Interpretation of Gel Points of an Epoxy–Amine System Including Ring Formation and Unequal Reactivity: Reaction Scheme and Gel-Point Prediction.

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ABSTRACT: First, the kinetics of the reaction of a polyyoxypropylene (POP) diamine and the diglycidyl ether of Bisphenol A (DGEBA), taking account of the induced unequal reactivity (substitution effect) of the hydrogen atoms of the amine groups, are analyzed. It is shown that a larger reduction in the reactivity of the second hydrogen atom of an amine group to react leads to a higher proportion of semireacted amine groups at a given overall extent of reaction. Second, the statistics of gelation of the amine–epoxy polymerization in the absence of intramolecular reaction but accounting for the aforementioned unequal reactivity are investigated. The description is cast in terms of an RA4 + R′B2 polymerization, where A represents a hydrogen atom of an amine group and B represents an epoxide group. It is shown that the induced unequal reactivity has only a very small effect on the gel point. For example, a decrease by a factor of 10 in the reactivity of the second hydrogen atom of an amine group to react leads to an increase in an extent of reaction at the gel point (pΓ) of only 0.022 over the Flory–Stockmayer value of 0.577. Third, a theory for predicting the gel point in RA4 + R′B2 type polymerizations accounting for intramolecular reaction is developed. The theory is an extension of Ahmed–Rolfes–Stepto (ARS) theory to include more detail of the molecular structures around pairs of reacting groups. The very small effects of induced unequal reactivity on the gel point mean that the probabilities of intramolecular reaction can be calculated assuming the equal reactivity of like reactive groups. ARS theory leads to a quadratic relationship between pΓ and the ring-forming parameter, λ0. The present, more comprehensive theory does not lead to an analytical relationship between pΓ and λ0, but numerical evaluation of pΓ as a function of λ0 shows that many more ring structures are accounted for than by ARS theory, even at small values of λ0. The present theory is applied to the experimental data in the following paper.

1. INTRODUCTION

This study, which is in two parts, is concerned with the measurement and interpretation of gel points in the polymerization of polyyoxypropylene (POP) amines and the diglycidyl ether of Bisphenol A (DGEBA). The first part, the present paper, describes the reaction scheme, the gel point condition and the results of calculations of the effects of unequal reactivity and ring formation on the gel point. In the second part, the following paper, the experimental determinations of conversion versus time curves and gel points through infrared and rheological measurements are described. The results are interpreted in terms of the theoretical expressions derived in the present paper and are compared with previously published results.

The type of polymerization considered is an RAa + R′Bb one, where fa and fb are the functionalities of the reactants bearing reactive A groups and B groups. In the present context, RAa is a primary diamine and A is used to denote the hydrogen atom of an amine group. R′Bb is a diepoxide, with B denoting an epoxy group. Thus, an RAa + R′Bb polymerization is considered.

At a critical extent of reaction, the size of the largest molecule formed spans the reaction volume and this extent of reaction is termed the gel point. Classical theories of gelation consider idealized reactions, which are defined based on two assumptions: (1) all like groups are equally reactive and (2) there is no intramolecular reaction. Many authors have considered such reactions, although in many real systems, the assumptions are not valid. Further, when more realistic models are used, they often remove only one of the assumptions. The present paper, in contrast, treats the gel points of an RAa + R′Bb epoxy–amine system accounting for both unequal reactivity and intramolecular reaction. The unequal reactivity considered is the induced unequal reactivity of hydrogen atoms on amine groups. Induced unequal reactivity is also known as the substitution effect and may be contrasted with intrinsic unequal reactivity, such as often occurs, for example, when primary and secondary hydroxyl groups react competitively with another type of group.

Intramolecular reaction leads to ring structures and delays the gel point. Further, ring structures bring about lower molecular weights at a given extent of reaction in the pregel regime than would be expected from theories using idealized reactions. They also preclude the formation of a perfect network and, hence, influence the elastic and viscoelastic properties of the final network. It is important, therefore, to describe quantitatively the ring structures that form.
are categorized as being in states H1, H2, and HR. Hydrogen atoms that belong to unreacted, primary amine groups are defined as H1, the unreacted hydrogen atoms that belong to semireacted amine groups are defined as H2, and reacted hydrogen atoms are defined as HR. In reaction 1, with rate constant $k_{H1}$, two H1 atoms are lost, and one H2 atom and one HR atom are formed. A hydrogen atom H2 on a secondary amine group and an epoxy group react to form a tertiary amine group as shown in reaction 2, with rate constant $k_{H2}$. In reaction 2, one H2 atom is lost and one HR atom is formed.

The rates of change of the concentrations of H1, H2, and HR are given by the following equations:

\[
\begin{align*}
\frac{dc_{H1}}{dt} &= -2k_{H1} \times c_{H1} \times c_{EP} \\
\frac{dc_{H2}}{dt} &= k_{H1} \times c_{H1} \times c_{EP} - k_{H2} \times c_{H2} \times c_{EP} \\
\frac{dc_{HR}}{dt} &= k_{H1} \times c_{H1} \times c_{EP} + k_{H2} \times c_{H2} \times c_{EP}
\end{align*}
\]

Here $c_{H1}$, $c_{H2}$, $c_{HR}$, and $c_{EP}$ are concentrations of H1, H2, HR atoms and epoxy groups, respectively. Let the concentrations of H1 and epoxy groups before the reaction (i.e., at $t = 0$) be $c_{H1}^0$ and $c_{EP}^0$, then $p_{HR}$, the extent of reaction of the hydrogen atoms, is

\[
p_{HR} = \frac{c_{HR}}{c_{H1}^0}
\]

It should be noted that the value of $p_{HR}$ is directly measurable using FT-IR spectroscopy, as described in the following paper. The fractional concentrations of H1 and H2 atoms and reacted epoxy groups can be defined as: $p_{H1} = (c_{H1}^0 / c_{H1}^0)$, $p_{H2} = (c_{H2}^0 / c_{H1}^0)$, $p_{EP} = (c_{EP}^0 / c_{EP}^0)$, where $c_{EP}^0 = c_{EP}^0 - c_{EP}$. The reactive-group ratio for the reaction mixture, $r_{HR}$, can be written as: $r_{HR} = (c_{H1}^0 / c_{EP})$. Further, at $t = 0$, $c_{HR}^0 = c_{HR}^0$, $c_{H2}^0 = 0$ and $c_{HR} = 0$. Also, $c_{HR} = c_{H1}^0 - c_{H1} - c_{H2}$, and $c_{HR} = c_{EP}$ during the course of reaction. Solving the differential eqs 1–3 and elimination of $t$ give $p_{H2}$ and $p_{HR}$ in terms of $p_{H1}$:

\[
\begin{align*}
p_{H2} &= \frac{1}{2 - \rho} (p_{H1}^{(\rho/2)} - p_{H1}) \\
p_{HR} &= 1 - \frac{1 - \rho}{2 - \rho} p_{H1} - \frac{1}{2 - \rho} p_{H1}^{(\rho/2)}
\end{align*}
\]

where

\[
\rho = k_{H2} / k_{H1}
\]

is the rate-constant ratio. Reactions 1 and 2 occur with equal probabilities for a random sample of the epoxy group as $\rho = 1$.

