Chain-Length Distributions in Living Copolymerization Systems

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ABSTRACT

An asymptotic theory for living copolymerization is
illustrated by comparison with numerical calculations
of the chain-length distribution (CLD). A new repre-
sentation of the CLD in reduced coordinates using
stretching parameters from the asymptotic theory is
seen to give much clearer insight into the system
behavior with time. Use of the asymptotic theory
for the prediction of the CLD properties when there
are large variations in monomer composition is
discussed.

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INTRODUCTION

The following copolymerization reactions will be considered:

$$p_j(\nu) + \mu_i \longrightarrow p_i(\nu + 1) \tag{1}$$

where μ_i denotes monomer i (i = 1, 2, ..., n) and $p_j(\nu)$ denotes a
polymer of chain length ν with a reactive end group corresponding
to monomer j. It will be assumed that initiation is instantaneous,
that there is no termination reaction, that the rate constants are
independent of chain length ν, and that the monomer concentrations
are kept constant (or their change with time can be neglected).
The problem under consideration is the computation of the chain
length distribution (CLD), p(ν,t), i.e., the relative concentration
of polymer with chain length ν at time t. The initial values of p
are then

$$p(1,0) = 1 \quad \text{and} \quad p(\nu,0) = 0, \quad \nu > 1 \tag{2}$$

Determination of p(ν, t) requires the integration of sets of differential
equations describing the dynamics of the reacting system.
    The distribution p(ν,t) becomes the Poisson distribution if n = 1
(homopolymerization) and if the rate constants of the reactions[1]
do not depend on ν. In the case n > 1, no such simple expression
for p(ν,t) exists except when certain relations between monomer
concentrations and the rate constants are satisfied [1]. However,
for n = 2 (binary copolymerization), one of us has derived an expres-
sion for p(ν,t) involving certain hypergeometric functions which
facilitates these calculations [2]. In addition, asymptotic proper-
ties of p(ν,t) can be derived easily from the rate constants for
general n [1]. In this paper, both the asymptotic theory and
numerical results will be combined to illustrate how the CLD
evolves with time.

ASYMPTOTIC PROPERTIES

The rate constant of reaction (1) will be denoted κ_{ij}. This is
consistent with the notation in the general field of linear kinetics;

however, the polymerization literature normally denotes the rate constant by κ_{ji}.

Since the monomer concentrations may be regarded constant, one can introduce pseudo-first-order constants k_{ij} by the transformation

$$k_{ij} = c^i \kappa_{ij} \tag{3}$$

where c^i is the concentration of μ_i (see also Ref. 1). The constants k_{ij} can be represented by a matrix K having entry k_{ij} at the intersection of i-th row and j-th column.

The center (number-average chain length) $\overline{\nu}(t)$ of the distribution is defined by

$$\overline{\nu}(t) = \sum_{\nu=1}^{\infty} \nu p(\nu, t) \tag{4}$$

and the variance $\sigma^2(t)$ by

$$\sigma^2(t) = \sum_{\nu=1}^{\infty} (\nu - \overline{\nu}(t))^2 p(\nu, t) \tag{5}$$

The following asymptotic relations (valid for sufficiently large t) have been established [1]:

$$\overline{\nu}(t) = vt + C_1 \tag{6}$$

$$\sigma^2(t) = v\theta t + C_2 \tag{7}$$

where v and θ depend only on K, and C_1 and C_2 depend on both K and the initial conditions. The approach to these relations is exponential with respect to time.

