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# Formation, Structure and Properties of Polymer Networks: Gel-Point Prediction in Endlinking Polymerisations

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SUMMARY: Gel points, predicted using Ahmed-Rolfes-Stepto (ARS) theory and a Monte-Carlo (MC) simulation method accounting for intramolecular reaction, are compared with experimental data for polyester (PES)-, polyurethane (PU)- and poly(dimethyhl siloxane) (PDMS)-forming polymerisations. The PES and PU polymerisations were from stoichiometric reactions at different initial dilutions and the PDMS ones were from critical-ratio experiments at different dilutions of one reactant. The predictions use realistic chain statistics to define intramolecular reaction probabilities and employ no arbitrary parameters. Universal plots of excess reaction at gelation versus ring-forming parameter are devised to enable the experimental data and theoretical predictions to be compared critically. It is shown that various gel points can be predicted by MC simulations, depending on the criterion for gelation used. Due to the lengthy computations needed and the uncertainties in the predictions, MC simulation is not a viable approach. Although inconsistencies are noted in the measured gel points, so that a unified interpretation of the data cannot be achieved, ARS theory is shown to be the preferred basis for gel-point prediction. It is also concluded that, before one can be certain of agreement between experiment and predictions, more experimental systems at different initial dilutions and ratios of reactants need to be studied and the various methods used for detecting gel points need to be compared.

## Introduction – Interpretation and Prediction of Gel Points

Previous studies have analysed experimental gel points obtained from polymerisations carried out at various dilutions and ratios of reactants and, using gelation theories, deduced values of ring-forming parameters that explain the excess extents of reaction at gelation over those predicted by Flory-Stockmayer (F-S) theory.[1-6] For polyester- (PES-), polyurethane- (PU-) and poly(dimethyl siloxane) (PDMS)-forming polymerisations, the values of the parameters have been shown to vary systematically with reactant chain structures and molar masses. Such results are expected theoretically. For example, in stoichiometric $RA_2 + R'B_f$ polymerisations, gel points are predicted[1,4,7] to be dependent solely on the functionality ($f$) and the ring-forming parameter

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$$\lambda_{ab0} = \frac{P_{ab}}{(c_{a0} + c_{b0})/2} \ , \tag{1}$$

where $P_{ab}$ represents the mutual concentration of A and B groups at the ends of the shortest sub-chain that can react intramolecularly. The structure of this sub-chain, consisting of $\nu$ skeletal bonds, and of root-mean-square end-to-end distance $<r^2>^{1/2}$ is illustrated in Fig. 1. In detail,[1,4,7)]

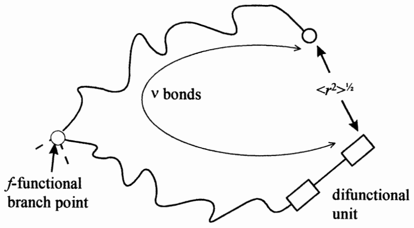

Fig. 1: Sub-chain forming a smallest loop structure illustrated with respect to an $RA_2+R'B_f$ polymerisation. The diagram shows the two arms of a star reactant, one arm having reacted with a difunctional monomer; the root-mean-square distance of the chain of $\nu$ bonds between the terminal groups is $<r^2>^{1/2}$.

$$P_{ab} = \frac{P(\underline{r} = \underline{0})}{N_{Av}} \ , \tag{2}$$

where $P(\underline{r} = \underline{0})$ is the probability-density of a zero end-to-end vector between reactive groups. If it is assumed that the end-to-end distance distribution can be represented by a Gaussian function, $P_{ab}$ is given by

$$P_{ab} = \frac{1}{N_{Av}} \left\{ \frac{3}{2\pi < r^2 >} \right\}^{3/2} . \tag{3}$$

$P_{ab}$ can be described as the mutual *internal concentration*, $c_{int}$, of a pair of reactive groups on the same molecule that can react intramolecularly to form the smallest loop. The concept is shown schematically in Fig. 2 for an A group, where the competition between intramolecular and intermolecular reaction with B groups is due to the (internal) concentration of B groups on the same molecule ($c_{b,int}$) relative to that of B groups on other molecules, the external concentration, $c_{b,ext}$. The external concentration will decrease automatically as a polymerisation proceeds but its initial value $c_{b0}$ will be characteristic of a given polymerisation. Further, $(c_{a0} + c_{b0})/2$ may be used to characterise external reaction with A and B groups in a nominally stoichiometric reaction mixture. Thus, the parameter $\lambda_{ab0}$ in equation (1) is a useful measure of the propensity of a system at a given ratio of reactants for intramolecular reaction. It captures the combined effects of reactant structure and reactive-group concentration on intramolecular reaction. A decrease in chain length or chain stiffness (i.e., a decrease in $\langle r^2 \rangle$) results in an increase in $P_{ab}$ and, hence, in the probability of intramolecular reaction and the formation of loop structures. Similarly, decreasing the concentration of reactive groups enhances the probability of intramolecular reaction.

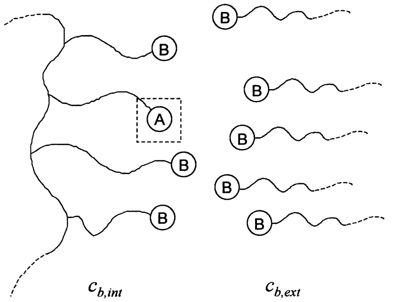

Fig. 2: Illustrating the concepts of internal and external concentrations of B-groups around a chosen A-group, leading, respectively, to intramolecular and intermolecular reaction.