The results of calculations of $p_{H1}$ and $p_{HR}$ in terms of $p_{H1}$ are displayed in Figure 2 as plots of $p_{H1}$ vs $p_{HR}$ and $p_{H2}$ vs $p_{HR}$ for different values of $\rho$. The increase in $p_{HR}$ from 0 to 1 describes the progress of a polymerization to completion. After H2 atoms are produced by reaction 1, their consumption follows reaction 2, resulting in the maxima in the $p_{H2}$ vs $p_{HR}$ curves. The curves clearly show dependences on $\rho$. The maximum in the $p_{H2}$ vs $p_{HR}$ curve for $\rho = 1$ occurs at $p_{HR} = 0.5$ and it shifts to higher values of $p_{HR}$ as $\rho$ decreases. Overall, as $\rho$ is decreased at a given $p_{HR}$, $p_{H1}$ decreases and $p_{H2}$ increases, showing that the secondary amine groups that are formed by reaction 1 react more slowly.

### 3. STATES OF THE DIAMINE UNIT

During a polymerization, six states of the diamine unit can be defined, as shown schematically in Figure 3. The classification of the diamine unit shown here is similar to that of Dušek et al.14 However, its use to define the gel point is different. The gel point in the study of Dušek et al. is defined as the point of divergence of the mass-average molar mass. Here, the gel point is derived in terms of the probabilities of continuing paths, as shown in the following sections. Second, ring formation was not considered by Dušek et al., whereas it is included in the present work.

With the progress of a reaction, the relative concentrations of the individual states change. State 1 is not included in growing chains. State 2 occurs at the ends of growing chains. States 3–6
form constituent parts of polymer chains and branching takes place at states 5 and 6. If the probabilities (mole fractions) of the six states are written as $X_i, i = 1, 2, ..., 6$, they can be expressed as functions of $P_{HR}$, which is experimentally measurable.

Let $X_u, X_d$ and $X_r$, respectively, be the mole fractions of unreacted, semireacted and fully reacted amino groups, with $X_u + X_d + X_r = 1$. State 1 consists of two unreacted amine groups. Hence, $X_1 = X_u^2$. State 2 consists of a semireacted amine group and an unreacted amine group and $X_2 = 2X_uX_d$. State 3 consists of a fully reacted amine group and an unreacted amine group, so that $X_3 = 2X_uX_r$. State 4 contains two semireacted groups and $X_4 = X_d^2$. Similarly, $X_5 = 2X_dX_r$ and $X_6 = X_r^2$. Furthermore, $\sum X_i = 1$.

The $X_i$ can now be calculated using the fractional concentrations of H1, H2 and HR atoms. State 1 contains four H1 atoms, and states 2 and 3 each contain two H1 atoms. Thus, $P_{H1} = (4X_1 + 2X_2 + 2X_3)/4$. Similarly, for H2 and HR atoms, $P_{H2} = (X_2 + 2X_3 + X_4)/4$ and $P_{HR} = (X_1 + 2X_2 + 3X_3 + 4X_4)/4$. Rearrangement of these equations gives the following expressions for the $X_i$:

$$X_1 = P_{H1}^2$$  \hfill (8)

$$X_2 = 4P_{H1}P_{H2}$$  \hfill (9)

$$X_3 = 2P_{H1}(P_{HR} - P_{H2})$$  \hfill (10)

$$X_4 = 4P_{H2}^2$$  \hfill (11)

$$X_5 = 4P_{HR}(P_{HR} - P_{H2})$$  \hfill (12)

$$X_6 = (P_{HR} - P_{H2})^2$$  \hfill (13)

From the results shown in Figure 2, $P_{H1}$ and $P_{H2}$ can be evaluated from $P_{HR}$. Hence, by means of eqs 8–13, the $X_i$ can be found from measured values of $P_{HR}$. Equations 8–13 can also be derived directly by assigning the probabilities $P_{H1}, 2P_{H2},$ and $P_{HR} - P_{H2}$ respectively, to unreacted, semireacted and fully reacted amine groups (see eqs 24–26, later).

### 4. GEL POINT IN THE ABSENCE OF INTRAMOLECULAR REACTION

To define the gel point statistically, the probability of path continuation is introduced.\(^1\)\(^9\)\(^{18}\)\(^{22}\) It is the probability that a randomly chosen reactive group has at least one path emanating from it that continues to infinity. This probability increases as a reaction proceeds and becomes equal to unity at the gel point. Here, the derivation of the expression for the gel point in terms of extent of reaction ($\rho$) proceeds and becomes equal to unity at the gel point.

Assume first that the randomly chosen group is an A group, denoted $A^1$ in Figure 4. The number of continuing paths ($\gamma_a$), given that an A group has been chosen, is the number of paths between the statistically equivalent points $A^1$ and $A^1$. $A^1\ldots$ denotes an A group can be reacted or unreacted.

$$\gamma_a = \left(\frac{3}{4}X_u + \frac{3}{2}X_d + \frac{3}{2}X_r + \frac{9}{4}X_s + 3X_a\right)P_b$$  \hfill (14)

$p_b$ is the extent of reaction of B groups.

