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The gel point and network formation – theory and experiment

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Summary

Gel points, accounting for intramolecular reaction, are predicted using Ahmed-Rolfes-Stepto (ARS) theory. They are compared with experimental gel points for polyester (PES)-forming, polyurethane (PU)-forming and poly(dimethylsiloxane) (PDMS) polymerisations. The PES and PU polymerisations were from stoichiometric reaction mixtures at different initial dilutions and the PDMS ones were from critical-ratio experiments at different fixed dilutions of one reactant. The ARS 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. Significant deviations between experiment and theory are found for the PU systems and the PDMS systems with higher molar-mass reactants. However, ARS theory fits well the results for the PES systems and the PDMS systems having lower molar-mass reactants. Possible reasons for these differences in behaviour are discussed in terms of the PU-forming reaction mechanism and the effects of entanglements in PDMS. Whilst ARS theory provides a good basis for gel-point predictions and can be applied to many types of polymerisation, more experimental systems at different initial dilutions and ratios of reactants still need to be studied and the various methods used for detecting gel points still need to be compared to enable a definitive assessment of its performance to be made.

Introduction

The present paper summarises and combines the results of previous papers [1-6] on gel-point prediction directly from formation conditions and reactant structures accounting for intramolecular reaction. Gelation results from a wide range of reaction

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systems, forming polyesters (PESs), polyurethanes (PUs) and poly(dimethylsiloxane)s (PDMSs), are interpreted using a universal approach based on Ahmed-Rolfes-Stepto (ARS) theory [7]. For a given system, the comparison of experimental and theoretical gel points at various dilutions of preparation enables the effective values of the ring-forming parameter, P_{ab}, to be evaluated. These effective values are compared with those expected from reactant structures and deviations discussed in terms of the ability of ARS theory to provide *ab initio* gel-point predictions and also possible special effects features of the poymerisations studied.

It perhaps should be mentioned that the experimental and theoretical gel points are interpreted in terms of deviations from Flory-Stockmayer (F-S) random-reaction statistics due to intramolecular reaction. The theory does not purport to account for the detailed molecular growth in the critical percolation regime, where all reaction groups are not equally accessible over the timescale of a polymerisation [8,9]. However, it will be seen that any effects of percolation on the observed gel points cannot explain the wide differences in agreement between the predictions of ARS theory and the experimental results for the various polymerisation systems.

Interpretation and Prediction of Gel Points – Ahmed-Rolfes-Stepto (ARS) Theory

It has been shown [10] that the accurate, direct Monte-Carlo modelling of gel points is not possible for finite populations of reactive groups. The best approach is to use a statistical theory that accounts reasonably completely for the ring structures that form during a polymerisation and can be applied to a wide range of polymerisations. To date, the statistical theory that accounts most completely for intramolecular reaction is ARS theory [7].

In its most general form, ARS theory treats polymerisations of mixtures of reactants bearing A groups and B groups, *i.e.* $RA_{faw} + R'B_{fbw}$ polymerisations, where f_{aw} and f_{bw} are the mass(weight)-average functionalities, defined originally by Stockmayer [11]. 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 Figure 1. Ring structures of all sizes are accounted for.

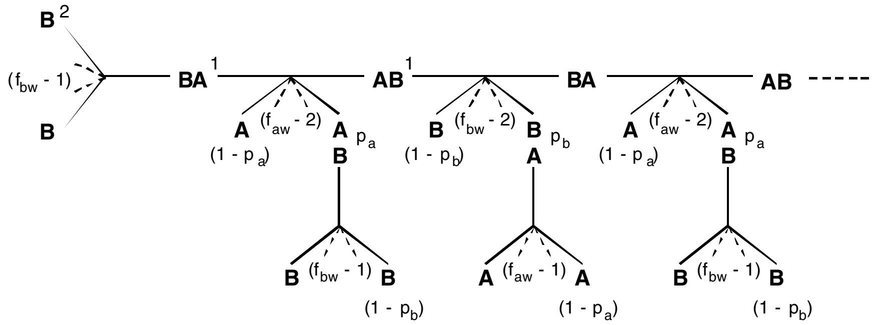

Figure 1. Sequence of structural units used to define gelation in an $RA_{faw} + R'B_{fbw}$ polymerisation in ARS theory [7]. Side chains up to two units long are considered. p_a and p_b are extents of reaction.