The gel points for the PES- and PU-forming polymerisations mentioned previously were for stoichiometric mixtures reacting at various initial dilutions of reactive groups.$^{1-5)}$ The PDMS gel points were obtained$^{6)}$ using various fixed dilutions of one reactant and varying the amount of the second until gelation was just observed at complete reaction of the minority component; the so-called critical ratio method. The results have been interpreted using Ahmad-Rolfes-Stepto (ARS) theory$^{8)}$ for $\Sigma_i RA_{fai}$ + $\Sigma_i RB_{fbj}$ (i.e. $RA_{faw}$ + $RB_{fbw}$) polymerisations. For such polymerisations, the theory evaluates the probability of growth between statistically equivalent points $B^1$ and $B^2$, in the molecular structure shown in Fig. 3.

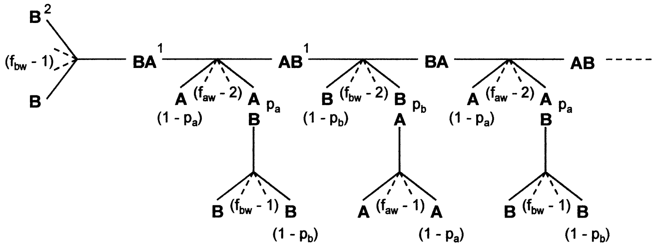

Fig. 3: Sequence of structural units used to define gelation in an $RA_{faw}$ + $RB_{fbw}$ polymerisation in ARS theory.$^{8)}$ Side chains up to two units long are considered. $p_a$ and $p_b$ are extents of reaction.

It is necessary to use the complex structure shown in order to define a reasonable approximation to the numerous opportunities for intramolecular reaction that exist. The resulting expression for the gel point, defining unit probability of growth from $B^1$ to $B^2$, is

$$r_a p_{ac}^2 (f_{aw}-1)(f_{bw}-1) = [1+(f_{aw}-2)\Phi(1,{}^3\!/_2)\lambda_{a0} + (f_{bw}-2)(f_{aw}-1)r_a\Phi(1,{}^3\!/_2)\lambda_{a0}p_{ac}]\cdot$$
$$[1+(f_{bw}-2)r_a\Phi(1,{}^3\!/_2)\lambda_{a0} + (f_{aw}-2)(f_{bw}-1)r_a\Phi(1,{}^3\!/_2)\lambda_{a0}p_{ac}], \quad (4)$$

where
$$r_a = \frac{c_{a0}}{c_{b0}} = \frac{p_b}{p_a}\ , \quad (5)$$

$$\lambda_{a0} = \frac{P_{ab}}{c_{a0}} = \lambda_{ab0} \text{ for } r_a = 1\ , \quad (6)$$

and
$$\Phi(1,{}^3\!/_2) = \left(\sum_1^\infty 1^i i^{-3/2}\right) = \sum_1^\infty i^{-3/2} = 2.612\ .$$

$p_{ac}$ and $p_{bc}$ are the overall extents of reaction of A and B groups at the gel point, $r_a$ is the initial molar ratio of A and B groups and $f_{aw}$ and $f_{bw}$ are the functionalities of the reactants. $\Phi(1,3/2)$ sums over one opportunity for forming each size of ring structure. The actual numbers of opportunities are accounted for by the various factors in $f_{aw}$ and $f_b$ in equation (4). When $\lambda_{a0} = 0$ the r.h.s. of equation (4) equals 1 and the F-S expression for the gel point is obtained.

Equation (4) is quadratic in both $p_{ac}$ and $\lambda_{a0}$ and may be arranged to solve analytically for either of these quantities.8) To *interpret* experimental gel points,1-6) equation (4) was solved for $\lambda_{a0}$ using the measured values of $p_{ac}$. The values of $\lambda_{a0}$ so obtained were then plotted versus $2/(c_{a0} + c_{b0})$, or another measure of dilution of the polymerisation, and $P_{ab}$ for the reactants evaluated from the slope of the linear plot, or the initial slope of the slightly curved plot so obtained. The value of $P_{ab}$ was then used with equation (3) to evaluate $<r^2>$, characteristic of the chain forming the smallest loop for the given reactants. As the $RA_2$ + $R'B_f$ polymersiations studied had only two reactants, the values of $<r^2>$ could then be interpreted simply according to Fig. 1 and the equation

$$<r^2> = vb^2\ , \quad (7)$$

where $v$ is the number of bonds and $b$ the effective bond length, a measure of chain stiffness. For the PES systems analysed, the values of $b$ were found to be broadly in agreement with those expected from solution properties and known characteristic ratios. For the PU systems, values of $b$ somewhat smaller than expected were found, indicating relatively more intramolecular reaction and a larger delay in gel point. Some of the PDMS systems gave values of $b$ larger than expected from the known value of $b$ for linear PDMS and some gave smaller values. Significantly, the values of $b$ for the PES and PU systems showed systematic variations with chain structure. They decreased with increases in the proportions, in the chains of $\nu$ bonds, of the more flexible units from the polyol arms.

The aim of the present paper is to reanalyse the PES, PU and PDMS results in a *predictive* rather than *interpretative* sense. Such an application of equation (4) was made by Stepto and Taylor[9)] using rotational-isomeric-state (RIS) statistics for the finite subchains forming the smallest loops and is also used in the Networks Module of the Polymer Software of Molecular Simulations Incorporated (MSI)[10)]. However, in the present work, universal plots of extents of reaction at gelation versus the ring-forming parameter $\lambda_{ab0}$ or $\lambda_{b0}$ (= $P_{ab}/c_{b0}$) will be used. Theoretically, for a given value of $r_a$ and functionalities of reactants, all gel points should lie on a single curve. The curves are derived using ARS theory and also a Monte-Carlo (MC) polymerisation algorithm developed by the authors[7,11-13)] linked with the use of various gel-point criteria. For the experimental systems, the values of $\lambda_{ab0}$ or $\lambda_{b0}$ required are derived from the known values of $c_{a0}$ and $c_{b0}$ of the reactions, together with the known values of $\nu$ and values of $b$ calculated *more rigorously* than hitherto. By considering gel points from eighteen systems covering two values of functionality and wide ranges of reactant molar masses, chain structures, dilutions and ratios, it is possible to look critically at the predictive capabilities of the ARS theory and MC simulations and also to comment on the consistency of experimentally determined gel points.