The terms in eq 14 are easily derived by reference to Figure 3. $X_1$ to $X_6$ are the probabilities that RA units in states 2 to 6, respectively, are chosen. If a unit in state 2 is chosen then the probability that an unreacted hydrogen atom (HU) is chosen for $A^1$ is equal to $3/4$ giving 1 path to a B–B unit. Following similar arguments, the origin of the numerical coefficients in eq 14, representing numbers of paths, may be summarized as follows:

$$X_1: \text{probability} = 1/2 \text{ that a HU atom is chosen for } A^1, \text{ giving 2 paths to B–B units, and}$$

$$X_2: \text{probability} = 1/2 \text{ that a HR atom is chosen for } A^1, \text{ giving 1 path to a B–B unit.}$$

Therefore, total number of paths = $1/2 \times 2 + 1/2 \times 1 = 3/2$. $X_3$ is same as $X_1$.

$$X_4: \text{probability} = 1/4 \text{ that a HU atom is chosen for } A^1, \text{ giving 3 paths to B–B units, and}$$

$$X_5: \text{probability} = 3/4 \text{ that a HR atom is chosen for } A^1, \text{ giving 2 paths to B–B units.}$$

Therefore, total number of paths = $1/4 \times 3 + 3/4 \times 2 = 9/4$. $X_6: \text{probability} = 1/2 \text{ that a HR atom is chosen for } A^1, \text{ giving 3 paths to B–B units.}$

To compare eq 14 with the conventional way,\(^1\)\(^9\) valid when $\rho = 1$, of defining $\gamma_a$ in terms of the fractions of unreacted and reacted A groups, $P_U$ and $P_R$, respectively, one has:

$$X_1 = P_U^4$$  \hfill (15)

$$X_2 = 4P_UP_R$$  \hfill (16)

$$X_3 = 2P_U^2P_R^2$$  \hfill (17)

$$X_4 = 4P_U^2P_R^2$$  \hfill (18)

$$X_5 = 4P_UP_R^3$$  \hfill (19)

$$X_6 = P_R^4$$  \hfill (20)

Substituting these relationships in eq 14 gives

$$\gamma_a = \left(\frac{3}{4}P_U^3P_R + \frac{3}{2}P_U^2P_R^2 + \frac{3}{4}P_U^2P_R^2 + \frac{9}{4}P_UP_R^3\right)P_b$$

$$= 3P_R(P_U^3 + 3P_U^2P_R + 3P_UP_R^2 + P_R^3)P_b$$

$$= 3P_R P_b$$  \hfill (22)

corresponding to $\gamma_a = (f_a - \text{1})p_aP_b$ for an RA$_a$ + R’B$_2$ polymerization, with

$$P_a \equiv P_R \text{ and } (1 - P_a) \equiv P_U$$  \hfill (23)

Comparison of eqs 15–20 with eqs 8–13 shows that, when $\rho = 1$

$$P_{H1} = P_U$$  \hfill (24)

$$P_{H2} = P_U \times P_R$$  \hfill (25)

and

$$P_{HR} - P_{H2} = P_R^2 = P_b^2$$  \hfill (26)

Furthermore, eqs 24, 25 and 26 show that
\[ p_{U} + p_{HR} = p_{U} \left( p_{U} + p_{R} \right) = p_{U} \left( 1 - p_{R} \right) \tag{27} \]

and
\[ p_{HR} = p_{R}^2 + p_{U} p_{R} - p_{R} \left( p_{R} + p_{U} \right) = p_{R} \tag{28} \]

Equations 24–26 also show that \( p_{HR} \), \( 2p_{HR} \), and \( p_{HR} - p_{HR}^2 \) are the probabilities of unreacted, semireacted and fully reacted amine groups occurring, with
\[
X_U + X_A + X_R = p_{HR} + 2p_{HR} + p_{HR} - p_{HR}^2
= p_{HR} + p_{HR} + p_{HR}
= 1
\]

In addition, eq 14 may be written in terms of \( p_{HR} \), \( 2p_{HR} \), and \( p_{HR} \) with
\[
\gamma_b = \left( 3p_{HR} + 3p_{HR} - p_{HR} + 6p_{HR}^2 \right)
+ 9p_{HR} \left( p_{HR} - p_{HR}^2 \right) + 3 \left( p_{HR} - p_{HR}^2 \right)^2 p_b
\tag{29} \]

Second, assume that the randomly chosen group is a B group, denoted \( B^\prime \) in Figure 5. The number of continuing paths (\( \gamma_b \)) is

\[
\gamma_b = p_b \times \text{number of paths from } B^\prime \text{ to } B^\prime \tag{30} \]

To evaluate the number of paths in eq 30, one needs to consider the fractions of reacted groups on the various states of a diamine unit, as defined in Figure 3. Summing the fractions of reacted groups gives the average number of reacted H groups on a diamine unit, namely,
\[
X_A + 2X_R + 3X_A + 4X_B
= 4p_{U}^3 p_{HR} + 4p_{U}^2 p_{HR}^2 + 5p_{U} p_{HR}^3 + 12p_{U}^2 p_{HR}^3 + 4p_{HR}^4
= 4p_{HR}
\tag{31} \]

Hence, the fractions of reacted groups that are on the various states and the numbers of continuing paths from those states are as defined in Table 1. Finally, from eq 30 and Table 1, the number of continuing paths from \( B^\prime \) to \( B^\prime \) is
\[
\gamma_b = p_b \left( p_{U}^2 p_{HR} + 2p_{U} p_{HR}^2 + 6p_{U} p_{HR}^3 + 3p_{HR} \right)
\tag{32} \]

i.e.,
\[
\gamma_b = 3p_{HR} p_{R}
\tag{33} \]

The expression for \( \gamma_b \) may be recast in terms of \( p_{HR} \), \( p_{HR} \), and \( p_{HR} \) by first rewriting eq 32 as
\[
\gamma_b = p_b \left( p_{U}^2 p_{HR} + 2p_{U} p_{HR}^2 + 6p_{U} p_{HR}^3 + 3p_{HR} \right)
\]

and then using eqs 24 to 28 to give
\[
\gamma_b = p_b \left( p_{U}^2 \left( p_{HR} - p_{HR}^2 \right) + 2p_{HR}^2 + 6p_{HR} \left( p_{HR} - p_{HR}^2 \right)
+ 3 \left( p_{HR} - p_{HR}^2 \right)^2 \right)
\tag{34} \]

Finally, adding the contributions from \( \gamma_a \) and \( \gamma_b \), the number of continuing paths from a randomly chosen group to a statistically equivalent point is
\[
\gamma = X_a \gamma_a + X_b \gamma_b
\tag{35} \]

where
\[
X_a = \frac{N_a}{N_a + N_b} \quad \text{and} \quad X_b = \frac{N_b}{N_a + N_b}
\tag{36} \]

are the mole fractions of A and B groups in the reaction mixture, with \( N_a \) and \( N_b \) the initial numbers of A and B groups, respectively, and
\[
X_a / X_b = r_a
\tag{37} \]

is the reactive group ratio of A groups relative to B groups. The full expression for \( \gamma \) in terms of \( p_{HR} \), \( p_{HR} \), and \( p_{HR} \) is
\[
\gamma = X_a 3p_{HR} \left( p_{HR} - p_{HR}^2 \right) + 2p_{HR} \left( p_{HR} - p_{HR}^2 \right)
+ 3p_{HR} \left( p_{HR} - p_{HR}^2 \right) + 3 \left( p_{HR} - p_{HR}^2 \right)^2
\]

\[
+ X_b \left( p_{HR} p_{HR} \right) \left( p_{HR} - p_{HR}^2 \right) + 2p_{HR} \left( p_{HR} - p_{HR}^2 \right)
+ 6p_{HR} \left( p_{HR} - p_{HR}^2 \right) + 3 \left( p_{HR} - p_{HR}^2 \right)^2
\tag{38} \]

