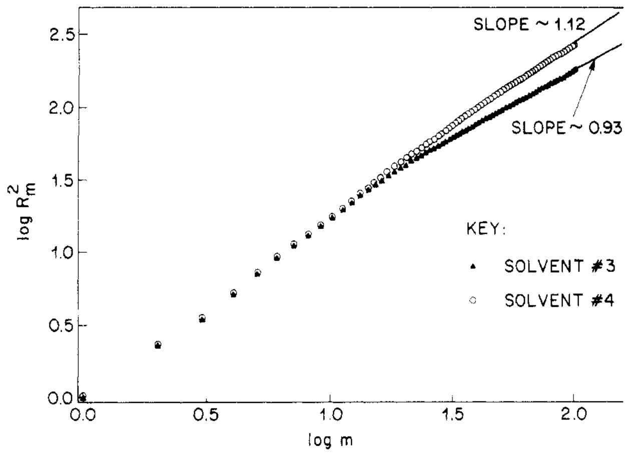

Figure 8. Mean-square distance between monomers separated by *m* polymer segments, in solvents with and without preferential affinity (solvents 3 and 4, respectively).

the results in the direction of better agreement with the theory. For N in the range 40–100, the scaling exponent 2ν (subject to finite size effects) is ~0.95 in this solvent. Figure 8 displays the internal polymer dimensions (R_m^2 versus m) in solvents 3 and 4 at $\eta\chi_{AP} = -2.40$. The limiting slope in Figure 8 for solvent 3 is 0.93, which is less than that observed for solvent 4 with $\gamma = 0$. This reduction in slope is indicative of the reduction in solvent quality attributable to preferential affinity. Note in Figure 8 that internal polymer dimensions are identical at low m in solvents with and without preferential affinity. We believe this is a reflection of the long range of the force causing the critical collapse. In contrast, the forces causing chain contraction are short ranged when $\eta = 0$, hence in solvent 1 we observed internal polymer dimensions to be affected by γ for all values of m. In solvent 1, we also determined that the probability of multiple polymer contacts per adsorbed solvent molecule increases as the chain contracts (see section IV.B); no such increase is observed as the chain contracts in solvent 3.

V. Summary

The simulation results for the effect of preferential affinity are consistent with the Shultz–Flory and Brochard–de Gennes theories. Preferential affinity causes both chain contraction and a buildup in concentration of the better solvent component near the polymer. As predicted by Brochard and de Gennes, a chain first contracts dramatically then reexpands as the consolute temperature is approached from above. However, preferential affinity also causes chain contraction far away from the critical point, as predicted by the Shultz–Flory theory. The effective range of the attractive force causing chain contraction is larger for the near-critical collapse. At large values of preferential affinity, the chain may contract below its dimensions in either of the pure solvent components. Also indicative of the decrease in solvent quality attributable to preferential affinity is the reduction of the Flory exponent ν.

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Molecular Weight Distribution and Moments for Condensation Polymerization with Variant Reaction Rate Constant Depending on Chain Lengths

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ABSTRACT: A new model for the chain length dependence of the reaction rate constant is proposed for the molecular weight distribution and averaged molecular weights obtained in linear condensation polymerization. An infinite molecular weight for a finite time is predicted if the reaction rate constant is increasing with chain length. The moments method is used and Gupta's model is reconsidered for analytic solutions. Both models are compared with available experimental data.

Introduction

The theory of molecular weight distribution of linear condensation polymers is well established on the principle of equal reactivity of Flory.[1] Even though experimental evidence seems to be generally in favor of this principle, it still seems to be interesting to investigate the systematic

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deviations from the most probable distribution of Flory. The reactivity of the functional groups is known to depend on the structures of monomers or polymers. There are monomers, especially those containing aromatic rings, for which the reactivity is different from those of higher homologues. Goel et al.[2] and recently Kumar[3] have considered such cases numerically in both batch and continuous reactors. Specifically Kumar[3] considered the reversible polymerization numerically and an analytic expression was obtained for irreversible polymerization in a continuous reactor. Here their case is reconsidered for the analytic results in a batch reactor which might be very useful for further engineering applications. A second possibility for the cause of the inequality in the reactivity could be the chain-length dependence. It is still unclear why the reactivities of higher chains are greater or less than those of shorter ones. External flow or other types of forces could alter the orientational distribution of the long-chain molecules, which eventually affects the reactivities of such chains. The highly oriented aromatic polyamide short fiber obtained by Yoon et al.[4] could be one such case. Nanda and Jain[5] were among the first workers to consider the chain-length dependence of the reaction rate constants of polymer chains. But their results were only useful for the early stage of polymerization since the reaction rate constants they used are decreasing as the chains grow so that eventually it becomes zero. A new model for chain-length dependence is proposed to predict that the molecular weight can reach infinity for a finite time of reaction if the reaction rate constant is an increasing function of chain length. The case of decreasing reaction rate constant is also considered to give a compact analytic expression which may be compared with an available set of data.