## Experimental Systems and Gel Points

The pairs of reactants used, together with their values of $\nu$, deduced from their molar masses, and values of $b$ are given in Table 1. The improved evaluations of $b$ were made using the RIS Metropolis Monte-Carlo (RMMC) software of MSI.[10)] The calculations for the more complex PES and PU chain structures, comprising two polyol arms and a difunctional residue, were based on detailed RIS modelling of the atactic polyoxypropylene chain,[14,15)] linked with RMMC analysis of the *complete*, branched structures of the polyols.[16)]

The PES experiments used stoichiometric mixtures reacting at 60 °C in bulk and various dilutions in diglyme.[1,2,4,5)] The PU experiments used stoichiometric mixtures reacting at 80 °C in bulk and various dilutions in nitrobenzene.[1-5)] The PDMS experiments used reactions at

25 °C in bulk and various dilutions in inert, linear PDMS. 3- and 4-functional DMS endlinkers ($RA_f$) with reactive –H groups were reacted with linear PDMS fractions with vinyl

Table 1: Experimental systems and their values of $\nu$, $\langle r^2 \rangle$ and $b$, characterising the chains forming the smallest loops.

| System | Reactants* | $\nu$ | $\langle r^2 \rangle$/nm$^2$ | $b$/nm |
|---|---|---|---|---|
| | | | | |
| Polyesters ($f$ = 3) | | | | |
| PES 1 | Adipoyl chloride + LHT240 | 37 | 3.68 | 0.315 |
| PES 2 | Sebacoyl chloride + LHT240 | 41 | 4.39 | 0.327 |
| PES 3 | Adipoyl chloride + LHT112 | 66 | 7.00 | 0.326 |
| PES 4 | Sebacoyl chloride + LHT112 | 70 | 7.52 | 0.328 |
| PES 5 | Adipoyl chloride + LG56 | 129 | 13.67 | 0.325 |
| PES 6 | Sebacoyl chloride + LG56 | 133 | 14.21 | 0.327 |
| | | | | |
| Polyurethanes ($f$ = 3,4) | | | | |
| PU 1 ($f$ = 3) | HDI + LHT240 | 33 | 3.72 | 0.337 |
| PU 2 ($f$ = 3) | HDI + LHT112 | 61 | 6.88 | 0.336 |
| PU 3 ($f$ = 4) | HDI + OPPE1 | 29 | 2.75 | 0.308 |
| PU 4 ($f$ = 4) | HDI + OPPE2 | 33 | 3.63 | 0.332 |
| PU 5 ($f$ = 4) | HDI + OPPE3 | 44 | 4.61 | 0.324 |
| PU 6 ($f$ = 4) | HDI + OPPE4 | 66 | 6.58 | 0.316 |
| | | | | |
| Poly(dimethyl siloxane)s ($f$ =3,4) | | | | |
| PDMS 1 ($f$ = 3) | A3 + 5k | 141 | 22.52 | 0.400 |
| PDMS 2 ($f$ = 4) | A4 + 5k | 141 | 22.52 | 0.400 |
| PDMS 3 ($f$ = 4) | A4 + 5k (short) | 141 | 22.52 | 0.400 |
| PDMS 4 ($f$ = 4) | A4 + 7k | 192 | 30.66 | 0.400 |
| PDMS 5 ($f$ = 4) | A4 + 11k | 315 | 50.31 | 0.400 |
| PDMS 6 ($f$ = 4) | A4 + 13k | 354 | 56.53 | 0.400 |

* LHT112, LHT240 and LG 56 are trifunctional polyoxypropylene (POP) triols; OPPE 1-4 are tetrafunctional POP tetrols; HDI is hexamethylene diisocyanate; A3 and A4 are trifunctional and tetrafunctional DMS –H functional endlinkers; 5k to 13k are vinyl terminated linear PDMS chains of molar masses 5 to 13 kg mol$^{-1}$, approximately; "short" denotes the use of a linear PDMS diluent low molar mass.

end groups ($R'B_2$).⁶⁾ At a given dilution of the $R'B_2$ reactant, the reactive-group ratio, $r_a$, was adjusted systematically, by increasing the initial concentration of the minority $RA_f$ endlinker until gelation was observed at complete reaction. The critical ratio, $r_{ac}$, for zero gel fraction at complete reaction was determined.

The experimental results for the stoichiometric PES and PU polymerisations are shown in Fig. 4, where $\alpha_{rc}$ is plotted versus the average initial dilution of reactive groups. $\alpha_{rc}$ is the excess of the product of the extents of reaction at gelation over the value predicted by F-S theory. That is,

$$\alpha_c = p_{ac} \cdot p_{bc} \tag{8}$$

$$\alpha_{rc} = \alpha_c - \alpha_c^o \tag{9}$$

$$\alpha_c^o = \frac{1}{f-1} \tag{10}$$

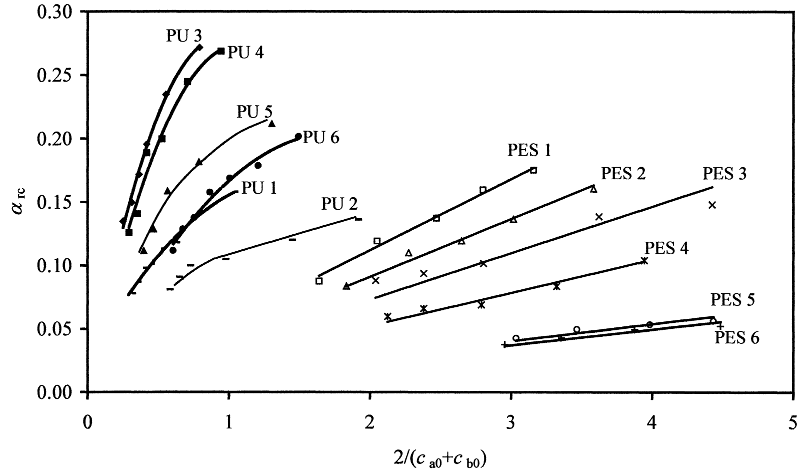

Fig. 4: Experimental gel points for stoichiometric PES $f = 3$, PU $f = 3$ (PU1,2) and PU $f = 4$ (PU3-6) polymerisations. $\alpha_{rc}$, the excess of the product of the extents of reaction at gelation as defined in equation (9), versus $2/(c_{a0} + c_{b0})$, the average initial dilution of reactive groups.