The results of calculations using eq 38 at \( r_a = 1 \), so that \( X_a = X_b = 1/2 \), are shown in Figure 6, with \( \gamma \) plotted as a function of \( p_{HR} \). The values of \( \rho \) used for the calculations were 1.5, 1, 0.5, and 0.1. It can be seen that \( \gamma \) increases from 0 to 3 as \( p_{HR} \) increases from 0 to 1. The result that \( \gamma \) is 3 as \( p_{HR} = 1 \) comes from the fact that, when all the A groups on the RA units are reacted, those units are all in state 6, which has three continuing paths from any randomly chosen group.

The curves of \( \rho \) vs. \( p_{HR} \) depend slightly on \( \rho \), as can be seen in the inset figure. Focusing on the gel point, the value of \( p_{HR} \) at \( \gamma = 1 \) is \( p_{HR} = 0.577 \) for \( \rho = 1 \), consistent with Flory-Stockmayer theory. In addition, as \( \rho \) decreases, \( p_{HR} \) increases, corresponding to a larger delay of the gel point. A smaller value of \( \rho \) means less of reaction 2 of Figure 1, resulting in the formation of states 3, 5, and 6 of the diamine unit being delayed (see Figure 3). States 5 and 6 bring about the bifurcation that leads to gelation. Hence, it can be considered that the delay of gel point caused by a decrease in \( \rho \) is due to the delay in the formation of states 5 and 6.

### Table 1: Fractions of Reacted Groups on the Various States of a Diamine Unit and the Numbers of Continuing Paths from Those States

<table>
<thead>
<tr>
<th>state</th>
<th>fraction of reacted groups</th>
<th>number of continuing paths</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \frac{X_a}{4p_{HR}} )</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{2X_a}{4p_{HR}} )</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{2X_a}{4p_{HR}} )</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{3X_a}{4p_{HR}} )</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>( \frac{4X_a}{4p_{HR}} )</td>
<td>3</td>
</tr>
</tbody>
</table>

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significantly delayed, $X_t$ and $X_o$ are nearly equal to zero up to $p_{HR} = 0.5$, whereas they increase very rapidly after $p_{HR} = 0.5$. In consequence, the increase in $p_c$ is not so large even for the small value of $\rho$. For $\rho = 0.1$, $p_c = 0.599$, an increase of only 0.022 over the Flory–Stockmayer value.

5. RING–FORMING PARAMETERS\textsuperscript{9,18,22}

In an $\text{RA}_A + \text{RB}_B$ type polymerization, competition always occurs between intermolecular and intramolecular reaction. To describe the competition, let $c_{a,\text{int}}$ be the (internal) concentration of $A$ groups from the same molecule around a $B$ group about to react and let $c_{a,\text{ext}}$ be the (external) concentration of $A$ groups from other molecules. Then, a ring–forming parameter, $\lambda_a$, can be defined as

$$\lambda_a = c_{a,\text{int}} / (c_{a,\text{ext}} + c_{a,\text{int}})$$  \hspace{1cm} (39)

Correspondingly, $c_{b,\text{int}}$ and $c_{b,\text{ext}}$ can be defined as the internal and external concentrations of $B$ groups around an $A$ group about to react, leading to the ring-forming parameter

$$\lambda_b = c_{b,\text{int}} / (c_{b,\text{ext}} + c_{b,\text{int}})$$  \hspace{1cm} (40)

The size of ring structure is denoted by $j$, as illustrated in Figure 7 with reference to an $\text{RA}_A + \text{RB}_B$ polymerization. The $\text{RA}_A + \text{RB}_B$ polymerization

![Figure 6. Number of continuing paths from a randomly chosen group, $\gamma$ as a function of $p_{HR}$ for different values of $\rho$. The inset shows the delay in gel point as $\rho$ decreases, that is, the increase in $p_{HR}$ at $\gamma = 1$.](image)

![Figure 7. Illustrating sizes of ring structures that can form in an $\text{RA}_A + \text{RB}_B$ polymerization.](image)

![Figure 7. Illustrating sizes of ring structures that can form in an $\text{RA}_A + \text{RB}_B$ polymerization.](image)

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available to form ring structures of all sizes with a reacting $A$ group on the same molecule, with

$$c_{b,\text{int}} = \sum_{j=1}^{\infty} c_{b,\text{int},j}$$  \hspace{1cm} (42)

When evaluating the contribution to the terms $c_{a,\text{int},j}$ and $c_{b,\text{int},\rho}$ from each pair of $A$ and $B$ groups that could react together, it is necessary to consider the probability that the end-to-end distance of the chain connecting them is equal to zero.\textsuperscript{34} It is assumed that the end-to-end distance distribution, i.e., the probability density $P(r_j)$ of an end-to-end vector equal to $r_j$, is a Gaussian distribution, with

$$P(r_j) = \left( \frac{3}{2\pi b^3} \right)^{3/2} \exp\left( -\frac{3r_j^2}{2\nu b^2} \right)$$  \hspace{1cm} (43)

and

$$\langle r_j^2 \rangle = \nu b^2$$  \hspace{1cm} (44)

$b$ is known as the effective bond length of the chain of $\nu$ bonds able to form the smallest ring structure ($j = 1$). $P(r_j)$ at $r_j = 0$, namely, $P(0)$, is the concentration of one chain end around the other chain end. Dividing $P(0)$ by $N_{Av}$, Avogadro’s number, gives the molar concentration of coincident chain ends that can form the smallest ring structure. This concentration is denoted $P_{ab}$, with

$$P_{ab} = P(0) / N_{Av} = \frac{1}{N_{Av}} \left( \frac{3}{2\pi \langle r_j^2 \rangle} \right)^{3/2}$$  \hspace{1cm} (45)

$\nu$ and $b$ can, in principle, be calculated from the molar masses and chain structures of the reactants. $P_{ab}$ is the molar concentration of $A$ or $B$ groups around a $B$ or $A$ group, respectively, that can form the smallest ring structure. Equation 45 neglects any effects of the branch units on the statistics governing the mutual separations of pairs of end groups in branched chains. Regarding this point, it is necessary to develop more realistic statistics, since ring structures can form through the branch units.

