Comparison of Ahmad–Rolfes–Stepto theory, rate theory and Monte-Carlo modelling of gel point and network modulus*

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The predictions of Ahmad–Rolfes–Stepto (ARS) theory, rate theory and Monte-Carlo (MC) modelling of gel points and network moduli at complete reaction are tested against published data from polyurethane-forming polymerizations. Gel points are predicted most accurately by ARS theory and the MC software of Lee and Eichinger. Rate theory and Biosym MC software underestimate extents of intramolecular reaction at gel. Network defects (M_c/M_c^0) are underestimated by the Lee and Eichinger and Biosym MC software and no distinction between trifunctional ($f=3$) and tetrafunctional ($f=4$) networks is apparent. Rate theory also underestimates M_c/M_c^0 but shows a distinction between $f=3$ and $f=4$ networks. At present, the best approach for predicting M_c/M_c^0 is: (1) to use ARS theory (or Lee and Eichinger MC software) to predict the gel point; (2) find the effective rate theory ring-forming parameter (λ_{a0}) for that gel point; and (3) use rate theory and that value of λ_{a0} to determine M_c/M_c^0.

(Keywords: gel points; networks; modulus)

INTRODUCTION

The performance of recent theoretical developments in gelation and network formation which include intramolecular reaction are compared using previously published data from polyurethane-forming polymerizations[1,2]. The theoretical developments are the Ahmad–Rolfes–Stepto (ARS) theory of gelation[3], a development of the Ahmad–Stepto (AS) theory[4], the rate theory of polymerizations[5–10] and Biosym's Monte-Carlo (MC) software (Networks module, Biosym Technologies Inc., San Diego, CA) based on the MC simulation method of Eichinger and co-workers[11–16].

The data and the present work are part of a collaborative IUPAC programme studying the experimental behaviour and theoretical interpretation of the formation, structure and properties of model networks[17]. The data are from uncatalysed reactions of two polyoxypropylene (POP) star-triols and four POP star-tetrols of various molar masses reacting in stoichiometric amounts with hexamethylene diisocyanate (HDI) at 80°C in bulk and at various initial dilutions in nitrobenzene[1,2,18].

RING-FORMING PARAMETER

All theories and simulations of polymerization and network formation require the definition of an intramolecular (*internal*) concentration of reactive groups. For RA_2+RB_3 and RA_2+RB_4 polymerizations and the present theoretical approaches, the concentration may be written[3–10]:

$$P_{ab}=\left(\frac{3}{2\pi\langle r^2\rangle}\right)^{3/2}/N_{AV} \qquad (1)$$

where P_{ab} is the mutual, internal concentration (in $\mathrm{mol\,l^{-1}}$) of an A and a B group on the same molecule which could react to form the smallest ring structure. The linear sequence of skeletal bonds connecting the A and B groups is assumed to obey Gaussian statistics and has a mean-square end-to-end distance, $\langle r^2\rangle$, given by:

$$\langle r^2\rangle=\nu b^2 \qquad (2)$$

Here ν is the number of skeletal bonds in the sequence and b is their effective bond length. ν and b can in principle be calculated from the molar masses, chemical functionalities and chain structures of the reactants.

As polymerization proceeds, different numbers of opportunities exist for forming ring structures with ν, 2ν, $3\nu, \ldots, i\nu$ bonds. By making different approximations to the changing distributions of molecular species, various theoretical approaches yield different approximations to these numbers of opportunities and their competition with the opportunities for intermolecular reaction. At the start of a polymerization, the opportunities for intermolecular reaction for a given reactive group ratio, r ($=c_{a0}/c_{b0}$), may be represented as c_{a0} (or c_{b0}), the initial concentration of A (or B) groups, which may be considered *external* to any molecule. The decrease in external concentration as polymerization proceeds is again taken into account by the approximations of the different theories to the distribution of molecular species. The result is that a dimensionless, ring-forming parameter

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may be defined[3,4,7-10]:

$$\lambda_{a0} = P_{ab}/c_{a0} \tag{3}$$

with each theory predicting extents of reaction at gelation and network defects which are universal functions of λ_{a0}.