The resulting expression for the gel point, defining unit probability of growth from B^1 to B^2, is

$$r_\mathrm{a} p_\mathrm{ac}^2 (f_\mathrm{aw}-1)(f_\mathrm{bw}-1) = [1+(f_\mathrm{aw}-2)\Phi(1,\tfrac{3}{2})\lambda_\mathrm{a0} + (f_\mathrm{bw}-2)(f_\mathrm{aw}-1) r_\mathrm{a} \Phi(1,\tfrac{3}{2})\lambda_\mathrm{a0} p_\mathrm{ac}] \cdot \\ [1+(f_\mathrm{bw}-2) r_\mathrm{a} \Phi(1,\tfrac{3}{2})\lambda_\mathrm{a0} + (f_\mathrm{aw}-2)(f_\mathrm{bw}-1) r_\mathrm{a} \Phi(1,\tfrac{3}{2})\lambda_\mathrm{a0} p_\mathrm{ac}] \quad \mathbf{(1)}$$

where

$$r_\mathrm{a} = \frac{c_\mathrm{a0}}{c_\mathrm{b0}} = \frac{p_\mathrm{b}}{p_\mathrm{a}} \quad \mathbf{(2)}$$

$$\lambda_\mathrm{a0} = \frac{P_\mathrm{ab}}{c_\mathrm{a0}} \quad \mathbf{(3)}$$

and

$$\Phi(1,\tfrac{3}{2}) = \left(\sum_1^\infty 1^i i^{-\frac{3}{2}} \right) = \sum_1^\infty i^{-\frac{3}{2}} = 2.612 \quad \mathbf{(4)}$$

p_ac and p_bc are the extents of reaction of A and B groups at the gel point and r_a is the initial molar ratio of A and B groups. λ_a0 is a ring-forming parameter, with c_a0 the initial concentration of A groups and 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 ν skeletal bonds, and of root-mean-square end-to-end distance $<r^2>^{½}$, is illustrated in Fig. 2. In detail [1, 4, 12],

$$P_\mathrm{ab} = \frac{P(\underline{r}=\underline{0})}{N_\mathrm{Av}} \quad \mathbf{(5)}$$

where $P(\underline{r}=\underline{0})$ is the probability-density of an end-to-end vector of magnitude equal to zero 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

$$P_\mathrm{ab} = \frac{1}{N_\mathrm{Av}} \left\{ \frac{3}{2\pi < r^2 >} \right\}^{3/2} \quad \mathbf{(6)}$$

and

$$<r^2> = \nu b^2 \quad \mathbf{(7)}$$

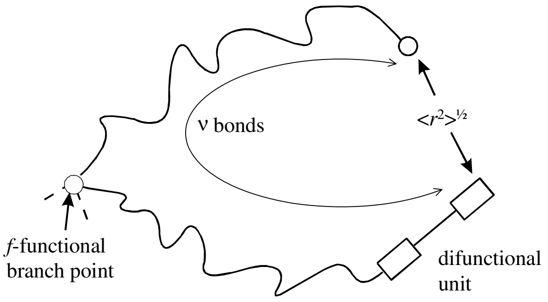

Figure 2. Sub-chain forming a smallest loop structure illustrated with respect to an RA_2+$R'B_f$ polymerisation. The diagram shows the two arms of a star reactant, one arm having reacted with a difunctional monomer; the root-mean-square end-to-end distance of the chain of ν bonds between the reactive terminal groups is $<r^2>^{½}$.

with b the effective bond length, a measure of chain stiffness. 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. Thus, the parameter λ_{a0} of Equation (3) 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 $<r^2>$) 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.

Returning to Equation (1), $\Phi(1,3/2)$ 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_{bw} in Equation (1). Finally, when $\lambda_{a0} = 0$, the r.h.s. of Equation (1) equals 1 and the F-S expression for the gel point is obtained.

Equation (1) is simple to apply. It is quadratic in both p_{ac} and λ_{a0} and may be arranged to solve analytically for either of these quantities [7]. To *interpret* experimental gel points, Equation (1) may be solved for λ_{a0} using the measured values of p_{ac}. The values of λ_{a0} so obtained may then plotted *versus* c_{a0}, 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} can then used with Equation (7) to evaluate $<r^2>$, characteristic of the chain forming the smallest loop for the given reactants, and the value can be compared with that expected from chain conformational calculations.