If there is only one opportunity to form a ring structure of each size, the sum over all sizes in eq 41 can be written

$$c_{a,\text{int}} = \sum_{j=1}^{\infty} \frac{1}{N_{Av}} \left( \frac{3}{2\pi \langle r_j^2 \rangle} \right)^{3/2} = P_{ab} \sum_{j=1}^{\infty} \left( \frac{1}{j} \right)^{3/2} = 2.61 P_{ab}$$  \hspace{1cm} (46)

where $\langle r_j^2 \rangle = \langle r_{1j}^2 \rangle$ and $\sum 1/j^{3/2} = \phi(1, 3/2) = 2.61$ is a Truesdell function.\textsuperscript{35} Similarly,

$$c_{b,\text{int}} = 2.61 P_{ab}$$  \hspace{1cm} (47)

can be derived from eq 42, assuming only one opportunity to form a ring structure of each size.

Alternative ring-forming parameters to those introduced in eqs 39 and 40 are

$$\lambda_{a0} = P_{ab} / c_{a0} \text{ and } \lambda_{b0} = P_{ab} / c_{b0}$$  \hspace{1cm} (48)

where $c_{a0}$ and $c_{b0}$ are the initial concentrations of $A$ and $B$ groups before reaction occurs. $\lambda_{a0}$ and $\lambda_{b0}$ have an advantage over $\lambda_a$ and $\lambda_b$, in that they can, in principle, be calculated directly from the molar masses and chain structures of the reactants and the initial concentrations of reactive groups, independent of the complex molecular structures forming during a polymerization.
6. GEL POINT ACCOUNTING FOR INTRAMOLECULAR REACTION

The derivation of an expression for the gel point in terms of extents of reaction follows the derivation in section 4, except that account is taken of the opportunities for intramolecular reaction. The derivation may be considered to be a development of Ahmed-Rolfe-Stepno (ARS) theory. The use of the different states of the diamine unit specified in Figure 3 to define opportunities for intramolecular reaction, rather than just a simplified linear sequence of branch units, such as that shown in Figure 7, means that more ring structures are accounted for.

As in the derivation of eq 38 in the absence of intramolecular reaction, an expression for the number of continuing paths from a randomly chosen group to a statistically equivalent point is required. γ is still given formally by eq 35, with γs and γb the number of continuing paths, given that an A group and B group, respectively, has been chosen. As in the absence of intramolecular reaction, assume first that an A group has been chosen. The opportunities for intramolecular reaction will depend on the state of the diamine unit to which the chosen A group belongs and the steps in the derivation of the expression for γs generally follow those that led to eq 14. However, because Figure 6 shows that unequal reactivity has a minimal effect on the relationship between $p_{\text{HR}}$ and γ, it is permissible to assume the equal reactivity of A groups when considering the probabilities of intramolecular reaction. This assumption greatly simplifies the probability considerations required. When more distant groups are considered for ring formation, it is necessary to include some topological effect as well as statistical probability of the group meeting. In addition, for the irreversible reactions, a kinetic development might be more appropriate than statistical considerations.

First, let the randomly chosen A group, namely, $A_i$, belong to an RA4 unit in state 2, as illustrated in Figure 8. As in eq 14, $\frac{3}{4}X_s$ is the probability that an unreacted A group on state 2 is chosen. In the absence of intramolecular reaction, this probability is multiplied by $p_b$, to give the probability $\frac{3}{4}X_s p_b$ that the group $A_i'$, which is statistically equivalent to $A_i$, is reached. Accounting for intramolecular reaction, the probability that the left-hand B group reacts intramolecularly with $A_i'$, rather than intermolecularly with the unreacted A groups on the unit bearing $A_i$, may be written $p_{a2}(1 - \lambda_{a2})$, where

$$\lambda_{a2} = \frac{3p_{ab}}{c_{a,\text{ext}} + 3p_{ab}}$$

(49)

$\lambda_{a2}$ is equivalent to $\lambda_a$ of eq 39 for the case of state 2 being the molecule under consideration, i.e.,

$$\lambda_{a2} = \frac{c_{a,\text{int}}}{c_{a,\text{ext}} + c_{a,\text{int}}} = \frac{3p_{ab}}{c_{a,\text{ext}}(1 - p_a) + 3p_{ab}}$$

(50)

with $c_{a,\text{int}} = 3p_{ab}$ accounting for the three A groups able to react intramolecularly with the left-hand B group, and $c_{a,\text{ext}} = c_{ao}(1 - p_a)$ being the instantaneous concentration of unreacted A groups in the polymerization. $P_{ab}$ is as defined in eq 45. Thus, the probability that the group $A_i'$ is reached from $A_i$ is $\frac{3}{4}X_s p_b (1 - \lambda_{a2})$ (51).

Next, assume that the randomly chosen A group belongs to an RA4 unit in state 3. This occurs with probability equal to $X_s$. There is a probability of 1/2 that the A group chosen, namely, $A_i$, is unreacted, as shown in Figure 9a, giving two possible continuing paths to R'B2 units. Select one of them, denoted $A_i^2$. There is a probability $(1 - p_b)$ that the other reacted A group of state 3 leads to an unreacted B group, $B_i^1$, as illustrated in Figure 9b. Hence, from eq 45, the internal concentration of B groups around $A_i^2$ available for intramolecular reaction is $(1 - p_b)P_{ab}$. Alternatively, the other reacted A group of state 3 leads to a reacted B group, $B_i^1$, with probability $p_b$. In that case, the infinite number of possible structures that could be connected to $B_i^1$ is approximated by a continuous chain of branch units, as depicted in Figure 9c. This structural approximation corresponds to that used previously and enables approximations to internal concentrations to be evaluated. Moving to the right of $B_i^1$, it can be seen that, at each RA4 unit of the continuing chain, there is a probability $(f - 2) p_{ab}(1 - p_b)$ that an unreacted B group exists. As one moves right along the chain, the size of the ring structure that can be formed by an unreacted B group reacting with $A_i^2$ increases and, following eq 46, the total internal concentration from all such unreacted B groups is
The last factor is \((\phi(1,3/2) - 1)\) because the smallest ring structure can be formed only when \(B^1\) is unreacted.