EXPERIMENTAL DATA AND VALUES OF P_{ab}

A summary of the polymerization systems studied experimentally is given in *Table 1*. The polyol functionalities (f) and the values of υ are listed. For the present systems, with star polyols, υ is the number of skeletal bonds in the linear chain consisting of two polylol arms and a HDI residue and terminated by a –OH and a –NCO group. M_c^0 is the molar mass of chains between junction points in the perfect network, again corresponding to chains consisting of two polyol arms and a HDI residue. (For schematic structures, see refs 1, 2 and 18.)

The values of $\langle r^2 \rangle$ were calculated using equation (2) with b taken from published values[19] of characteristic ratios of the polymethylene (PM) and POP chains. The PM chain was used to represent the HDI residue in the chain of υ bonds. If the HDI residue contributes υ_a (= 10) bonds and the POP residue υ_b ($=\upsilon-\upsilon_a$) bonds to the chain of υ bonds, then, assuming no interdependence between the conformational states of the PM and POP residues:

$$\langle r^2 \rangle = \upsilon b^2 = \upsilon_a b_a^2 + (\upsilon - \upsilon_a) b_b^2 \tag{4}$$

b_a and b_b, the effective bond lengths of the PM and POP residues, were put equal to their values for infinite chain length, namely 0.396 and 0.34 nm, respectively. The values of P_{ab} in *Table 1* were calculated using equation (1) and the tabulated values of $\langle r^2 \rangle$.

The data to be interpreted are summarized in *Figures 1* and *2*. *Figure 1* shows the extent of intramolecular reaction at gel ($p_{r,c}$) *versus* initial dilution of reactive groups $[(c_{a0}+c_{b0})^{-1}]$. The Flory–Stockmayer gel point corresponds to $p_{r,c}=0$ and, for stoichiometric reaction mixtures ($r=1$):

$$p_{r,c} = (p_{ac}p_{bc})^{1/2} - (f-1)^{-1/2} \tag{5}$$

with $p_{ac}=p_{bc}$ the overall extent of reaction at gel. The results in *Figure 1* show that $p_{r,c}$ increases with initial dilution of reactive groups. The point at the lowest value of $p_{r,c}$ for each polymerization system is from reaction in bulk, where the dilution of reactive groups by the inert parts of the reactant molecules results in 5–10% intramolecular reaction. In addition, as discussed previously[1,2,18], intramolecular reaction increases with functionality ($f=4$, systems 3–6, cf. $f=3$, systems 1 and 2) and with a decrease in υ or $\langle r^2 \rangle$ (systems 6→3 and systems 2→1). The increase with functionality occurs because for higher functionalities there are on average more groups per molecule which can undergo intramolecular reaction. The change with υ is that expected from equation (1).

Figure 2 shows network defects (M_c/M_c^0) *versus* initial dilution of reactive groups. M_c is the average molar mass between junction points in a network at complete

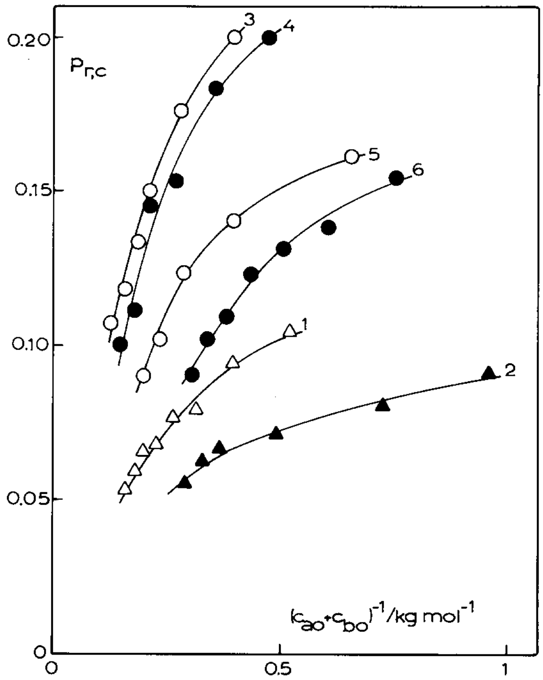

Figure 1 Experimental values[1,2] of the extent of intramolecular reaction at the gel point ($p_{r,c}$) *versus* initial dilution $[(c_{a0}+c_{b0})^{-1}]$ for polymerization systems 1–6 of *Table 1*