The principal aim of the present paper is the analysis of gel-point results in a *predictive* rather than *interpretative* manner (*cf.* [13]). Universal plots of extents of reaction at gelation versus the ring-forming parameter λ_{a0} will be used. Theoretically, according to ARS theory, for a given value of r_{a} and given functionalities of reactants, all extents of reaction at gelation should lie on a single curve. Experimentally, knowing the molar masses and the functionalities of the reactants, the values of λ_{a0} required may be derived from the values of c_{a0} of the reactions, together with the values of $<r^2>$ of the finite sub-chains forming the smallest loop structure (see Equations (3), (6) and (7)). In the present work, the values of $<r^2>$ have been calculated rigorously using rotational-isomeric-state (RIS) statistics and the RIS Metropolis Monte-Carlo (RMMC) software of Molecular Simulations Incorporated (now Accelrys) [14]. By considering gel points from eighteen PES, PU and PDMS systems covering two values of branch-point functionality and wide ranges of reactant molar masses, chain structures, dilutions and ratios, it is possible to look critically at the predictive capability of ARS theory and also to comment on the consistency of experimentally determined gel points across the systems.

Experimental Systems and Gel Points

The pairs of reactants used, together with their values of ν, deduced from their molar masses, and the calculated values of $<r^2>$ and effective bond length b are given in Table 1. As stated, the calculations were made using the RMMC software of MSI. The values of $<r^2>$ for the more complex PES and PU chain structures, comprising two polyoxypropylene polyol arms and a difunctional residue, were based on detailed RIS modelling of the atactic polyoxypropylene chain [15,16], linked with RMMC analysis of the *complete*, branched structures of the polyols [17].

Table 1. Experimental systems and their values of ν, $<r^2>$ and b characterising the chains forming the smallest loops.

System	Reactants*	ν	$<r^2>$/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(dimethylsiloxane)s (f =3,4)				
PDMS 1 (f = 3)	5k + B3	141	22.52	0.400
PDMS 2 (f = 4)	5k + B4	141	22.52	0.400
PDMS 3 (f = 4)	5k + B4 (short)	141	22.52	0.400
PDMS 4 (f = 4)	7k + B4	192	30.66	0.400
PDMS 5 (f = 4)	11k + B4	315	50.31	0.400
PDMS 6 (f = 4)	13k + B4	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; 5k to 13k are vinyl terminated linear PDMS chains of molar masses 5 to 13 kg mol^{-1}, approximately; B3 and B4 are trifunctional and tetrafunctional (R′B$_f$) DMS H-functional endlinkers; “short” denotes the use of a linear PDMS diluent low molar mass.

The PES experiments used stoichiometric mixtures reacting at 60 °C in bulk and various dilutions in diglyme [1, 2, 4].The PU experiments used stoichiometric mixtures reacting at 80 °C in bulk and various dilutions in nitrobenzene [1-5].The PDMS experiments [6] used reactions at 25 °C in bulk and various dilutions in inert, linear PDMS. 3-functional and 4-functional DMS endlinkers (R′B$_f$) with reactive H groups were reacted with linear PDMS fractions with vinyl end groups (RA$_2$). At a given dilution of the RA$_2$ reactant, the reactive-group ratio, r_a, was adjusted systematically, by increasing the initial concentration of the minority R′B$_f$ 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. 3, where α_{rc} is plotted versus the average initial dilution of reactive groups. α_{rc} is the excess of the product of the extents of reaction at gelation over the value predicted by F-S theory. That is,

