 + \bar{r}t + \tfrac{1}{2}\bar{r}^2) + [2 + \alpha(1-t)]\left(t + \frac{\bar{r}}{2}\right) \right.$$

$$\left. + (2 - \alpha t) \right\}$$

$$= \frac{\bar{r}}{2} \exp\left(\frac{-2t}{\bar{r}}\right) \left\{ t\left(2 + \frac{\alpha\,\bar{r}}{2}\right) + \frac{\alpha\,\bar{r}^2}{2} + \bar{r}\left(1 + \frac{\alpha}{2}\right) + 2 \right\}$$

$$= \bar{r} \exp\left(\frac{-2t}{\bar{r}}\right) \left[t\left(1 + \frac{\alpha\,\bar{r}}{4}\right) + \frac{\alpha\,\bar{r}^2}{4} + \frac{(\alpha+2)\bar{r}}{4} + 1 \right]$$

$$\therefore \quad N_t(\alpha) = \frac{4N}{\bar{r}^2} (1-\alpha)^{t-1} \exp\left(\frac{-2t}{\bar{r}}\right) \left\{ t + \alpha\,\bar{r} \exp\left(\frac{-2}{\bar{r}}\right) \right.$$

$$\left. \left[t\left(1 + \frac{\alpha\,\bar{r}}{4}\right) + \frac{\alpha\,\bar{r}^2}{4} + \frac{(\alpha+2)\bar{r}}{4} + 1 \right] \right\}$$

which may be written in the form

$$N_t(\alpha) = K_1 (K_2 t + K_3) \exp\left(\frac{-2t}{\bar{r}}\right) (1-\alpha)^{t-1}$$

where

$$K_1 = \frac{4N}{\bar{r}^2}$$

$$K_2 = 1 + \alpha\,\bar{r}\left(1 - \frac{\alpha\bar{r}}{4}\right) \exp\left(\frac{-2}{\bar{r}}\right)$$

$$K_3 = \alpha\bar{r}\left[1 + \frac{(\alpha+2)\bar{r}}{4} + \frac{\alpha\,\bar{r}^2}{4}\right] \exp\left(\frac{-2}{\bar{r}}\right)$$

APPENDIX 2

This appendix deals with the integration by parts of

$$J_{(1)} = \int_0^\infty t N_t(\alpha)\,dt$$

and

$$J_{(1+a)} = \int_0^\infty t^{1+a} N_t(\alpha)\, dt$$

Consider the integral

$$J_{(p)} = \int_0^\infty t^p (1-\alpha)^{t-1} e^{-kt}\, dt \quad \text{where } k = \frac{2}{r}$$

$$(1-\alpha)^{t-1} = e^{[(t-1)\ln(1-\alpha)]}$$

$$\therefore J_{(p)} = e^{-\ln(1-\alpha)} \int_0^\infty t^p e^{-t[k-\ln(1-\alpha)]} dt$$

Let $S = [k - \ln(1-\alpha)]t$. Therefore,

$$dS = [k - \ln(1-\alpha)]\, dt$$

$$dt = \frac{dS}{k - \ln(1-\alpha)}$$

$$\therefore \quad J_{(p)} = e^{-\ln(1-\alpha)} \int_0^\infty \frac{S^p}{[k-\ln(1-\alpha)]^p} e^{-S} \frac{dS}{k-\ln(1-\alpha)}$$

$$= \frac{e^{-\ln(1-\alpha)}}{[k-\ln(1-\alpha)]^{p+1}} \int_0^\infty S^p e^{-S}\, dS$$

But

$$\int_0^\infty S^p e^{-S}\, dS = \Gamma(p+1)$$

$$e^{-\ln(1-\alpha)} = \frac{1}{1-\alpha}$$

$$\therefore \quad J_{(p)} = \frac{\Gamma(p+1)}{(1-\alpha)\,[k-\ln(1-\alpha)]^{p+1}}$$

First,

$$\int_0^\infty t N_t(\alpha)\, dt = \int_0^\infty K_1(K_2 t^2 + K_3 t)(1-\alpha)^{t-1} \exp\left(\frac{-2t}{r}\right) dt$$

$$= K_1 K_2 J_{(2)} + K_1 K_3 J_{(1)}$$

$$= K_1 \left\{ \frac{2K_2\Gamma(2)}{(1-\alpha)[(2/\bar{r})-\ln(1-\alpha)]^3} \right.$$

$$\left. + \frac{K_3\Gamma(3)}{(1-\alpha)[2/\bar{r})-\ln(1-\alpha)]^2} \right\}$$

$$= \frac{K_1\{2K_2 + K_3[(2/\bar{r})-\ln(1-\alpha)]\}}{(1-\alpha)[2/\bar{r}-\ln(1-\alpha)]^3}$$