The results show the expected general trends. There are significant delays beyond the F-S gel point. For each group of systems (PES $f = 3$, PU $f = 3$ and PU $f = 4$), intramolecular reaction increases with dilution and decreases as $\nu$ increases. Also more intramolecular reaction occurs in the PU polymerisations for $f = 4$ than for $f = 3$. A higher functionality means more opportunities for intramolecular reaction. The PU systems undergo more intramolecular reaction than the PES systems. The reason for this difference is not understood, especially as Table 1 shows that for similar lengths of chain for $f = 3$ systems, the PES chains have smaller values of $b$ than the PU chains and should, therefore, have larger values of $P_{ab}$ and undergo more intramolecular reaction at a given dilution.

## ARS Modelling

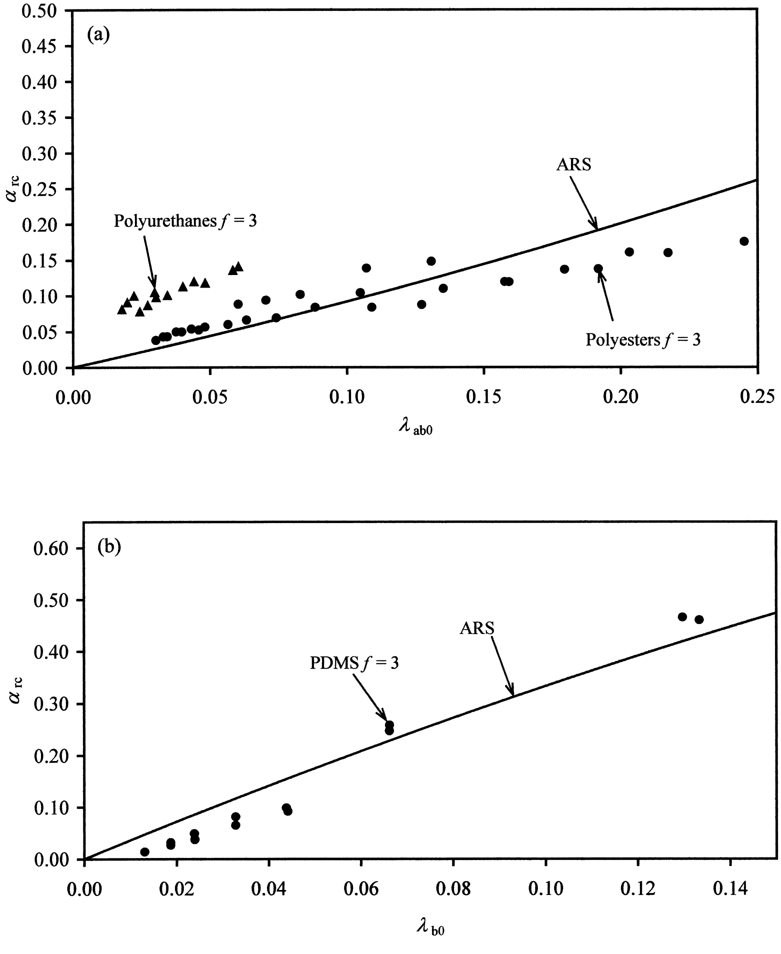

Fig. 5: Comparison of ARS theory and experiment for $f = 3$ systems. Universal representations of $\alpha_{rc}$ versus (a) $\lambda_{ab0}$ for PES and PU, $r_a = 1$ polymerisations and (b) $\lambda_{b0}$ for PDMS, $r_a < 1$ critical-ratio polymerisations.

The values of $<r^2>$ given in Table 1 were used to calculate, using equation (3), values of $P_{ab}$ for each of the reaction systems. For the PES and PU reactions at $r_a = 1$, the values of $P_{ab}$ and the initial dilutions of reactive groups were used in equation (6) to define values of $\lambda_{ab0}$ (= $\lambda_{a0}$) for the individual polymerisations studied. The experimental values of $\alpha_{rc}$ were then plotted versus $\lambda_{ab0}$. The results for the trifunctional systems are shown in Fig. 5(a), together with the theoretically predicted universal curve obtained by solving equation (4) for $p_{ac}$ in terms of $\lambda_{ab0}$ with $f_{aw} = 2$ and $f_{aw} = 3$ and using equations (5), (8) and (9) to evaluate $p_{bc}$, $\alpha_c$ and, finally, $\alpha_{rc}$.

Importantly, the use of $\lambda_{ab0}$ as a variable reduces the distinct plots in Fig. 4 for the individual PES and PU systems to essentially single curves. This reduction means that the combined effects of dilution, functionality ($f$), molar mass ($\nu$) and chain stiffness ($b$) are, in relative terms, correctly accounted for in $\lambda_{ab0}$. For the PES systems, good agreement with the predicted ARS universal behaviour is found, especially at the lower values of $\lambda_{ab0}$. For the PU systems, the measured values of $\alpha_{rc}$ are higher than predicted by ARS theory. This is a real difference between the results of the PES and PU systems that cannot be resolved without investigations into the possible effects of the detailed reaction mechanisms on the probabilities of intramolecular reaction. Other possible factors should have similar influences on both types of system. For example, nominally the same triols were used in the PU systems as in four of the PES systems so that any slight reduction in the functionality below the value of 3 should affect both types of system similarly. In addition, preliminary calculations16) evaluating $P(\underline{r} = \underline{0})$ directly, avoiding the Gaussian approximation of equation (3), show that the values of $P_{ab}$ for the PES and PU chains are affected approximately equally.

