A. The distribution function of a random variable is rarely available in polymer science except for the chain length distributions when the polymerization mechanisms are known. This problem is to focus on the moments of a distribution with a known distribution function, i.e., the probability that the random variable N is picked randomly from the entire population {N}. In general, kth moment of the distribution function F_N in the discrete form of a random variable N with its sample space $1 \le N \le \infty$ is defined as

$$m_k \equiv \sum_{N=1}^{\infty} N^k \cdot F_N \tag{1}$$

and the corresponding moments generating fucntion is given by

$$g(N,s) \equiv \sum_{N=1}^{\infty} s^N \cdot F_N \tag{2}$$

(1) Derive that kth moment of the distribution is given by

$$m_k = \left[\left(s \cdot \frac{d}{ds}\right)^{(k)} g(N,\ s)\right]_{s=1} \tag{3}$$

where the superscript (k) denotes the kth successive operation of the operator s(d/dt) on g(N, s).

(2) If F_N is the discrete form of the most probable distribution, find 0th to 4th moments of the distribution,

$$F_N = (1-p) \cdot p^{N-1}, \quad (0 < p < 1) \tag{4}$$

(3) Derive that kth moment of the distribution in the continuous limit is given by

$$m_k = \left[\left(\frac{d}{ds}\right)^{(k)} G(N,\ s)\right]_{s=0} \tag{5}$$

where kth moment and the moments generating function in the continuous limit are defined, respectively, as

$$m_k \equiv (-1)^k \cdot \int_0^{\infty} N^k \cdot F(N) dN \tag{6}$$

and

$$G(N,s) \equiv \int_0^{\infty} e^{-sN} \cdot F(N) dN, \text{ Laplace Tranform of } F(N) \tag{7}$$

B. Two other distributions of polymer chain length are given by the mechanisms of

1) free radical polymerization with termination by recombination only, and
2) anionic polymerization without termination (Poisson distribution).

The discrete distribution functions in terms of weight fraction are given, respectively, as follows.

1) $$w_N = \frac{N(N-1)}{2}\alpha^{N-2}(1-\alpha)^3, \ (\alpha \le 1, \ 2 \le N \le \infty) \text{ (see Problem 1.36)} \tag{8}$$

2) $$w_N = \frac{Ne^{-(N_n-1)}(N_n-1)^{N-1}}{N_n(N-1)!} \tag{9}$$

or $$w_N = \frac{N(N_n-1)^{N-1}}{N_n(N-1)!}\cdot e^{1-N_n}, \quad \left(1 \le N \le \infty, \ \left|\frac{N-N_n}{N_n}\right| << 1\right) \tag{9'}$$

Derive the corresponding distribution in the continuous limit in terms of n(N, p), and find the weight average and z-average degrees of polymerzation.

Note: You may need to use Stiring's approximation for 2);

$$x! \cong \sqrt{2\pi x}\cdot(x/e)^x \tag{10}$$

The discrete form of n_N of the Poisson distribution is given as Equation 1.68, p. 44.

C. Problem 1.35
D. Problem 1.36
E. Problem 1.37
F. Problem 1.40