According to these equations the distribution will approach a constant velocity v and the width of the distribution (to be interpreted as σ) will asymptotically increase proportional to $\sqrt{t}$. The asymptotic

parameters v and θ can be computed easily from K (see Ref. 1). For binary (n = 2) copolymerization one obtains [1]

$$v = \frac{k_{12}d_1 + k_{21}d_2}{k_{12} + k_{21}} \tag{8}$$

$$\theta = 1 + \frac{2k_{12}k_{21}(d_1 - d_2)^2}{(k_{12} + k_{21})^2(k_{12}d_1 + k_{21}d_2)} \tag{9}$$

where

$$d_1 = k_{11} + k_{21}, \qquad d_2 = k_{12} + k_{22} \tag{10}$$

As can be seen, it is necessary to exclude the case $k_{12} = k_{21} = 0$ which corresponds to two independent homopolymerizations (unlinked) case in Ref. 1). We shall be particularly interested in the case where k_{12} and k_{21} are nonzero but small because of the very interesting transient phenomena which occur.

EVOLUTION OF THE DISTRIBUTION

The evolution of $p(\nu,t)$ with time has been studied numerically using the relations derived in Ref. 2. The K matrix used in this example is given by

$$K = \begin{bmatrix} 5 & 0.1 \\ 0.1 & 1 \end{bmatrix} \tag{11}$$

For t = 0, equal concentration of $p_1(1)$ and $p_2(1)$ have been assumed. Results are shown in Fig. 1, where it can be seen that at first two peaks evolve which later combine into a single peak. The two peaks for small t can be explained by the dominance of k_{11} and k_{22} over the other rate constants. The system can be approximated for small t by two independent homopolymerizations ($k_{12} = k_{21} = 0$). The peaks corresponding to these move with velocities k_{11} and
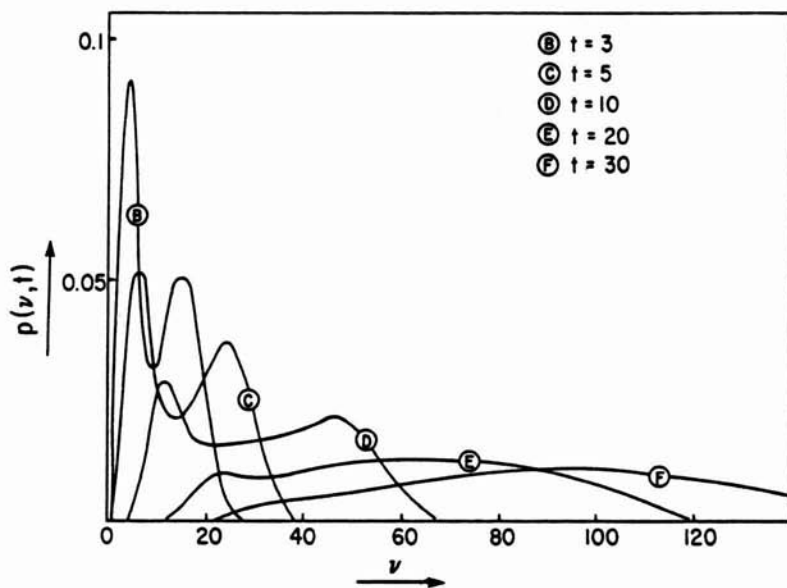
FIG. 1. Chain-length distribution for several t for the binary system with K given by Eq. (11). At t $\approx$ 0, equal concentrations of $p_1(1)$, $p_2(1)$ are assumed. p = fraction of polymer molecules having chain length ν.

k_{22}, respectively. However, a two-peak situation with different peak velocities may not persist according to the asymptotic theory (if k_{12} and k_{21} are not exactly zero) since for the two-peak case the width σ increases proportional to t, not$\sqrt{t}$ as required by the theory. Because of the nonzero crossover constants, k_{12} and k_{21}, the faster peak which initially corresponds to polymers $p_1(\nu)$ will lose chains of $p_2(\nu)$ type at its rear. Conversely the slower peak, initially consisting of $p_2(\nu)$ polymers, will send off $p_1(\nu)$ chains at its front. Eventually one single peak is established corresponding to a mixture of $p_1(\nu)$ and $p_2(\nu)$ chains.

These phenomena occur in all systems in which the diagonal terms of the matrix K dominate. The choice of $k_{11} \gg k_{22}$ for this example was made to clearly emphasize the difference in peak velocities.