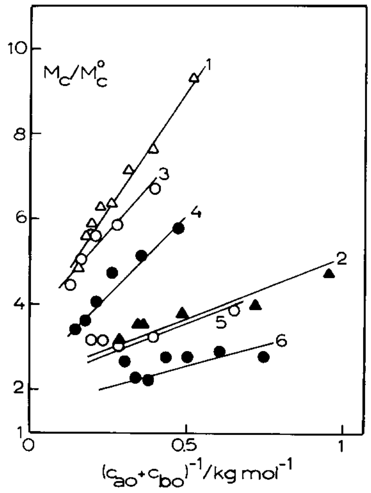

Figure 2 Experimental values[1,2] of network defects represented as M_c/M_c^0 (see text) *versus* initial dilution $[(c_{a0}+c_{b0})^{-1}]$ for polymerization systems 1–6 of *Table 1*

Table 1 Characteristics of the polymerization systems[1,2] and values of $\langle r^2 \rangle$ and P_{ab} used in the present calculations

System[a]	f[b]	υ[c]	M_c^0 (g mol^{-1})[d]	$\langle r^2 \rangle$ (nm^2)[e]	P_{ab} (mol l^{-1})[f]
1. HDI+LHT240	3	33	635	4.230	0.06297
2. HDI+LHT112	3	61	1168	7.471	0.02683
3. HDI+OPPE1	4	29	500	3.768	0.07490
4. HDI+OPPE2	4	33	586	4.230	0.06297
5. HDI+OPPE3	4	44	789	5.503	0.04244
6. HDI+OPPE4	4	66	1220	8.049	0.02399

[a] POP triols (LHT240 and LHT112) from the chain extension of 1,2,6-hexane triol. POP tetrols (OPPE1–4) from the chain extension of pentaerythritol. Stoichiometric polymerizations using each system were carried out at 80°C in bulk and at various initial dilutions in nitrobenzene. Gel points and moduli at complete reaction were measured

[b] Functionality of polyol

[c] Number of skeletal bonds in the chain capable of forming the smallest ring structure

[d] Molar mass of elastic chain in the perfect network

[e] Mean-square end-to-end distance of the chain of υ bonds

[f] Mutual, internal concentration of a pair of A and B groups consistent with $\langle r^2 \rangle$, according to equation (1)

reaction, as deduced from modulus measurements[1,2]. For dry networks, M_c/M_c^0 is equal to the factor by which the modulus of the actual network is reduced relative to that of the perfect network. For a given functionality, network defects increase as M_c^0 decreases (systems 6→3; systems 2→1). Also $f=3$ networks show more defects for similar values of M_c^0 (system 1 cf. system 4; system 2 cf. system 6). The general trends in the results are consistent[1,2,18] with loss of elastic chains being dominated by smallest ring structures. They are in contrast with delays in gel points, which depend on the total amount of intramolecular reaction, irrespective of the size of the ring structures formed. (See refs 1, 2 and 18 for detailed discussions.)

RESULTS OF THEORETICAL CALCULATIONS

The present calculations using ARS theory, rate theory and MC simulations were all performed using the values of $\langle r^2 \rangle$ listed in *Table 1*. In this way, it was possible to compare directly the relative performance of the three theoretical approaches. A detailed description of the present application of the Biosym MC software is published elsewhere[20].

Predictions of the gel points for systems 1 and 5 in comparison with the experimental data are shown respectively in *Figures 3a* and *b*. The earlier MC results of Lee and Eichinger[15,21] are also shown in *Figure 3b*. The behaviours depicted are typical of those for all the polymerization systems. The MC calculations of Lee and Eichinger (carried out for systems 5 and 6 only and effectively using different values of $\langle r^2 \rangle$) give good gel-point predictions. The present MC calculations for systems 1 to 6 using Biosym software underestimate $p_{r,c}$ and show more scatter. The rate theory, which counts only the smallest ring structures, seriously underestimates $p_{r,c}$. The ARS theory, which results[3] in a quadratic expression between p_{ac} and λ_{a0}, is the simplest to use and, overall, gives reasonable predictions of $p_{r,c}$. The underestimation of $p_{r,c}$ by ARS theory, apparent in *Figures 3a* and *b*, may well be attributable to the approximations used in evaluating $\langle r^2 \rangle$ (see later).