Finally, summing the two contributions corresponding to \(B^1\) being unreacted and reacted, the total internal concentration of \(A\) groups around \(A^5\) in state 3 of an RA4 unit is

\[
c_{b3,int} = p_{ab}(1 - p_b) + p_b[(f_a - 2)p_a'(1 - p_a)]
\]

and the probability that intramolecular reaction, rather than intermolecular reaction, occurs is

\[
\lambda_{b3} = \frac{c_{b3,int}}{c_{b,ext} + c_{b3,int}} = \frac{c_{b3,int}}{c_{b0}(1 - p_b) + c_{b3,int}}
\]  
\[(53)\]

Conversely, the probability that \(A^5\) has reacted intermolecularly with a \(B\) group is

\[
(1 - \lambda_{b3})
\]  
\[(54)\]

This leads to the structure depicted in Figure 9d. Then, applying to the reaction of \(B^2\) the preceding arguments regarding the intramolecular versus intermolecular reaction of \(A^5\), one finds that the total internal concentration of \(A\) groups around \(B^2\) is

\[
c_{a3,int} = 2p_{ab} + p_b[(f_a - 2)(1 - p_a)p_{ab}(\phi(1,3/2) - 1)]
\]

\[
= p_{ab}[(2 + p_b)(f_a - 2)(1 - p_a)(\phi(1,3/2) - 1)]
\]  
\[(55)\]

The probability of intramolecular reaction rather than intermolecular reaction is

\[
\lambda_{a3} = \frac{c_{a3,int}}{c_{a,ext} + c_{a3,int}}
\]  
\[(56)\]

And the probability that \(B^2\) has reacted intermolecularly leading to \(A^5\), a statistically equivalent group to \(A^5\), is

\[
p_b(1 - \lambda_{a3})
\]  
\[(57)\]

Expressions 54 and 57 show that the total probability that \(A^5\) is reached from \(A^5\), when \(A^5\) is an unreacted group on state 3, is

\[
\frac{1}{2} \times 2X_4(1 - \lambda_{b3})p_b(1 - \lambda_{a3})
\]  
\[(58)\]

Now assume that \(A^4\), the randomly chosen \(A\) group on state 3, is a reacted \(A\) group, giving one possible path through \(A^2\) to \(A^5\). There is a probability equal to \(1/2\) that \(A^4\) is reacted. The possible resulting structures are depicted in Figure 10a. The \(R'B_4\) unit attached to \(A^4\) ends in an unreacted \(B\) group with probability \((1 - p_b)\) resulting in an internal concentration of \(B\) groups around \(A^5\) of \((1 - p_b)p_{ab}\). Conversely, it ends in a reacted \(B\) group with probability \(p_b\) when it is assumed that the same structure as depicted in Figure 9(c) exists, and the internal concentration of \(B\) groups around \(A^5\) is

\[
p_b[(f_a - 2)p_a'(1 - p_a)]p_{ab}(\phi(1,3/2) - 1)
\]

Giving a total internal concentration of \(B\) groups of \(c_{b3,int}\) the same as that in eq 52 and a probability \(\lambda_{b3}\) as in eq 53, that intramolecular reaction occurs.

Proceeding left from \(A^5\) to an intermolecularly reacted \(B\) group, with probability \((1 - \lambda_{b3})\), the other end of the \(R'B_4\) unit, \(B^4\), is reacted with probability \(p_b\). Figure 10(b) shows that the opportunities for the intramolecular reaction of \(B^2\) with an \(A\) group are similar to those depicted in Figure 9(d), leading to a probability \(\lambda_{a3}\) of intramolecular reaction, as defined in eq 56. Hence, \((1 - \lambda_{a3})\) is the probability that \(B^2\) reacts intermolecularly, leading to \(A^5\) a statistically equivalent group to \(A^5\), and the probability of passing from \(A^4\), a reacted \(A\) group on state 3, to \(A^5\) is

\[
\frac{1}{2} X_4(1 - \lambda_{b3})p_b(1 - \lambda_{a3})
\]  
\[(59)\]

Thus, adding expressions 58 and 59, the total contribution to \(\gamma_a\) when an \(A\) group on state 3 is chosen, irrespective of it being reacted or unreacted, becomes

\[
\frac{3}{2} X_4(1 - \lambda_{b3})p_b(1 - \lambda_{a3})
\]  
\[(60)\]

If the randomly chosen \(A\) group is on state 4, the same probabilities ensue as when the group is on state 3. Hence, one may formally write the contribution to \(\gamma_a\) as

\[
\frac{3}{2} X_4(1 - \lambda_{b4})p_b(1 - \lambda_{a4})
\]  
\[(61)\]

where \(\lambda_{b4} = \lambda_{b3}\) and \(\lambda_{a4} = \lambda_{a3}\).

Next assume that the randomly chosen \(A\) group is an unreacted \(A\) group on state 5, giving three possible continuing paths, as depicted in Figure 11a. An unreacted \(A\) group on state 5 is chosen with a probability equal to \(1/4\). Let the \(A\) group on one of the continuing paths be denoted \(A^5\). Figure 10(b) shows that this group experiences an internal concentration of \(B\) groups

