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Gel-gel reaction in RA_f and $RA_2 + RB_f$ polymerisations

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Summary

The amount of gel-gel reaction in RA_f and $RA_2 + RB_f$ random polymerisations is evaluated. For a given functionality f and stoichmetric amounts of reactants, half as much gel-gel reaction occurs in $RA_2 + RB_f$ polymerisations by complete reaction as in RA_f polymerisations. This difference is readily understandable in that the formation of a loop requirestwice as many pairs of groups to react in the former type of polymerisation as in the latter. Gel-gel reaction is necessary for the formation of the network structure at complete reaction. However, it also leads to network imperfections,viz. inelastic loops.

Introduction

Statistical derivations of the equations for the molecular distributions in the two types of polymerisation are given in classical works by Flory(1) and by Stockmayer(2). The statistics used assumes the random reaction of groups, with the exclusion of pre-gel intramolecular reaction and post-gel intramolecular reaction in the sol fraction. Gel-gel reaction must occur and is intramolecular. It is the mechanism by which a network structure is formed from the tree-like structure at the gel point. However, some of it will lead to inelastic loops.

It is now well-established, both experimentally and theoretically(3,4) and from computer simulations(5),that intramolecullar reaction between finite species can justifiably be excluded only in linear polycondensations in bulk. The present consideration of gel-gel reaction using the random reaction of groups refers to the limit of no spatial correlations between reacting groups, namely reactants of infinite molar mass or zero flexibility(4). In actual polymerisation, groups are spatially correlated and more intramolecular reaction will occur. Thus, the present, limiting treatment provides a basis for understanding the growth from tree-like structure to network. The treatment may be developed further to account for spatially-correlated reacting groups and structures occurring in real networks.

Dedicated to Prof. Walther Burchard on the occasion of his 60th birthday

RA_f Polymerisations

A polymerisation contains N_f monomers. At extent of reaction p, the number of x-mers in the sol is

$$N_{x,s} = N_f\omega'_x(1 - p)^2\beta^x \tag{1}$$

$$\omega'_x = \frac{f((f-1)x)!}{x!((f-2)x+2)!} \tag{2}$$

and

$$\beta = p(1-p)^{f-2} = p^*(1-p^*)^{f-2} \tag{3}$$

p^* denotes the lowest, real positive root of eqn(3). For the pre-gel regime, $p \leq p_c = 1/(f-1)$, $p = p^*$, and the whole polymerising mixture is sol.

The number of unreacted groups on x-mers in the sol(4)

$$\Gamma_{x,s} = (fx - 2x + 2)N_{xs} \tag{4}$$

and the total number of unreacted groups on sol molecules

$$\Gamma = \sum_1^\infty (fx - 2x + 2)N_{xs} \tag{5}$$

Evaluation of the summation gives(4)

$$\Gamma_s = fN_f(1-p).\frac{(1-p)}{p}.\frac{p^*}{(1-p^*)} \tag{6}$$

At extent of reaction p, the total number of unreacted groups is

$$\Gamma = fN_f(1-p) \tag{7}$$

and the number on the gel

$$\Gamma_g = \Gamma - \Gamma_s \tag{8}$$

The fractions of unreacted groups on sol and gel are

$$\gamma_s = \frac{(1-p)}{p}.\frac{p^*}{(1-p^*)} \tag{9}$$

and

$$\gamma_g = 1 - \gamma_s \tag{10}$$

Given random reaction, γ_g is the probability that a randomly chosen unreacted group is on the gel.

The progress of the polymerisation may formally be represented as the integral

$$\Gamma_p = \int_o^p \frac{fN_f}{2} dp \qquad (11)$$

where Γ_p is the number of **pairs** of groups which have reacted by extent of reacion p. Accordingly, the reaction of pairs of goups can be divided into sol-sol, sol-gel and gel-gel reaction with

$$\Gamma_p = \int_0^p \frac{fN_f}{2} (\gamma_s^2 + 2\gamma_s\gamma_g + \gamma_g^2) dp \qquad (12)$$

(The version of eqn(12) given in ref(4) erroneouusly contains a factor (1 - p)). Division of Γ_p by $fN_f/2$ give the fraction of bonds formed up to p. The fraction which results from gel-gel reaction

$$\gamma_{gg} = \int_o^p \gamma_g^2 dp \qquad (13)$$

where the lower limit may be replaced by 1/(f - 1) as $\gamma_g = 0$ for $p \leq 1(f - 1)$.

The terms in the integrand of eqn(12) represent the fractional rates of sol-sol reaction(γ_s^2), conversion of sol to gel ($2\gamma_s\gamma_g$), in which sol forms tree-like, pendant structures on the gel, and network growth (γ_g^2), through the formation of both elastic and inelastic loops.

$RA_2 + RB_f$ Polymerisations

The equations corresponding to eqn(6) for numbers of unreacted groups are(6)

$$\Gamma_{b,s} = fN_f \frac{(1 - \alpha)}{\alpha} \cdot \frac{\alpha}{(1 - \alpha^*)}^{*} (1 - p_b) \qquad (14)$$

$$\Gamma_{a,f,s} = fN_f \frac{(1 - \alpha)}{\alpha} \cdot \frac{\alpha^*}{(1 - \alpha^*)} p_b (1 - pa) \qquad (15)$$

and

$$\Gamma_{a,2} = 2N_2(1 - pa)^2 \qquad (16)$$

The polymerisation contains N_2 RA_2 monomers and N_f RB_f monnomers. $\Gamma_{b,s}$ is the number of unreacted B groups in the sol. $\Gamma_{a,f,s}$ is the number of unreacted A groups on molecules containing RB_f units. $\Gamma_{a,2}$ is the number of unreacted A groups on RA_2 monomers. p_a is the extent of reaction of A groups, p_b that of B groups and $\alpha = p_a p_b$. α^* is the lowest root of the equation

$$\beta = (1 - \alpha)^{f-2}\alpha \tag{17}$$

with $\alpha = \alpha^*$ for $\alpha \le \alpha_c = 1/(f - 1)$, when the whole polymerising mixture is sol.