General Kinetic Equations

Irreversible polycondensation reactions are represented as an infinite set of elementary reactions:

$$P_m + P_n \underset{k_{m,n}}{\rightarrow} P_{m+n} \qquad m, n = 1, 2, ... \tag{1}$$

where P_m is molecules having m repeating units and $k_{m,n}$ is reaction rate constant of P_m and P_n. Of course the reversible polymerization should be treated especially for high conversion, but it is still interesting to consider the irreversible case if the removal of byproduct is instantaneous due to the high vacuum applied. It can serve an important role in the further numerical calculation for the reversible case pointed by Kumar.[3] The following set of differential equations generally characterizes the irreversible condensation polymerization process:

$$\mathrm{d}P_1/\mathrm{d}t = -P_1 \sum_{n=1}^{\infty} k_{1n}P_n - k_{11}P_1^2 \tag{2}$$

$$\mathrm{d}P_m/\mathrm{d}t = -P_m \sum_{n=1}^{\infty} k_{mn}P_n - k_{mm}P_m^2 + \sum_{n=1}^{m^*} k_{n,m-n}P_nP_{m-n} \tag{3}$$

where m^* is the integer part of $m/2$. For the illustrative purpose, let us consider the Gupta's case first.

Gupta's Model

In this kinetic scheme, the polymerization process is modeled by two parameter k_1 and k only:

$$\begin{aligned} k_{11} &= k_1/2 \qquad k_{m,n} = k \quad m \neq n \\ k_{n,n} &= k/2 \quad n \geq 2 \end{aligned} \tag{4}$$

If k_1 is equal to k, it is the case of equal reactivity. It is easy to construct a set of nondimensionalized equations for a given initial condition. Here the simplest initial condition is used, that is the only monomer exists at the beginning with the concentration M_0.

$$\mathrm{d}P_1/\mathrm{d}\tau = -2P_1Q_0 - 2(g-1)P_1^2 \tag{5}$$

$$\mathrm{d}P_2/\mathrm{d}\tau = -2P_2Q_0 + gP_1^2 \tag{6}$$

$$\mathrm{d}P_m/\mathrm{d}\tau = -2P_mQ_0 + \sum_{n=1}^{m-1} P_nP_{m-n} \qquad (m > 2) \tag{7}$$

where $g = k_1/k$ and $\tau = kM_0t/2$. Moments, Q_i, are defined by eq 8 and every Q_i and P_m is nondimensionalized by M_0.

$$Q_i = \sum_{n=1}^{\infty} n^iP_n \tag{8}$$

In order to calculate the number-averaged and weight-averaged molecular weight, only Q_0, Q_1, and Q_2 are necessary. It is easy to construct a Q_i equation in general by summing eq 5–7.

$$\mathrm{d}Q_0/\mathrm{d}\tau = -Q_0^2 - (g-1)P_1^2 \tag{9}$$

$$\mathrm{d}Q_1/\mathrm{d}\tau = 0 \tag{10}$$

$$\mathrm{d}Q_i/\mathrm{d}\tau = \sum_{j=1}^{i-1} {}_iC_jQ_jQ_{i-j} + (g-1)(2^i - 2)P_1^2 \tag{11}$$

where ${}_iC_j$ is the permutation symbol. These sets of equations permit the exact analytic solutions which were not noticed by the inventor of the model. The detail is shown in Appendix. The results are

$$Q_0 = \frac{1 + \tau - \beta^2}{[(1 + \tau)^2 - \beta^2]} \tag{12}$$

$$Q_1 = 1 \tag{13}$$

$$Q_2 = 2 + 2\tau - \frac{(1 - \beta^2)(1 + \tau)}{[(1 + \tau^2) - \beta^2]} + \frac{(1 - \beta^2)}{2\beta} \ln \frac{(1 + \tau + \beta)(1 - \beta)}{(1 + \tau - \beta)(1 + \beta)} \tag{14}$$