The experimental and theoretical results for the trifunctional PDMS system are compared in Fig. 5(b). For the non-stoichiometric polymerisations used with gelation at complete reaction of the minority A group on the $RA_f$ reactant, $\alpha_{rc}$ was evaluated using the relationships

$$p_{ac} = 1; \; p_{bc} = r_{ac} \tag{11}$$

$$\alpha_c = p_{ac} \cdot p_{bc} = r_{ac} \tag{12}$$

$$\alpha_{rc} = r_{ac} - \alpha_c^o \tag{13}$$

with $\alpha_c^o$ given by equation (10). The reactions were carried out at fixed values of $c_{b0}$ of the $R'B_2$ reactant. Hence, $\lambda_{b0}$ is the natural ring-forming parameter to use. To derive the predicted values of $\alpha_c$ (= $r_{ac}$), equation (4) was used with $r_a \cdot p_{ac}^2 = r_{ac}$, $\lambda_{a0} = \lambda_{b0} / r_{ac}$, $r_a \cdot \lambda_{a0} \cdot p_{ac} = \lambda_{b0}$ and $r_a \cdot \lambda_{a0} = \lambda_{b0}$. Fig. 5(b) shows that there is good agreement between ARS theory and experiment for the trifunctional PDMS system.

The results for the tetrafunctional PU and PDMS systems are shown in Figs. 6(a) and 6(b). The results for the PU systems from Fig. 3 again normalise to essentially a single curve and again it lies above the universal curve predicted by ARS theory. The results for the PDMS systems split into two, with the values of $\alpha_{rc}$ for the linear PDMS chains of higher molar mass (11k and 13k) lying above the curve predicted by ARS theory and those for the chains of lower molar mass (5k and 7k) lying generally below, but in reasonable agreement with the theoretical curve. No effect of the molar mass of the PDMS diluent was apparent. The splitting of the results into two branches could indicate a reduced accessibility of the reactive groups of the higher molar mass PDMS chains for intermolecular reaction.

## MC Modelling

The MC polymerisation algorithm developed[7,11-13)] uses Flory-Stockmayer (FS) random-reaction statistics coupled with intramolecular reaction allowed on a correctly weighted basis. It can be used to simulate, $RA_f$ self-polymerisations and $RA_{fa}$ + $R'B_{fb}$ polymerisations. It follows the formation of *all* of the connections and counts *all* of the ring structures as a function of extents of reaction. It also enables polymerisations and network structures to be simulated *efficiently* up to *complete* reaction. The same ring-forming parameters $P_{ab}$, $\lambda_{ab0}$ and $\lambda_{b0}$ are used as in the ARS modelling. Thus, direct comparisons of the results from the two approaches can be made.

The MC simulations were carried out using total initial populations of 12,000 reactive groups. This size of population has been shown to provide reproducible results for extents of intramolecular reaction and distributions of loop sizes.[7,11-13)] Because all connecting paths between reactant units are monitored during a polymerisation, the maximum population possible is 40,000, giving 16,000,000 array elements, the maximum allowed by the compiler. For 12,000 reactive groups, simulations of complete polymerisations took between 12 and 20 hours on a Silicon Graphics O2 R10000 Workstation, depending on the value of the ring-forming parameter. Time increased as the cube of the population of reactive groups. Such long computing times are typical for MC simulations of gelling polymerizations.[17-19)]

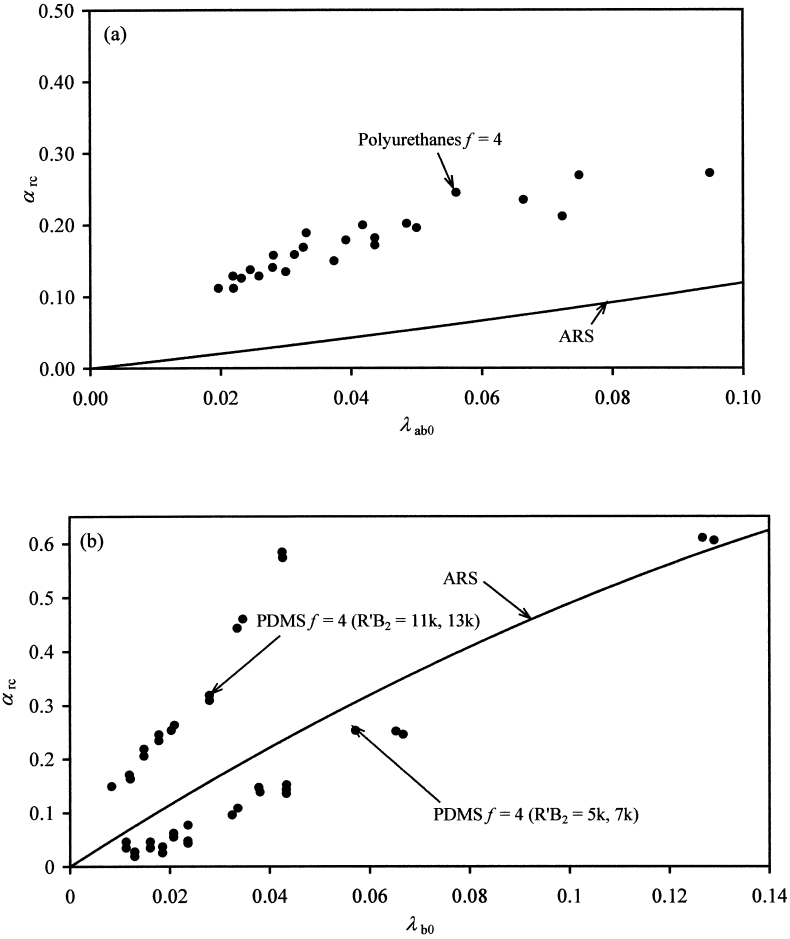

Fig. 6: Comparison of ARS theory and experiment for $f = 4$ systems. Universal representations of $\alpha_{rc}$ versus (a) $\lambda_{ab0}$ for PU, $r_a = 1$ polymerisations and (b) $\lambda_{b0}$ for PDMS, $r_a < 1$ critical-ratio polymerisations.