\[
c_{b3,int} = 2(1 - p_b)p_{ab} + p_b[(f_a - 2)p_a'(1 - p_a)]p_{ab}(\phi(1,3/2) - 1)
\]  
\[(62)\]
Thus, $A^2$ reacts intramolecularly with $B^1$ with a probability
\begin{equation}
\lambda_{b5} = \frac{c_{b5,\text{int}}}{c_{b,\text{ext}} + c_{b5,\text{int}}}
\end{equation}
and intermolecularly with a probability $(1 - \lambda_{b5})$. Also, comparison with eq 52 shows that
\begin{equation}
c_{b5,\text{int}} = 2c_{b3,\text{int}}
\end{equation}
The group $B^2$ experiences an internal concentration of $A$ groups of $P_a$ from $A^1$ and
\begin{equation}
2p_b(f_a - 2)(1 - p_b)p_a(\phi(1, 3/2) - 1)
\end{equation}
from unreacted A groups on the continuing sequences shown in Figure 11a. Thus,
\begin{equation}
c_{a5,\text{int}} = p_a[1 - 2p_b(f_a - 2)(1 - p_a)](\phi(1, 3/2) - 1)
\end{equation}
and the probability that $B^2$ reacts intramolecularly is
\begin{equation}
\lambda_{a5} = \frac{c_{a5,\text{int}}}{c_{a,\text{ext}} + c_{a5,\text{int}}}
\end{equation}
The probability that it reacts intermolecularly is $(1 - \lambda_{a5})$ and, hence, the contribution to $\gamma_a$ when an unreacted A group on an RA$_4$ unit in state 5 is chosen, is
\begin{equation}
\frac{3}{4} \times 3X_b(1 - \lambda_{b5})p_b(1 - \lambda_{a5})
\end{equation}
and, summing expressions 67 and 68, the total contribution to $\gamma_a$ when a reacted or unreacted A group on an RA$_4$ unit in state 5 is chosen, is
\begin{equation}
\frac{9}{4}X_b(1 - \lambda_{b5})p_b(1 - \lambda_{a5})
\end{equation}
Finally, if the A group chosen, $A^1$, is on state 6, all the arms are equivalent to each other and there are three possible continuing paths. Considering the reaction of $A^2$ on one of these paths, it experiences an internal concentration of $B$ groups
\begin{equation}
c_{b6,\text{int}} = 3(1 - p_b)p_a + 3p_b(f_a - 2)p_a(1 - p_b)p_a(\phi(1, 3/2) - 1)
\end{equation}
and, summing expressions 67 and 68, the total contribution to $\gamma_a$ is
\begin{equation}
\lambda_{b6} = \frac{c_{b6,\text{int}}}{c_{b,\text{ext}} + c_{b6,\text{int}}}
\end{equation}
Furthermore, comparison with eq 52 shows that
\begin{equation}
c_{b6,\text{int}} = 3c_{b3,\text{int}}
\end{equation}
Turning to the reaction of $B^2$, the internal concentration of A groups is
\begin{equation}
c_{a6,\text{int}} = 3p_b(f_a - 2)(1 - p_a)p_b(\phi(1, 3/2) - 1)
\end{equation}
Thus, the probability of intermolecular reaction of $B^2$ leading to $A^1$, a statistically equivalent group to $A^1$, is equal to $(1 - \lambda_{a6})$, where $\lambda_{a6}$ is given by
\begin{equation}
\lambda_{a6} = \frac{c_{a6,\text{int}}}{c_{a,\text{ext}} + c_{a6,\text{int}}}
\end{equation}
The total contribution to $\gamma_a$ when the randomly chosen A group belongs to an RA$_4$ unit in state 6 is
\begin{equation}
3X_a(1 - \lambda_{b6})p_a(1 - \lambda_{a6})
\end{equation}
Summing the contributions to $\gamma_a$ given in expressions 51, 60, 61, 69, and 75 gives
\begin{equation}
\gamma_a = \left[\frac{3}{4}X_b(1 - \lambda_{b5}) + \frac{3}{2}X_b(1 - \lambda_{b5})(1 - \lambda_{a5}) + \frac{3}{2}X_b(1 - \lambda_{b6})(1 - \lambda_{a6}) + \frac{9}{4}X_b(1 - \lambda_{b5})(1 - \lambda_{a6}) + 3X_a(1 - \lambda_{b6})(1 - \lambda_{a6})\right]p_b
\end{equation}
where, for $i = 2-6$
$\lambda_{ii} = \frac{c_{ii,\text{int}}}{c_{ii,\text{int}} + c_{ii,\text{ext}}}$ (77)

with

$\begin{align*}
c_{ii,\text{int}} &= 3P_{ab}c_{ii,\text{int}} \\
c_{ii,\text{ext}} &= P_{ab}[2 + P_b\{(f_a - 2)(1 - P_b)(1, 3/2) - 1\}] \\
c_{ii,\text{int}} &= P_{ab}[1 - 2P_b\{(f_a - 2)(1 - P_b)(1, 3/2) - 1\}] \\
c_{ii,\text{int}} &= P_{ab}[3 - 3P_b\{(f_a - 2)(1 - P_b)(1, 3/2) - 1\}]
\end{align*}$

and

$\begin{align*}
c_{ii,\text{int}} &= P_{ab}^2\{(1 - P_a)\{1 + P_b\{(f_a - 2)(1 - P_b)(1, 3/2) - 1\}\}\} \\
c_{ii,\text{int}} &= 2c_{ii,\text{int}} \\
c_{ii,\text{int}} &= 3c_{ii,\text{int}} \\
c_{ii,\text{int}} &= 3c_{ii,\text{int}}
\end{align*}$

Returning to eq 35, it is now required to evaluate $\gamma_{b_i}$ the number of continuing paths if a B group, B1, is randomly chosen. B1 can be reacted or unreacted, as depicted in Figure 12. B2, the RA4 unit that has reacted with group B2 can give a continuing chain provided it is in state 3–6, as depicted in Figure 12. The probability that an RA4 unit in state i is attached to B2 is equal to $Q_i$, the probability of choosing a reacted A group on state i. The expressions for $Q_i$, i = 2–6, are

$\begin{align*}
Q_2 &= \frac{X_2}{(X_2 + 3X_5 + 4X_6)} \\
Q_3 &= \frac{2X_3}{(X_2 + 3X_5 + 4X_6)} \\
Q_4 &= \frac{X_4}{(X_2 + 3X_5 + 4X_6)} \\
Q_5 &= \frac{3X_5}{(X_2 + 3X_5 + 4X_6)} \\
Q_6 &= \frac{4X_6}{(X_2 + 3X_5 + 4X_6)}
\end{align*}$

As can be seen from Figure 3, the denominator in each case is the total number of reacted A groups per unit. State 2 has only one reacted A group and, hence, cannot give a chain continuing on from group A2 in Figure 12.

If B2 in Figure 12 has reacted with an RA4 unit in state 3, there is only one continuing path to B1′, that passing through A2 and this A group experiences an internal concentration of B groups equal to $c_{b3,int}$ of eq 52. Thus, the probability that A2 has reacted intramolecularly to reach B1′ and given a continuing chain is $(1 - \lambda_{b3})$, where $\lambda_{b3}$ is given by eq 33. Hence, the contribution to $\gamma_{b_i}$ when an RA4 unit in state 3 has reacted with B2 is

$\begin{align*}
p_{b_i}(1 - \lambda_{b_i})Q_3(1 - \lambda_{b3})
\end{align*}$

If the RA4 unit that has reacted with B2 is in state 4, the same opportunities for intramolecular reaction exist as for state 3; $c_{b4,int}$ and $\lambda_{b4} = \lambda_{b3}$. Also, the contribution to $\gamma_{b_i}$ is