Eqn(14) and (15) sum to give

$$\Gamma_{f,s} = fN_f(1 - \alpha)\left(\frac{1 - \alpha}{\alpha}\right)\cdot\frac{\alpha^*}{1 - \alpha^*} \tag{18}$$

corresponding to eqn(6) for RA_f polymerisations. Thus, the total number of unreacted groups on branched species, follows the same law as in RA_f polymerisations, provided α rather than a single extent of reaction is used as variable. Note that this simple scaling does not apply to the constituent expressons for $\Gamma_{b,s}$ and $\Gamma_{a,f,s}$.

The sum of eqn(15) and (16) gives the total number of unreacted A groups in the sol

$$\Gamma_a = 2N_2(1 - pa)\left(\left(\frac{1 - \alpha}{\alpha}\right)\cdot\frac{\alpha^*}{1 - \alpha^*}\, pa + (1 - pa)\right), \tag{19}$$

where use has been made of the equality of the number of A groups and number of B groups reacted ($2N_2pa = fN_fpb$). The fractions of unreacted A groups and B groups in the sol are

$$\gamma_{a,s} = \frac{1 - \alpha}{\alpha}\cdot\frac{\alpha^*}{1 - \alpha^*}\, pa + 1 - pa \tag{20}$$

and

$$\gamma_{b,s} = \frac{1 - \alpha}{\alpha}\cdot\frac{\alpha^*}{1 - \alpha^*} \tag{21}$$

For the gel

$$\gamma_{a,g} = 1 - \gamma_{a,s} \tag{22}$$

and

$$\gamma_{b,g} = 1 - \gamma_{b,s} \tag{23}$$

Dividing the progress of the polymerisation into sol-sol, sol-gel and gel-gel reactions, one has, corresponding to eqn(12),

$$\Gamma_p = \int_0^{pa} 2N_2(\gamma_{a,s}\cdot\gamma_{b,s} + \gamma_{a,s}\gamma_{b,g} + \gamma_{a,g}\gamma_{a,s} + \gamma_{a,g}\gamma_{b,g})dpa, \tag{24}$$

where the upper limit of the integration can extend to complete reaction of the A groups, viz. 1 for r(= $2N_2/fN_f$) $\leq$ 1 and 1/r for r > 1. Integration can also be with respect to pb(= rpa) when the upper limit can extend to r for r $\leq$ 1 and 1 for r > 1.

Corresponding to eqn(13), the fraction of bonds formed which have resulted from gel-gel reaction

$$\gamma_{gg} = \int_0^{pa} \gamma_{a,g}\gamma_{b,g} dpa \qquad (25).$$

Results

Fig 1 shows γ_g^2 versus p for the RA_3 polymerisation and $\gamma_{a,g}\gamma_{b,g}$ versus α for the RA_2+ RB_3 polymerisation at r = 1. It is clear that a simple scaling between the two cases from p to α does not apply.

The integrals of γ_g^2 and $\gamma_{a,g}\gamma_{b,g}$ up to the end of reaction ($\gamma_{gg,e}$) according to eqn(13) and (25) are given in table 1 for

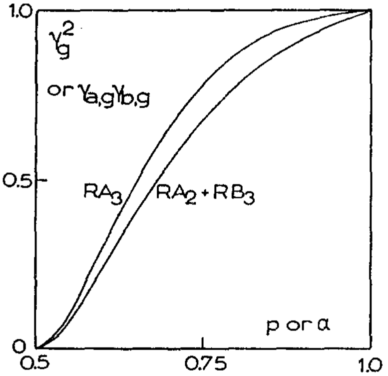

Fig 1. Instantaneous probabilities of gel-gel reaction in (1)RA_3 and (2)RA_2 + RB_3 polymerisations versus (1)p and (2)α.

	$\gamma_{gg,e}$	
f	RA_f	RA_2 + RB_f
3	1/3	1/6
4	1/2	1/4
5	6/10	3/10
10	8/10	4/10

Table 1. Fractions of gel-gel reaction (gel-gel bonds) formed from gel point to complete reaction ($\gamma_{gg,e}$) in RA_f polymerisations and RA_2 + RB_f polymerisations at r = 1.

various values of f. An interesting relationship is apparent in that the amounts of gel-gel reaction in the $RA_2 + RB_f$ polymerisations are just one half those in the corresponding RA_f polymerisations. This phenomenon is rationalised when one realises that to **complete** a loop (of any size) two branch branch points must be joined. In an RA_f polymerisation this occurs by the direct reaction of a pair of groups on two branch units. In an $RA_2 + RB_f$ polymerisation, two branch points are linked through an RA_2 unit requiring two pairs of groups to be reacted only one of which can be through gel-gel reaction.

The values in table 1 for the $RA_2 + RB_f$ polymerisations are larger than the extents of post-gel intramolecular reaction leading to inelastic loops in actual $RA_2 + RB_3$ and $RA_2 + RB_4$ polymerisations. From correlations of modulus and gel-point point measurements it has been deduced(4) that, of the bonds formed by complete reaction, about 10% have led to inelastic loops due to gel-gel reaction and sol-sol reaction in the post-gel regime. Thus, theory and experiment are broadly consistent. More detailed theoretical analyses, including spatial correlations, are required for interpretations of the data and defining the structures actually formed.

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