Because finite populations of reactive groups are used, approximate conditions need to be employed to define the gel point. Two conditions, introduced by Lee and Eichinger,$^{17)}$ are the extent of reaction ($p$) at which the reduced weight-average degree of polymerisation ($x_{w,r}$) reaches a maximum and the extent of reaction at which $dx_w/dp$ is a maximum. $x_{w,r}$ is the weight-average degree of polymerisation evaluated over all species except the largest. According to Lee and Eichinger, the true gel point will lie between the two estimates. The conditions of maxima in $x_{w,r}$ and $dx_w/dp$ may be termed ***whole-system gel-point criteria.*** To these may be added the extent of reaction at the maximum in $x_{n,r}$, the reduced number-average degree of polymerisation. Examples of the detection of gel points using $x_{w,r}$ and $dx_w/dp$ for stoichiometric $RA_2$ + $R'B_4$ polymerisations are given in Figs. 7(a) and 7(b). It can be seen that $x_{w,r}$ does have a clearly defined maximum that become less sharp as $\lambda$ increases. The value of $p_c$ in the Flory-Stockmayer simulation ($\lambda = 0$, sol-sol intramolecular reaction excluded and gel-gel intramolecular reaction random) is 0.560 less than the expected value of $1/\sqrt{3} = 0.577$.

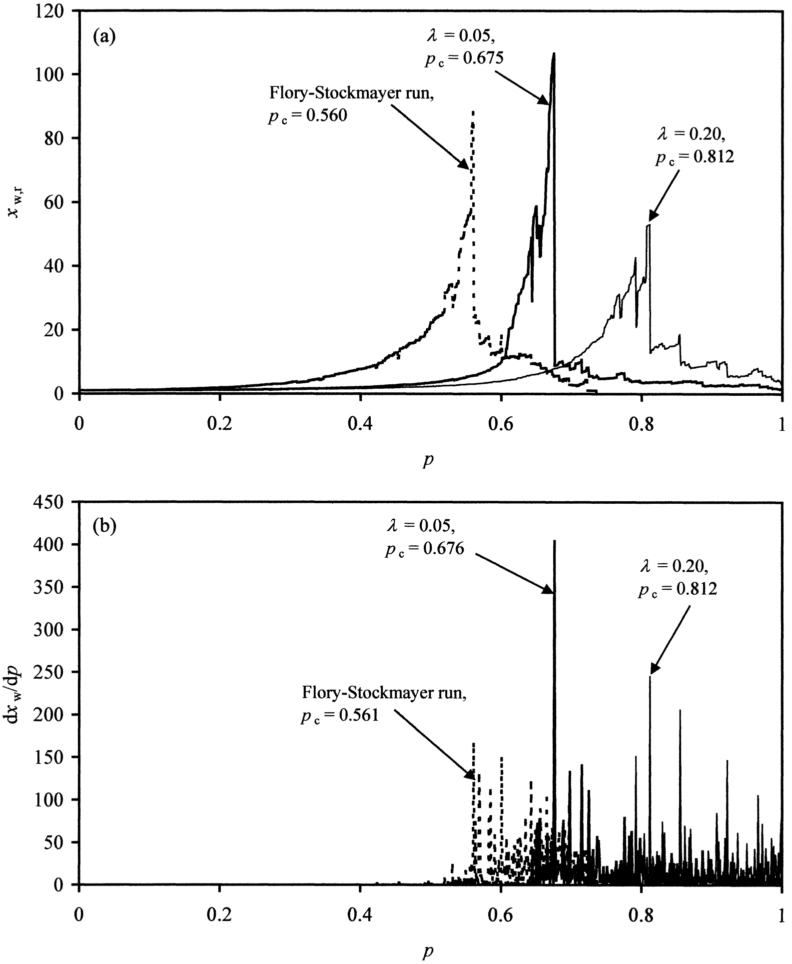

Fig. 7: Detection of gel points in stoichiometric $RA_2$ + $R'B_4$ polymerisations; (a) $x_{w,r}$ versus $p$ and (b) $dx_w/dp$ versus $p$. The values of $\lambda$ (= $\lambda_{ab0}$) used and the extents of reaction at gelation $p_c$ (= $p_{ac} = p_{bc}$) determined are indicated.

The detection of the maximum in $dx_w/dp$ is less certain because of the greater numerical errors in evaluating a gradient.

Values of $\alpha_{rc}$ for stoichiometric $RA_2 + R'B_4$ polymerisations, calculated using the maxima in $x_{w,r}$, $dx_w/dp$ and $x_{n,r}$, are plotted in Fig. 8 versus $\lambda_{ab0}$. Use of the mean of the values of the extent of reaction predicted by the maxima in $x_{w,r}$ and $dx_w/dp$ was proposed by Lee and Eichinger[17)]. The curves drawn are through values of $\alpha_{rc}$ averaged over six simulations at each value of $\lambda_{ab0}$ used. The maximum-to-minimum error bars are shown. There are significant uncertainties in and significant differences between the gel points predicted by the individual criteria. In addition the curves do not pass through $\alpha_{rc} = 0$ at $\lambda_{ab0} = 0$, as they should.