Figures 4a and *b* show the values of M_c/M_c^0 for systems 1 and 5 predicted by MC simulations and rate theory. The earlier MC results of Lee and Eichinger[15,21] for system 5 are also shown. Again, the behaviours depicted are typical of those for all the polymerization systems. The distinction between the calculations of Lee and Eichinger and those using the Biosym software, apparent in the gel-point predictions, is *not* apparent in the values of M_c/M_c^0. *Both* sets of MC simulations seriously underestimate M_c/M_c^0, as does rate theory.

DISCUSSION

MC simulations

The larger scatter in the gel-point results using the Biosym software, compared with those obtained by Lee and Eichinger[15,16] for systems 5 and 6 (see *Figure 3b*), indicates that larger populations of molecules are needed to obtain reproducible answers. It is estimated that in excess of 20000 molecules are required[20]. The smaller values of $p_{r,c}$ found, compared with those calculated by Lee and Eichinger, are probably attributable[20] to the more exact representation used by Lee and Eichinger of the rotational-isomeric-state conformational statistics, $\langle r^2 \rangle$, of the branched POP tetrol reactants of the particular molar masses used in systems 5 and 6.

The overall performance of the MC simulations can be seen in *Figure 5*, where M_c/M_c^0 is plotted *versus* $p_{r,c}$. The MC values of M_c/M_c^0 are uniformly too low and do not reflect the experimental differences between $f=3$ and $f=4$ networks. The better agreement of Lee and Eichinger's analysis of systems 5 and 6 with the experimental gel points is apparent (cf. *Figure 3b*), but very similar, low values of M_c/M_c^0 are predicted using both the Lee and Eichinger and the Biosym software,