$$\alpha_c = p_{ac} \cdot p_{bc} \qquad \mathbf{(8)}$$

$$\alpha_{rc} = \alpha_c - \alpha_c^o \qquad \mathbf{(9)}$$

$$\alpha_c^o = \frac{1}{f-1} \qquad \mathbf{(10)}$$

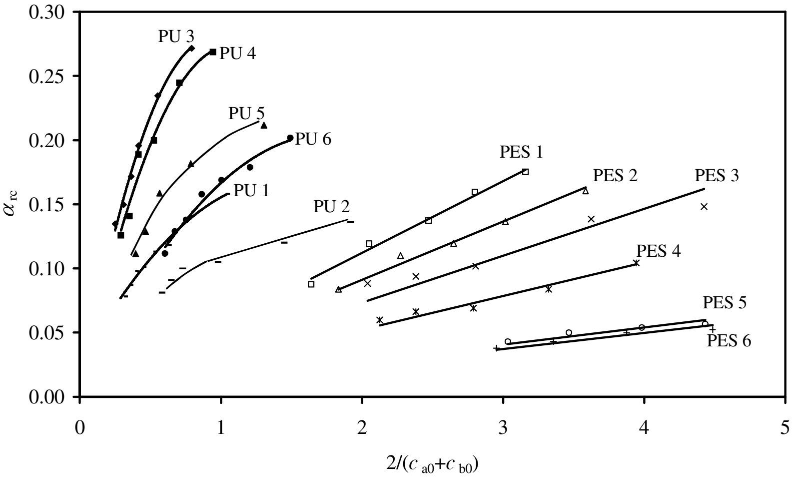

Figure 3. Experimental gel points for stoichiometric PES $f = 3$, PU $f = 3$ (PU1, 2) and PU $f = 4$ (PU3-6) polymerisations. α_{rc}, the excess of the product of the extents of reaction at gelation as defined in Equation (9), versus $2/(c_{a0} + c_{b0})$, the average initial dilution of reactive groups.

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 ν 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. This difference is seen more clearly in the next section on the basis of the universal ARS plots. The reason for it 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.

The experimental results for the PDMS systems are shown in the next section on the basis of universal ARS plots.

Universal Plots - ARS Modelling

To convert the experimental gel-point results into universal plots of α_{rc} versus λ_{a0} for given reactant functionalities and ratios of reactive groups, the values of λ_{a0} need to be calculated. The values of $<r^2>$ given in Table 1 were used to calculate, using Equation (6), 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 (3) to define values of λ_{a0} for the individual polymerisations studied. The experimental values of α_{rc} were then plotted versus λ_{a0}. The results for the trifunctional systems are shown in Fig. 4(a), together with the theoretically predicted universal curve, obtained by solving Equation (1) for p_{ac} in terms of λ_{a0} with $f_{aw} = 2$ and $f_{bw} = 3$ and using Equations (2), (9) and (10) to evaluate p_{bc}, α_c and, finally, α_{rc}. Significantly, the use of λ_{a0} as a variable reduces the distinct plots in Fig. 3 for the individual PES and PU systems to essentially single curves. This reduction means that

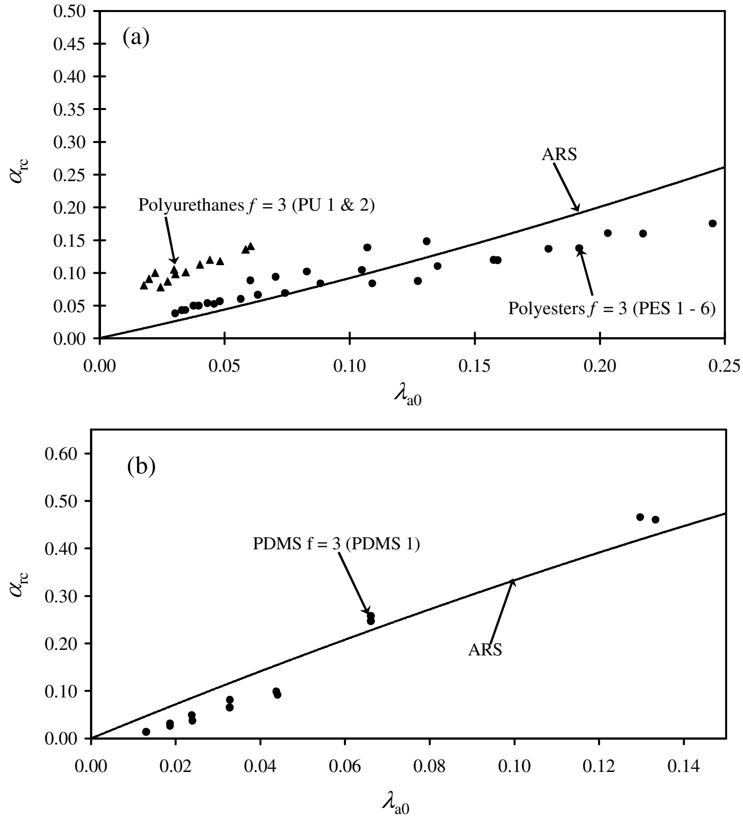

Figure 4. Comparison of ARS theory and experiment for $f = 3$ systems. Universal representations of α_{rc} versus λ_{a0} for (a) PES and PU, $r_a = 1$ polymerisations and (b) PDMS, $r_a > 1$ critical-ratio polymerisations.

the combined effects of dilution, functionality (f), molar mass (ν) and chain structure (b) are, in relative terms, correctly accounted for in λ_{a0}. For the PES systems, good agreement with the predicted ARS universal behaviour is found, especially at the lower values of λ_{a0}.