and

$$P_1 = \frac{(1 - \beta^2)}{[(1 + \tau)^2 - \beta^2]} \tag{15}$$

$$P_2 = \left[\frac{(1 - 2\beta^2)}{2\beta^2[(1 + \tau)^2 - \beta^2]}\right]\left[\frac{(1 + \tau - \beta)(1 + \beta)}{[(1 + \tau + \beta)(1 - \beta)^{\beta} - 1]}\right] \tag{16}$$

where $\beta^2 = (g - 1)/g$ and these results are good for $g \geq 1$. It is possible to calculate Q_i and P_m successively. For the case of $g \leq 1$, similar results can be obtained as follows. Here β^2 is redefined by $(1 - g)/g$.

$$Q_0 = \frac{(1 + \tau + \beta^2)}{[(1 + \tau)^2 + \beta^2]} \tag{17}$$

$$Q_1 = 1 \tag{18}$$

$$Q_2 = 2 + 2\tau - \frac{(1 + \beta^2)(1 + \tau)}{[(1 + \tau)^2 + \beta^2]} + \frac{(1 + \beta^2)}{\beta}\left[\arctan\left(\frac{1}{\beta}\right) - \arctan\left(\frac{1 + \tau}{\beta}\right)\right] \tag{19}$$

and

$$P_1 = \frac{(1 + \beta^2)}{(1 + \tau)^2 + \beta^2} \tag{20}$$

$$P_2 = \left[\frac{(1 + \beta^2)}{2\beta^2[(1 + \tau)^2 + \beta^2]}\right] \times \left[1 - 2\beta\left[\arctan\left(\frac{1}{\beta}\right) - \arctan\left(\frac{1 + \tau}{\beta}\right)\right]\right] \quad (21)$$

According to the definition of number-averaged and weight-averaged chain lengths L_n and L_w it is easy to have the following relationships.

$$L_n = Q_1/Q_0 \quad (22a)$$

$$L_w = Q_2/Q_1 \quad (22b)$$

Comparison with Experimental Results

The theoretical results shown in the previous section can be indirectly checked by $L_n(\tau)$ data available in the literature.[1] This reaction was modeled by several workers in the past. The details are documented by Odian[6] in his textbook, but none of the kinetic plots come close to being as useful as Flory's original study. Therefore it is still interesting to consider another type of kinetic model for the engineering purpose to fit the data of higher L_n. It can still be treated as low conversion as far as the real synthesis of commercial polymers is concerned so that the irreversibility is not too difficult to be obtained since the byproduct can be removed easily in this range of low conversion. Figure 1 shows the data of Fory and the theoretical calculation with $g = 5.08$ and $kM_0 = 0.909 \times 10^{-2}$/min. g value is calculated by the following formula.

$$g = \frac{\lim_{t \to 0} (\mathrm{d}L_n/\mathrm{d}t)}{\lim_{t \to \infty} (\mathrm{d}L_n/\mathrm{d}t)} \quad (23)$$

The initial data are well-fitted with Gupta's model and the final data are fitted reasonably well with the predictions of new model proposed in the next paragraph as explained in the Figure 1.

New Model Proposed

Here a new model is proposed with the variant reaction rate constant which depends slightly on the chain length. It is not claimed that such a dependence corresponds to any real situation, but there is a strong possibility that polymerization could be accelerated by the external field such as shear flow. If the reaction rate varies as given in eq 24 then it is easy to construct not only the mass balance equation but also corresponding moment equations.

$$k_{m,n} = k[1 + q^2mn] \qquad m \neq n \quad (24a)$$

$$k_{n,n} = \frac{k[1 + q^2n^2]}{2} \qquad n = 1, 2, \ldots \quad (24b)$$

$$\mathrm{d}P_1/\mathrm{d}\tau = -2P_1Q_0 - 2q^2P_1Q_1 \quad (25)$$

$$\mathrm{d}P_2/\mathrm{d}\tau = -2P_2Q_0 - 4q^2P_2Q_1 + (1 + q^2)P_1^2 \quad (26)$$

$$\frac{\mathrm{d}P_m}{\mathrm{d}\tau} = -2P_mQ_0 - 2mq^2P_mQ_1 + \sum_{n=1}^{m-1}[1 + q^2n(m - n)]P_nP_{m-n} \quad (27)$$

and

$$\frac{\mathrm{d}Q_0}{\mathrm{d}\tau} = -Q_0^2 - q^2Q_1^2 \quad (28)$$

$$\mathrm{d}Q_1/\mathrm{d}\tau = 0 \quad (29)$$

$$\mathrm{d}Q_i/\mathrm{d}\tau = \sum_{j=1}^{i-1} {}_iC_j[Q_jQ_{i-j} + q^2Q_{j+1}Q_{i-j+1}] \quad (30)$$