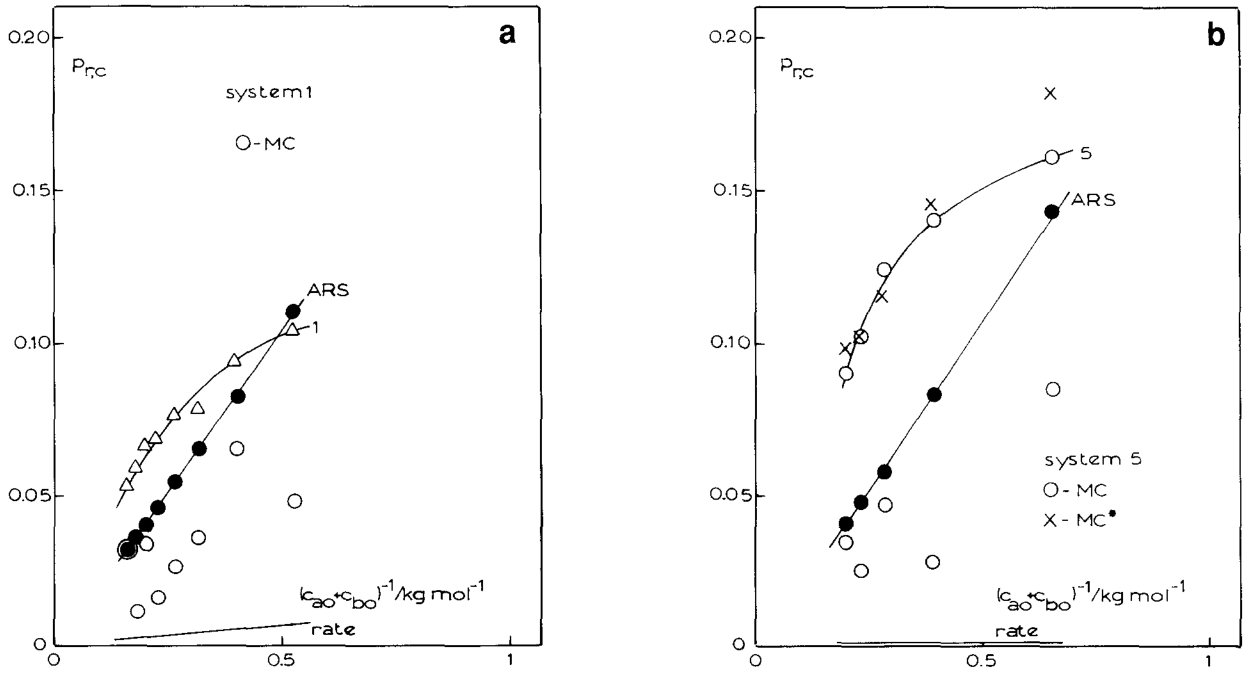

Figure 3 Experimental and calculated values of $p_{r,c}$ *versus* initial dilution $[(c_{a0}+c_{b0})^{-1}]$: (a) system 1; (b) system 5. (△, ○) Experimental data; (●) ARS theory; (——) rate theory; (○) MC, Biosym software; (×) MC*, Lee and Eichinger[15,21]

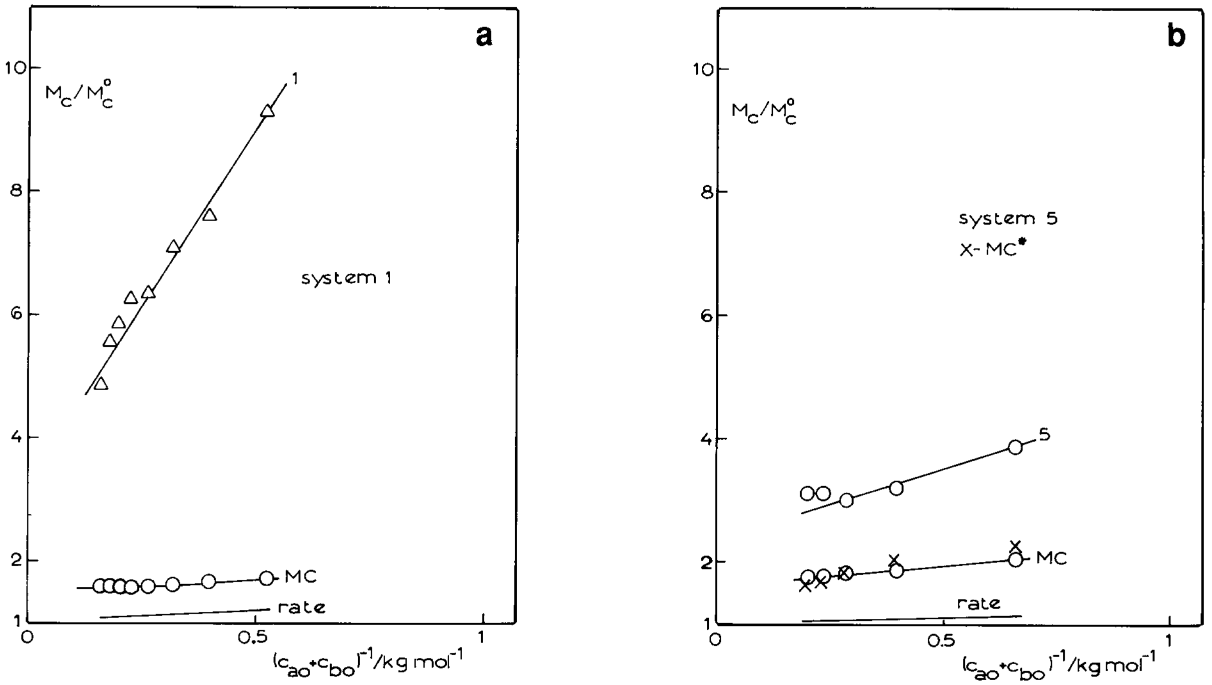

Figure 4 Experimental and calculated values of M_c/M_c^0 *versus* initial dilution $[(c_{a0}+c_{b0})^{-1}]$: (a) system 1; (b) system 5. Symbols as in *Figure 3*