For the PU systems, the measured values of α_{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 (LHT240 and LHT112) so that any slight reduction in the functionality below the value of 3 should affect both types of system similarly. In addition, preliminary calculations [17] evaluating $P(\underline{r} = \underline{0})$ directly (Equation (5)), avoiding the Gaussian approximation of Equation (6), show that the values of P_{ab} for the PU and PES chains are affected approximately equally.

The experimental and theoretical results for the trifunctional PDMS system are compared in Fig. 4(b). For the non-stoichiometric polymerisations used with gelation at complete reaction of the minority B group on the R′B$_f$ reactant, the experimental values of α_{rc} were evaluated using the relationships

$$p_{bc} = 1 \quad p_{ac} = r_{ac}^{-1} \qquad \textbf{(11)}$$

$$\alpha_c = p_{ac} \cdot p_{bc} = r_{ac}^{-1} \qquad \textbf{(12)}$$

$$\alpha_{rc} = r_{ac}^{-1} - \alpha_c^o \qquad \textbf{(13)}$$

with α_c^o given by Equation (10). The reactions were carried out at fixed values of c_{a0} of the RA$_2$ reactant. Hence, λ_{a0} is still the natural ring-forming parameter to use for these non-stoichiometric polymerisations. To derive the predicted values of α_c (= r_{ac}^{-1}), Equation (1) was used with $r_a \cdot p_{ac}^2 = r_{ac}^{-1}$, and $p_{ac} = r_{ac}^{-1}$. Fig. 4(b) shows that there is good agreement between the universal ARS plot and experiment for the trifunctional PDMS system.

The results for the tetrafunctional PU and PDMS systems are shown in Figs. 5(a) and 5(b). Significantly, the results for the PU systems from Fig. 3 again normalise to

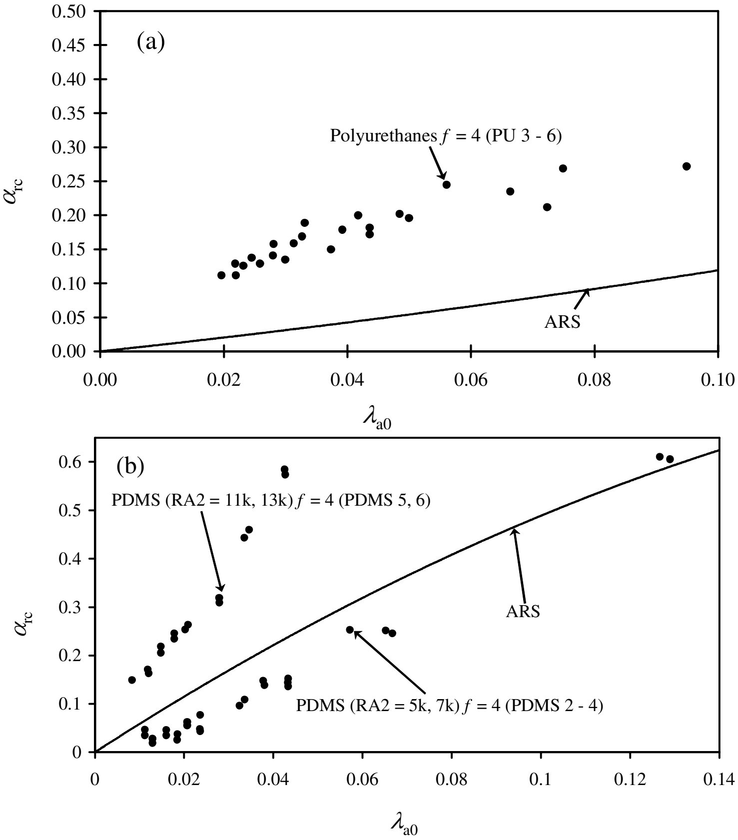

Figure 5. Comparison of ARS theory and experiment for f = 4 systems. Universal representations of α_{rc} versus λ_{a0} for (a) PU, r_a = 1 polymerisations and (b) PDMS, r_a > 1 critical-ratio polymerisations.