$\begin{align*}
p_{b_i}(1 - \lambda_{b_i})Q_4(1 - \lambda_{b4})
\end{align*}$

State 5 of an RA4 unit has three reacted groups. Hence, reaction of B2 with an RA4 unit in state 5 gives two continuing paths. One of these contains A2′, which experiences an internal concentration of B groups equal to $c_{b5,int}$ of eq 62. Hence, A2′ reacts intramolecularly with B1′ with probability $(1 - \lambda_{b5})$, where $\lambda_{b5}$ is given by eq 63 and gives a contribution to $\gamma_{b_i}$ of

$\begin{align*}
p_{b_i}(1 - \lambda_{b_i})Q_5(1 - \lambda_{b5})
\end{align*}$

Finally, intermolecular reaction of B2 with an RA4 unit in state 6 gives three continuing paths and A2′ experiences an internal concentration of B groups equal to $c_{b6,int}$ of eq 70. Hence, A2′ reacts intramolecularly with B1′ with probability $(1 - \lambda_{b6})$, where $\lambda_{b6}$ is given by eq 71 and gives a contribution to $\gamma_{b_i}$ of

$\begin{align*}
p_{b_i}(1 - \lambda_{b_i})Q_6(1 - \lambda_{b6})
\end{align*}$

Collecting the individual contributions to $\gamma_{b_i}$ defined by expressions 82 to 85 shows that

$\begin{align*}
\gamma_{b_i} = p_{b_i}(1 - \lambda_{b_i})[Q_3(1 - \lambda_{b3}) + Q_4(1 - \lambda_{b4}) + 2Q_5(1 - \lambda_{b5}) + 3Q_6(1 - \lambda_{b6})]
\end{align*}$

The gel point is defined by $\gamma$ in eq 35 equal to one, namely

$\gamma = X_{b_i}'X_{b_i} + X_{b_i}'X_{b_i} = 1$

with $\gamma_{b_i}$ and $\gamma_{b_i}$ given by eqs 76 and 86, respectively.

7. GEL POINT CALCULATIONS AND DISCUSSION

Calculations of extents of reaction at the gel point have been carried out for reactions at equal initial concentrations of A and B.
groups, i.e., \( r = 1 \), giving \( c_{i0} = c_{0i} = c_p \) and using different values of the ring-forming parameters of eq 48 with
\[
\lambda_{0i} = \lambda_{00} = P_{ab}/c = \lambda_0
\]  
(87)

The value of \( \lambda_0 \) is sufficient to allow the \( \lambda_{0i} \) and \( \lambda_i \) of eqs 77, 78, and 80 to be evaluated. Equation 50 shows that \( \gamma \) is independent of \( Stockmayer \) theory. Figure 13 again shows that the ring-forming parameters of eq 48 with \( \gamma \) can be determined.

Inspection of eqs 77, 78, and 80 shows that the expressions for the ring-forming parameters all contain a factor \( P_{ab} \). Hence, the factors \( (c_{i0}/P_{ab}), (c_{i0}/P_{ab}) \), and \( (c_{i0}/P_{ab}) \) in eqs 88 to 90 are independent of \( P_{ab} \) and depend only on \( p_z \) and \( P_b \).

As stated previously, the gel point is defined as the extent of reaction \( p_x \) or \( p_b \) that makes \( \gamma \) equal to 1, with \( \gamma_x \) and \( \gamma_b \) given by eqs 76 and 86, respectively. \( p_z \) and \( P_b \) are related through
\[
\frac{P_b}{P_z} = \frac{X_b}{X_z} = \frac{c_{i0}}{c_{0i}} = r_z
\]
(91)

Equations 76, 81, 86, and 88–90 show that \( \gamma_x \) and \( \gamma_b \) are functions of \( X_z \) and \( X_b \). In addition, eqs 8 to 13 show that \( X_z \) and \( X_b \) can be defined in terms of \( P_{13} \), \( P_{12} \), and \( P_{11} \), allowing the effects of unequal reactivity \( (\rho \neq 1) \) to be accounted for using eqs 5 to 7. Alternatively, eqs 16–20 can be used to evaluate \( X_z \) and \( X_b \) when \( \rho = 1 \).

Figure 13 shows the (critical) extent of reaction at gelation \( (p_x) \) versus \( \lambda_0 \) for reaction mixtures with \( r_z = 1 \). At the gel point

![Figure 13](image)

**Figure 13.** Critical extent of reaction, \( p_x \) versus the ring-forming parameter \( \lambda_0 \) for \( RA_4 + R'B_2 \) polymerizations with \( r_z = 1 \) and different values of \( \rho \).

when \( r_z = 1 \), \( p_x = p_{bc} = p_c \). Further, the value of \( p_x \) when \( \rho = 1 \) and \( \lambda_0 = 0 \) is \( 3^{1/2} = 0.577 \), in agreement with Flory–Stockmayer theory. Figure 13 again shows that \( p_z \) is relatively insensitive to changes in \( \rho \) (compare Figure 6). However, the amount of intramolecular reaction and, hence, \( p_z \) increase markedly as \( \lambda_0 \) increases, and, when \( \lambda_0 = 0.073 \), the gel point occurs only at complete reaction.

The present predictions of the gel point and its variation with ring-forming parameter for \( \rho = 1 \) are compared in Figure 14 with those given by ARS theory for \( RA_4 + R'B_2 \) polymerizations.\(^{22,24}\) Here, \( \alpha_i = \alpha_c \cdot \alpha_c \) is plotted versus \( \lambda_0 \) for reaction mixtures with \( r_z = 1 \). \( \alpha_c = \lambda_{0a} \) and \( \alpha_c = \lambda_{0b} \) are the extents of reaction of A and B groups at gelation in the absence of intramolecular reaction. According to Flory–Stockmayer theory, \( \alpha_c = 1/3 \) and \( p'_{ac} = p'_{bc} = 3^{1/2} \) for \( RA_4 + R'B_2 \) polymerizations with \( r_z = 1 \). It can be seen that, using the present predictions, significantly more ring structures are accounted for than when using ARS theory. This improvement can be attributed to the detailed consideration of the opportunities for intramolecular reaction depicted in Figures 9–12, rather than, as in ARS theory, just those predicted by linear sequences of branch units, such as those shown in Figure 7 and the continuing arms in Figures 9 and 12. Moreover, comparison with ARS interpretations\(^{22,24}\) of existing experimental data on the gel points of tetrafunctional polyurethane-forming reactions shows that the present predictions lie closer to the experimental gel points. Further interpretation of published experimental data using the present theoretical predictions will be the subject of future work. Meanwhile, the following paper presents the results of measurements of gel points in polymerizations involving POP diamines and DGEBA and the application of the present theoretical interpretation to the results obtained.

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