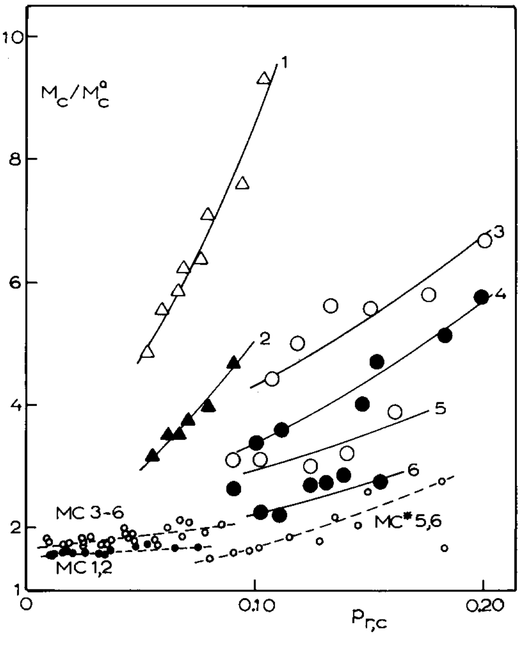

Figure 5 MC values of M_c/M_c^0 *versus* $p_{r,c}$ in comparison with the experimental values from *Figures 1* and *2*. (MC) Biosym software, systems 1–6; (MC*) Lee and Eichinger[15,21], systems 5 and 6

independent of junction-point functionality. There seems to be a serious undercounting of inelastic chains in both versions of the software.

ARS theory

The ARS theory[3] takes account of more ring structures than the AS theory[4]. Application of ARS theory[3] to gel-point data from polyester-forming polymerizations indicates that agreement with experimental gel points is given using more realistic values of P_{ab}, i.e. $\langle r^2 \rangle$, than those needed by AS theory. ARS theory is easy to apply, as the gel point is given by a quadratic relationship between λ_{a0} and p_{ac}, with numerical coefficients defined by reactant functionalities, reactive-group ratio and expressions for numbers of opportunities for intramolecular reaction to form ring structures of all sizes. It can also be used for general mixtures of reactants of different functionalities.

Comparison of *Figures 3a* and *b* shows that ARS theory predicted $p_{r,c}$ values better for the $f=3$ than for the $f=4$ systems. The underestimation of $p_{r,c}$ in both cases is in part probably due to the values of $\langle r^2 \rangle$ estimated for the polymerization systems (*Table 1*) being too large as they are based on effective bond lengths for infinite chains. The predictions are better than those using the Biosym MC software. Given the previous correlations with data from polyester-forming systems[3] and the present calculated values of $p_{r,c}$, ARS theory is obviously capable of predicting gel points with good accuracy. Realistic values of $\langle r^2 \rangle$, evaluated by separate calculation, are of course required to define P_{ab} and, hence, λ_{a0}. Such work is in progress.

Rate theory

Figures 3a and *b*, and *4a* and *b* show that the amount of intramolecular reaction is underestimated by rate theory. This is undoubtedly due to it allowing for only the smallest ring structures. However, as noted previously[10], rate theory does distinguish between $f=3$ and $f=4$ networks. In that work, experimental gel points of the present set of data were fitted using appropriate values of P_{ab}. The values were much larger than those in *Table 1*, consistent with the undercounting of opportunities for intramolecular reaction. If the gel points were fitted, reasonable predictions of M_c/M_c^0 could be made. The behaviour is illustrated in *Figure 6*, where experimental and rate theory results are plotted as M_c/M_c^0 *versus* $p_{r,c}$. Notice that the rate theory distinguishes between $f=3$ and $f=4$ systems, but a universal curve (for a given value of r) is predicted in each case. In order to reflect the experimental dependence on M_c^0 (or v), different sizes of ring structure would have to be counted. The gel point is delayed by all intramolecular reaction. In contrast, M_c/M_c^0 is affected only by inelastic loops. Such loops are principally the smallest ring structures[1,2,18], although larger ring structures can cause some loss in number of elastic chains. Thus, rate theory, which at present counts only the smallest ring structures, provides reasonable predictions of M_c/M_c^0 for *given* values of $p_{r,c}$.