P_m has the following types of analytic solutions:

$$P_m = A_m(q)\left[\frac{\tan(q\tau)}{q}\right]^{m-1} \frac{[1 + \tan^2(q\tau)]}{\left[1 + \frac{\tan(q\tau)}{q}\right]^{m+1}} \times \exp[-2mq^2\tau] \quad (31)$$

where $A_m(q)$ is given by eq 32.

$$A_1(q) = 1 \quad (32a)$$

$$A_m(q) = \frac{1}{m - 1}\sum_{n=1}^{m-1}[1 + q^2n(m - n)]A_nA_{m-n} \quad (32b)$$

Q_i can be also obtained successively by

$$Q_0 = \frac{[1 - q\tan(q\tau)]}{\left[1 + \frac{\tan(q\tau)}{q}\right]} \quad (33)$$

$$Q_1 = 1 \quad (34)$$

$$Q_2 = \frac{\left[1 + \frac{\tan(2q\tau)}{q}\right]}{[1 - q\tan(2q\tau)]} \quad (35)$$

L_n and L_w are obtained from Q_0, Q_1, and Q_2:

$$L_n = \frac{\left[1 + \frac{\tan(q\tau)}{q}\right]}{[1 - q\tan(q\tau)]} \quad (36)$$

$$L_w = Q_2 \quad (37)$$

It is clear that dimensionless time τ should be less than a certain finite time of acrtan $[1/q]/2q$. The time to give an infinite L_n is longer than this time. After that time, the weight-averaged molecular weight reaches infinity. It is worthwhile to notice that if q approaches zero, then the formula reduces to the case of Flory. These results are applicable for the case $q = iq^*$, that is, the case when the rate constant decreases with increasing chain length. Here i is the base of the imaginary number ($i^2 = -1$), and by using $q = iq^*$ and $\tan[iq^*] = i\tanh[q^*\tau]$ every results can be rewritten. As mentioned in the Introduction, it is only valid for the early stage of polymerization due to the limitation of the molecular size.

Limit of Infinite q

If q is infinite, it is better to redimensionalize the time scale by defining $\tau_1 = q^2\tau$ since the reaction rate constant for monomers becomes infinite like $(1 + q^2)k$. Then it is easy to evaluate P_m and Q_0, Q_1, and Q_2.

$$P_m = a_m\tau_1^{m-1}\exp(-2m\tau_1) \quad (38)$$

where a is the constant evaluated by the following recursive formula:

$$a_m = \frac{1}{m - 1}\sum_{n=1}^{m-1} n(m - n)a_na_{m-n} \quad (39a)$$

$$a_1 = 1 \quad (39b)$$

And 1

$$Q_0 = 1 - \tau_1 = 1/L_n \quad (40)$$

$$Q_1 = 1 \quad (41)$$

$$Q_2 = \frac{1}{[1 - 2\tau_1]} = L_w \quad (42)$$

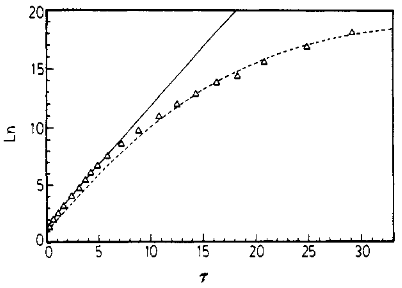

Figure 1. Number-averaged chain length (L_n) versus the dimensionless time τ. Solid line is based on (22a) with $g = 5.08$ and $kM_0 = 0.909 \times 10^{-2}$/min, dotted line is based on (36) with $q = 0.051i$ and the same kM_0, and Δ is from the data of Flory[7] for the reaction between diethylene glycol and adipic acid.

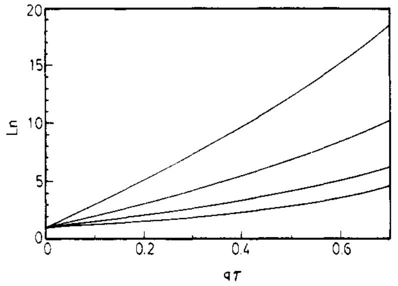

Figure 2. Number-averaged chain length (L_n) versus the dimensionless time ($q\tau$) based on (36). From the top, q = 0.05, 0.1, 0.2, and 0.5, respectively.