Second, $\int_0^\infty t^{1+a}N_t(\alpha)\,dt$

$$= \int_0^\infty t^{1+a}K_1(K_2t^2 + K_3t)(1-\alpha)^{t-1}\exp\left(\frac{-2t}{\bar{r}}\right)dt$$

$$= K_1K_2J_{(2+a)} + K_1K_3J_{(1+a)}$$

$$= K_1 \left\{ \frac{K_2\Gamma(a+3)}{(1-\alpha)[k-\ln(1-\alpha)]^{3+a}} + \frac{K_3\Gamma(a+2)}{(1-\alpha)[k-\ln(1-\alpha)]^{2+a}} \right\}$$

$$= \frac{K_1\{K_2\Gamma(a+3) + K_3\Gamma(a+2)[(2/\bar{r})-\ln(1-\alpha)]\}}{(1-\alpha)[(2/\bar{r})-\ln(1-\alpha)]^{3+a}}$$

$$\therefore \quad [\eta] = \frac{KM_0^a \int_0^\infty t^{1+a}N_t(\alpha)\,dt}{\int_0^\infty tN_t(\alpha)\,dt}$$

$$= \frac{KM_0^a K_1 \Gamma(a+2)\{K_2(2+a) + K_3[(2/\bar{r})-\ln(1-\alpha)]\}}{(1-\alpha)[(2/\bar{r})-\ln(1-\alpha)]^{3+a}}$$

$$\times \frac{(1-\alpha)[(2/\bar{r})-\ln(1-\alpha)]^3}{K_1\{2K_2 + K_3[(2/\bar{r})-\ln(1-\alpha)]\}}$$

$$= \frac{KM_0^a \Gamma(a+2)\{K_2(2+a) + K_3[(2/\bar{r})-\ln(1-\alpha)]\}}{[(2/\bar{r})-\ln(1-\alpha)]^a\{2K_2 + K_3[(2/\bar{r})-\ln(1-\alpha)]\}}$$

where K_2 and K_3 have the same significance as in Appendix 1.

APPENDIX 3

This appendix evaluates the integral

$$J = \int_0^{p+1} t^{1+a}\alpha(1-\alpha)^{t-1}[2+(p-t)\alpha]\,dt$$

Let

$$J = \int_0^{p+1} t^{1+a}\alpha(1-\alpha)^{t-1}[2+(p-t)\alpha]\,dt$$

$$= \int_0^{p+1} t^{1+a}\alpha e^{-(t-1)\ln(1/1-\alpha)}\,[2+(p-t)\alpha]\,dt$$

$$= \alpha e^{\ln(1/1-\alpha)}\int_0^{p+1} t^{1+a}e^{-t\ln(1/1-\alpha)}[2+(p-t)\alpha]\,dt$$

Let $Z = t\ln(1/1-\alpha)$. Therefore, $dZ = dt\ln(1/1-\alpha)$ and

$$J = \frac{\alpha}{1-\alpha}\int_0^{(p+1)\ln(1/1-\alpha)}\left[\frac{Z}{\ln(1/1-\alpha)}\right]^{1+a}$$

$$e^{-Z}\left[2+\left(p-\frac{Z}{\ln(1/1-\alpha)}\right)\alpha\right]\frac{dZ}{\ln(1/1-\alpha)}$$

Let

$$\theta = (p+1)\ln(1/1-\alpha) \text{ and}$$

$$\gamma[p,\theta] = \int_0^\theta Z^{p-1}e^{-Z}\,dZ$$

Then

$$J = \frac{\alpha}{1-\alpha}\left\{\frac{Z+p\alpha}{[\ln(1/1-\alpha)]^{2+a}}\int_0^\theta Z^{1+a}e^{-Z}\,dZ\right.$$

$$\left.-\frac{\alpha}{[\ln(1/1-\alpha)]^{3+a}}\int_0^\theta Z^{2+a}e^{-Z}\,dZ\right\}$$

$$= \frac{\alpha}{(1-\alpha)[\ln(1/1-\alpha)]^{3+a}}$$

$$\left\{(2+p\alpha)\ln\frac{1}{1-\alpha}\gamma[a+2,\theta]-\alpha\gamma[a+3,\theta]\right\}$$

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