Use of the whole-system criteria to model the gel points of the $f = 3$ systems is shown in Figs. 9(a) and 9(b). For the stoichiometric polymerisations in Fig. 9(a), the MC curves, unlike the ARS curve, seem to give better predictions of the PU results than the PES results. The PU $f =$ 4 systems (not shown in the present paper) are best modelled by the $dx_w/dp$ criterion. The results in Fig. 9(b) show that the whole-system criteria do not work for the non-stoichiometric PDMS polymerisations. It is clear that the use of such criteria with finite populations does not allow a well-defined gel point to be predicted. To obtain good accuracy, long computations

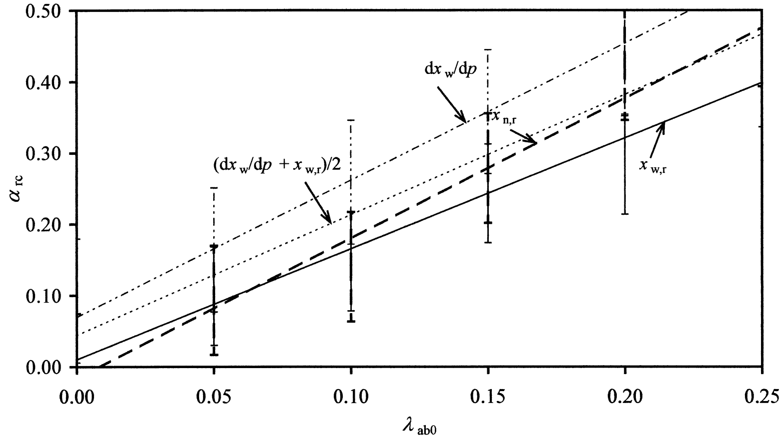

Fig. 8: $\alpha_{rc}$ versus $\lambda_{ab0}$ for stoichiometric $RA_2 + R'B_4$ polymerisations predicted by whole-system criteria. The curves are the averages of six simulations at each value of $\lambda_{ab0}$ used. Maximum-to-minimum error bars are shown. $(dx_w/dp + x_{w,r})/2$ denotes the mean of the values of the extent of reaction predicted by the maxima in $x_{w,r}$ and $dx_w/dp$.

are generally required and if *all* connections are recorded, as in the present algorithm, there is a compiler limitation that is computationally difficult to overcome. Also, it is not advisable to use the condition of connectivity throughout a finite population as condition for connectivity for an infinite population without investigating the effects of size of population. It should be noted that a MC approach is needed if an investigation of molecular growth in the critical, gel-point regime is the aim. However, there are no clear advantages to gained over the use of an analytical approach, such as the ARS theory, for gel-point prediction.

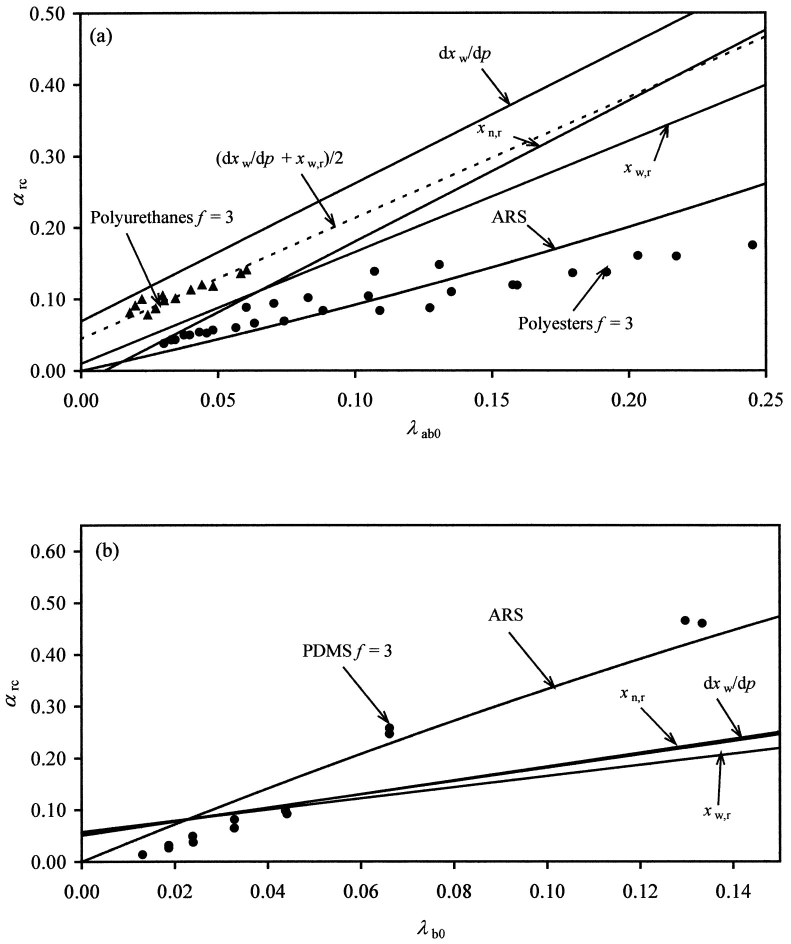

Fig. 9: Comparison of experimental gel points with predictions using MC simulations and whole-system gel-point criteria and ARS theory for $f = 3$ systems. $\alpha_{rc}$ versus (a) $\lambda_{ab0}$ for PES and PU, $r_a = 1$ polymerisations and (b) $\lambda_{b0}$ for PDMS, $r_a < 1$ critical-ratio polymerisations.