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 α_{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) generally lying below, but in reasonable agreement with the theoretical curve. Again, the points for the two groups of systems (PDMS 2-4 and PDMS 5,6) reduce to single curves. No effect of the molar mass of the PDMS diluent is apparent (PDMS 3). The splitting of the PDMS results into two branches seems to indicate a reduced accessibility of the reactive groups of the higher molar mass PDMS chains for intermolecular reaction.

Discussion and conclusions

The gel point is neither an easy quantity to measure nor to model and, by analysing experimental and theoretical gel points for several systems in terms of universal plots, it has been possible to highlight significant variations in the closeness of agreement between experiment and theory. ARS theory attempts to provide an absolute prediction of the gel point, with its ring-forming parameter established (independent of the polymerisation) from the conformational behaviour of reactant sub-chains. It performs well for the PES systems (Fig. 4(a)) and the $f = 3$ PDMS system and the $f = 4$ PDMS systems of lower molar mass (PDMS 2-4) (Figs. 4(b) and 5(b)). Also, as mentioned previously, the reduction of the results for the various systems in Fig. 3 to single curves for the PES and PU systems in Figs. 4(a) and 5(a), and the reduction of the results for systems PDMS 2-4 and PDMS 5,6 to single curves in Fig 5(b) show that the use of ARS theory and the single parameter λ_{a0} accounts well in relative terms for the combined effects of dilution (c_{a0}) and reactant functionalities (f), molar masses (v) and chain structures (b).

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. In this respect, it could be significant that the molar masses of the linear (RA_2) reactants of the higher molar-mass systems, PDMS 5,6 (≈11,000 and 13,000 g mol^{-1}) are approximately equal to the entanglement molar mass of 12,000 g mol^{-1} [18].

The unexpectedly high extents of reaction at gelation shown by the PU systems may be summarised in terms of the larger values of P_{ab} needed to fit the experimental results as plotted in Fig. 3 on the basis of the ARS expression (Equation (1)) compared with the values predicted from the independently-evaluated values of $<r^2>$ in Table 1. The comparison between the predicted and ARS-gel-point values of P_{ab} is made in Table 2, where it can be seen that the values of P_{ab} consistent with the experimental data are four to seven times larger than the predicted values. The corresponding comparison between fitted and predicted values of P_{ab} for the results for the PDMS systems of higher molar mass (PDMS 5, 6) in Fig. 5(b) shows similar relative values.

It does appear that experimentally determined gel points are extremely sensitive to what may be termed “non-random” effects that lead to excess intramolecular reaction. In the PU-forming polymerisations, the reaction mechanism probably causes a bias that favours intramolecular reaction. In the PDMS polymerisations using the higher molar-mass linear reactants, entanglements probably reduce the mutual accessibility of pairs of groups for intermolecular reaction. The PES-forming polymerisationa and the PDMS polymerisations using reactants below the entanglement threshold appear to show negligible "non-random" effects. ARS theory performs well for these systems and any effects of percolation phenomena on the extents of reaction at gelation are not seen. To improve the agreement between theory and experiment for such systems, the development of ARS theory, taking account of a more complex structure than that shown in Fig. 1 and improvements to the assumption of Gaussian statistics for the ring-forming sub-chains would seem to be the best way forward.

Table 2. Predicted and fitted values of P_{ab} characterising ring formation in the PU- forming polymerisations of Table 1. The predicted values were derived using Equation (7) and the values of $<r^2>$ given in Table 1. The fitted values are averages for each system, derived using the experimental extents of reaction at gelation in the ARS expression (Equation (1)) to evaluate λ_{a0} and, hence, P_{ab} from Equation (3) and the known value of c_{a0}.

System	Reactants	ν	P_{ab}/ mol l^{-1} predicted from $<r^2>$	P_{ab}/ mol l^{-1} gel-point fitting
PU 1 ($f = 3$)	HDI + LHT240	33	0.076	0.267
PU 2 ($f = 3$)	HDI + LHT112	61	0.030	0.150
PU 3 ($f = 4$)	HDI + OPPE1	29	0.120	0.409
PU 4 ($f = 4$)	HDI + OPPE2	33	0.079	0.337
PU 5 ($f = 4$)	HDI + OPPE3	44	0.033	0.228
PU 6 ($f = 4$)	HDI + OPPE4	66	0.032	0.153

Regarding the experimental gel points considered in this paper, 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 the predictions of 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 (see [19]). 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.

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