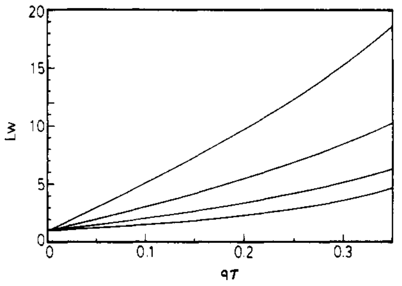

Figure 3. Weight-averaged chain length (L_w) versus the dimensionless time ($q\tau$) based on (37). From the top, q = 0.05, 0.1, 0.2, and 0.5, respectively.

Here we are have another kind of interesting molecular weight distribution.

Discussions and Conclusions

The number-averaged chain length and weight-averaged chain length are plotted against the dimensionless time $q\tau$ in Figures 2 and 3. As far as the molecular weights are concerned, the new time scale $q\tau$ governs the situations. The polydispersity index (PDI) defined by L_w/L_n is also plotted as a function of $q\tau$ in Figure 4. As expected, PDI deviates much from 2 as q increases. The time τ_g for the infinite L is plotted against q in semilog scale in Figure 5. For small q, τ_g varies with $1/q$, and for large q, τ_g varies with $1/q^2$. Experimental evidence for the proposed theory is not available right now, it is not yet known whether it is possible to have such an acceleration phenomenon during linear condensation polymerization and if possible whether the theoretical predictions are good quantitatively. Of course it is very difficult to obtain the high conversion which can be carried out in this manner not only due to the reversibility of the reaction but also due to the precipitation of high molecular weight polymers. In order to mimic the real situation more precisely, attempts are being carried out for a more accurate rate dependence model of the small molecules. One of them could be the combination of the two models given in this paper. The other unsolved problem is the rheokinetic origin of the variant kinetic constant like the expression given by eq 24. And reversibility should be considered in detail for both a batch reactor and a continuous-type reactor in the future.

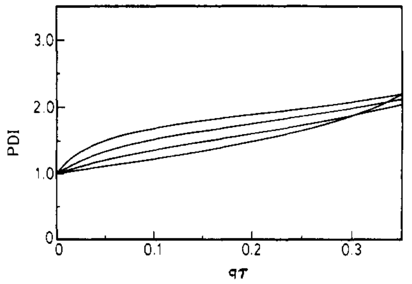

Figure 4. Polydispersity index (L_w/L_n) versus the dimensionless time ($q\tau$). From the top, q = 0.05, 0.1, 0.2, and 0.5, respectively.

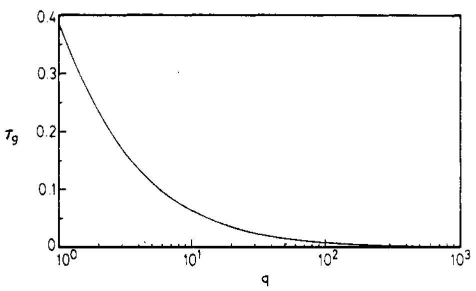

Figure 5. Time (τ_g) for an infinite L_w versus the parameter q.

Appendix Q_0 and P_1 for $g \geq 1$

From eq 5 and 9 it is easy to obtain the following equation:

$$\frac{dQ_0}{dP_1} = \frac{(Q_0/P_1)^2 + (g-1)}{(Q_0/P_1) + 2(g-1)} \tag{A1}$$

If we define $v = Q_0/P_1$, (A1) can be converted into (A2).

$$\frac{P_1\, dv}{dP_1} = \frac{[-v^2 - 2(g-1)v + (g-1)]}{[2v + 2(g-1)]} \tag{A2}$$

It can be integrated by using initial condition $P_1 = v = 1$ at $\tau = 0$.

$$g/P_1 = v^2 + 2(g-1)v - (g-1) \tag{A3}$$

By combining (5), (A2), and (A3) for v, it is easy to have

$$dv/d\tau = g \tag{A4}$$

which gives us $v = 1 + g\tau$. Then Q_0 and P_1 are obtained successively. Exactly the same is true for g less than 1.

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Registry No. (diethylene glycol)(adipic acid) (copolymer), 9010-89-3; (diethylene glycol)(adipic acid) (SRU), 25036-49-1.

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