As stated, MC simulations of the size reported can be used[7,11-13)] to calculate accurately the populations of loop structures forming during polymerisations. Because only finite structures are being enumerated, numerical uncertainties are greatly reduced over those of gel points when whole-system criteria are used. Similarly, it is possible to define *extent-of-reaction criteria* for gel points that are also subject to much less numerical uncertainty. Thus, we may propose in an $RA_2 + R'B_f$ polymerisation that

$$\alpha_{inter} = p_{a,inter} \cdot p_{b,inter} = 1/(f-1) \tag{14}$$

defines gelation, where "inter" means "leading to intermolecular growth". $p_{a,inter}$ and $p_{b,inter}$ cannot be defined rigorously using finite structures, but approximations can be proposed. For example, for either A or B groups,

$$p_{inter} = p_{total} - p_{intra} , \tag{15}$$

where

$$p_{intra} = \sum_{i=1}^{\infty} p_{r,i} , \tag{16}$$

with $p_{total}$ the overall extent of reaction, $p_{intra}$ the extent of intramolecular reaction and $p_{r,i}$ the extent of reaction forming an *i*-meric loop structure. Another approximation is

$$p_{inter} = p_{total} - 2\, p_{r,1} , \tag{17}$$

limiting wasted reaction to the formation of smallest loops and recognising that two pairs of groups need to react to form such loops in $RA_2 + RB'_f$ polymerisations. The predictions of some selected extent-of-reaction criteria are shown in Figs. 10(a) and 10(b), along with the trifunctional experimental data and ARS predictions. In this case, all the criteria give curves that pass through the origin. However, it can be seen that there is again a wide spread of predictions that can be made. Also, some of the criteria can be applied only over limited ranges of $\lambda_{ab0}$ or $\lambda_{b0}$. To empirically model gel points, in the sense of choosing a gel-point criterion to fit a given system, extent-of-reaction criteria are preferable to whole-system criteria.

## Summary and Conclusions

The gel point is neither an easy quantity to measure nor to model and, by analysing experimental and theoretical gel points in terms of universal plots, it has been possible to highlight inconsistencies and uncertainties in the experimental determinations of gel points and in theoretical predictions. Both ARS theory and the MC simulations attempt to provide absolute predictions of the gel point, with their ring-forming parameters established independently from the conformational behaviour of reactant subchains. ARS theory performs well for the PES systems and the PDMS systems of lower molar mass. The relatively larger amounts of intramolecular reaction for the PU systems and the PDMS systems of higher molar mass would seem to indicate special effects, such as groups being inaccessible for intermolecular reaction in the PDMS systems or, for the PU systems, side reactions or a bias towards intramolecular reaction due to the complex reaction mechanism.

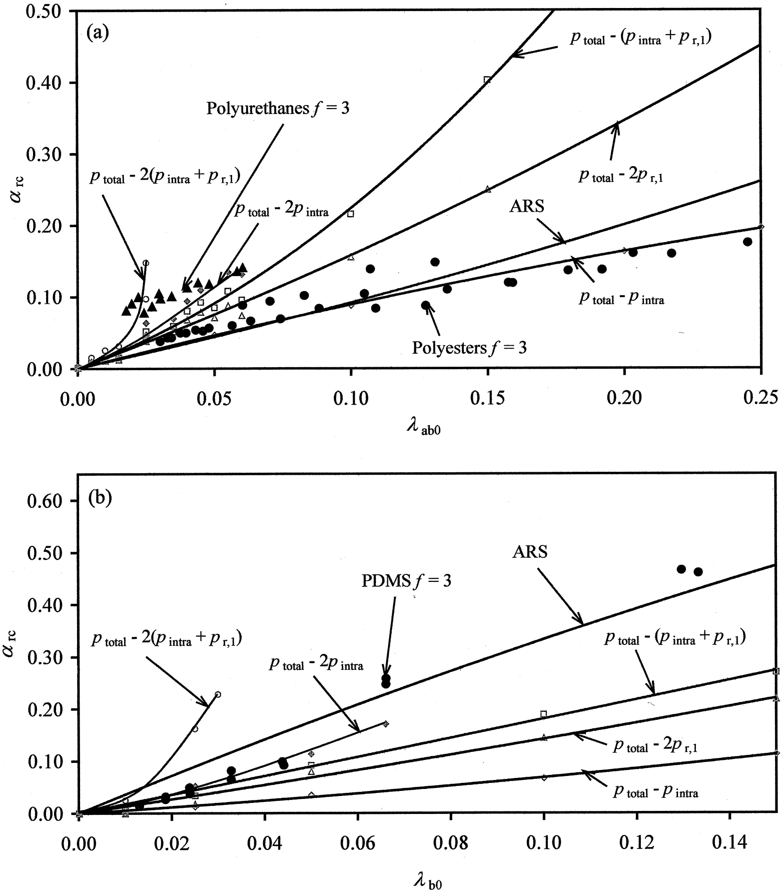

Fig. 10: Comparison of experimental gel points with predictions using (i) MC simulations and extent-of-reaction gel-point criteria and (ii) ARS theory for $f = 3$ systems. $\alpha_{rc}$ versus (a) $\lambda_{ab0}$ for PES and PU, $r_a = 1$ polymerisations and (b) $\lambda_{b0}$ for PDMS, $r_a < 1$ critical-ratio polymerisations.

The uncertainties in predicting gel points using a MC approach have been highlighted. Given these uncertainties and the long computational times needed, MC simulations are not a viable approach to gel-point prediction. ARS theory is more viable. Moreover, it can be further improved by using a more complex growth structure than that shown in Fig. 3 and improvements to the assumption of Gaussian statistics for the ring-forming subchains could be made. It is also possible to generalise the theory to include induced or intrinsic unequal reactivities of like functional groups.

Regarding the experimental gel points considered, it should be recalled that these were obtained using two different methods; the onset of the Weissenberg effect in a stirred reaction flask (PES and PU systems) and the measurement of gel fraction (PDMS systems). Although the differences between ARS theory and experiment do not depend on which method was used, the experimental methods do need to be examined critically and compared with the modulus self-similarity criterion of Winter and Chambon.20) Overall, the present comparison of theory and experiment has highlighted the fact that the measurement of gel points is not fully understood. The methods used need to be reviewed critically and the gel points of even more systems as functions of dilution and ratios of reactants need to be studied. The shortcomings of MC simulations for gel-point predictions are clearly shown and the ARS theory, or some development of it, would appear to be the best way forward, subject to experimental uncertainties being resolved.

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