The asymptotic relations suggest introduction of a coordinate system which moves with velocity v and is contracted proportionally

to$\sqrt{v\theta t}$. In order to adjust for decreasing peak heights, it will be convenient to stretch the ordinate by $\sqrt{v\theta t}$. Mathematically this corresponds to the transformation

$$q(\mu,t) \;=\; \sqrt{v\theta t}\; p(vt + \mu \;\; v\theta t, t) \tag{12}$$

The coordinates μ and q will be called reduced coordinates. In the reduced coordinate system both the position of the center and the width of the distribution must approach time invariant values. For our example, results are plotted in reduced coordinates in Fig. 2.
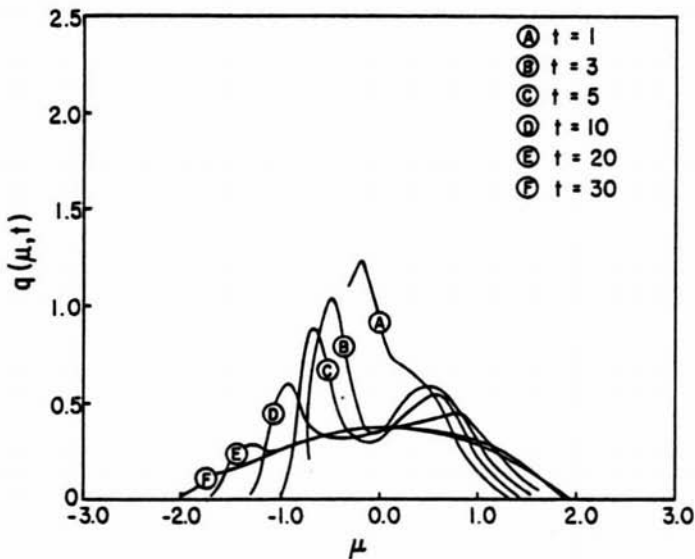

FIG. 2. The results of Fig. 1 in reduced coordinates q and μ. These are defined by Eq. (12).

In this representation the initial evolution of two peaks, the combination to one peak, and the asymptotic behavior as indicated by the approach to a stationary shape can be seen much clearer than in the original coordinates. The time constant [1] for the approach to the asymptotic distribution is 5 for this example, so that in about

6 time constants the distribution is invariant in reduced coordinates and centered about $\mu = 0$ (see Fig. 2).

The parameters v and θ for computing the reduced coordinates are obtained from the asymptotic theory. The relevant equations for arbitrary n are discussed in detail in Ref. 1.

Reduced coordinates can also be used if the monomer concentration changes. The dynamic equations of the system must then include a balance over the monomers. It is well known that, in general, certain states of the system can be approximated at any time by the steady state belonging to the monomer conditions at that time (quasi-steady state). From this the following transformation for the general reduction follows

$$q(\mu,t) = \hat{\theta}(t)\, p(\hat{\nu}(t) + \mu\hat{\theta}(t),t) \tag{13}$$

where

$$\hat{\nu} = \int_0^t v(t)\, dt \tag{14}$$

$$\hat{\theta}^2 = \int_0^t v(t)\theta(t)\, dt \tag{15}$$

v and θ are to be determined by the relations given in Ref. 1 from the magnitudes $k_{ij}(t)$. The latter must be computed from Eq. (3) with c^i equal to the μ_i concentration prevailing at time t. $c^i(t)$ must be determined from a mass balance on the monomers.

This will be a very good approximation if the time scale for the dissipation of the effect of initial conditions on the polymer is short compared to the time scale for a change in monomer concentrations.

For n = 2, Eqs. (8)-(10) can be used with k_{ij} replaced by $k_{ij}(t)$.

In certain cases, such as azeotropism, it is convenient to introduce a dimensionless time variable related to real time by an integral transformation. This is discussed in Ref. 2.

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