For modelling purposes, one wishes to predict values of M_c/M_c^0 given the reactant structures and initial concentrations of reactive groups. If experimental gel points are available, they may be fitted using rate theory and the values of λ_{a0} required for this fitting can be used to predict values of M_c/M_c^0. Plots of M_c/M_c^0 *versus* initial dilution derived in this way are shown, together with the experimental data, in *Figures 7a* and *b*. Although $p_{r,c}$ and M_c/M_c^0 are universal functions of λ_{a0} for given values of r and f (*Figure 6*), the various polymerization systems show different dependences on $(c_{a0}+c_{b0})$, resulting from the different scaling between λ_{a0} and $(c_{a0}+c_{b0})^{-1}$ as P_{ab} changes [equation (3)]. The changes in calculated curves with M_c^0 (or υ) are not as large as those observed experimentally, probably reflecting the effects of different proportions of larger ring structures in the different polymerization systems.

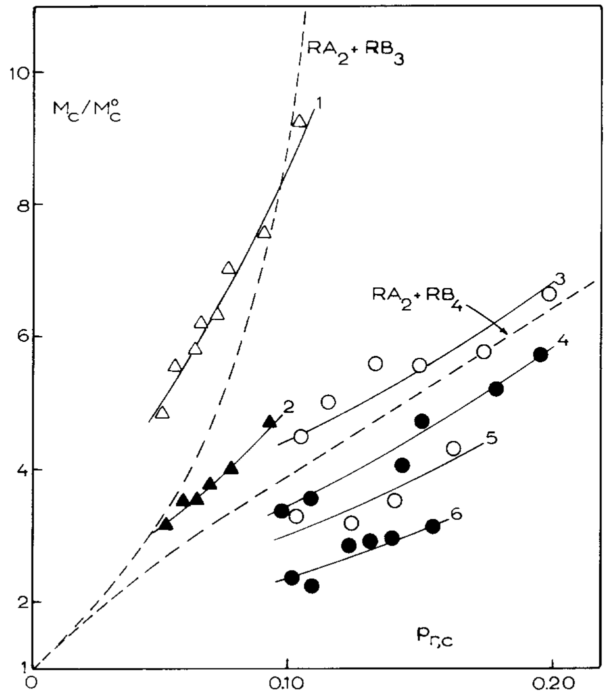

Figure 6 M_c/M_c^0 *versus* $p_{r,c}$ experimental values (curves 1–6) and rate theory values for RA_2+RB_3 and RA_2+RB_4 polymerizations (– – –)

In terms of modelling unknown polymerizations of the types RA_3, RA_4, RA_2+RB_3 and RA_2+RB_4, for which rate theory has so far been developed, the best results at present can be achieved by:

1. Using ARS theory (or the MC programs of Lee and Eichinger) to predict gel points with P_{ab} based on realistic chain statistics.
2. Fitting the predicted gel points using rate theory through the choice of new (larger) values of P_{ab}.
3. Using the gel-point, rate theory values of P_{ab} to predict values of M_c/M_c^0.

CONCLUSIONS

1. Reductions in modulus are underestimated by the MC method and no distinction between $f=3$ and $f=4$ networks is apparent. The way in which inelastic chains are counted needs investigation.
2. ARS theory[3], which only requires the solution of a quadratic equation, provides quicker and more accurate predictions of gel points than the Biosym MC software. Its accuracy is probably comparable to that of Lee and Eichinger's software, provided accurate values of $\langle r^2 \rangle$ are used. It can also be applied to a wide range of polymerization systems.
3. Presently, the best prediction of M_c/M_c^0 from reactant structures and reaction formulation can be achieved by using ARS theory (or Lee–Eichinger MC software) to predict the gel point, finding the value of λ_{a0} needed by rate theory consistent with that gel point and using that value of λ_{a0} and rate theory to calculate M_c/M_c^0. For polymerizations in bulk or concentrated solutions, Figures *7a* and *b* show that values of M_c/M_c^0 will probably be predicted to within an accuracy of 10–50%.

The application of rate theory to polymerizations of the general type $RA_{fa}+RB_{fb}$ is straightforward. Its development to count larger ring structures is underway[22]. Hence, more accurate predictions for a wider range of polymerization systems should soon be possible.

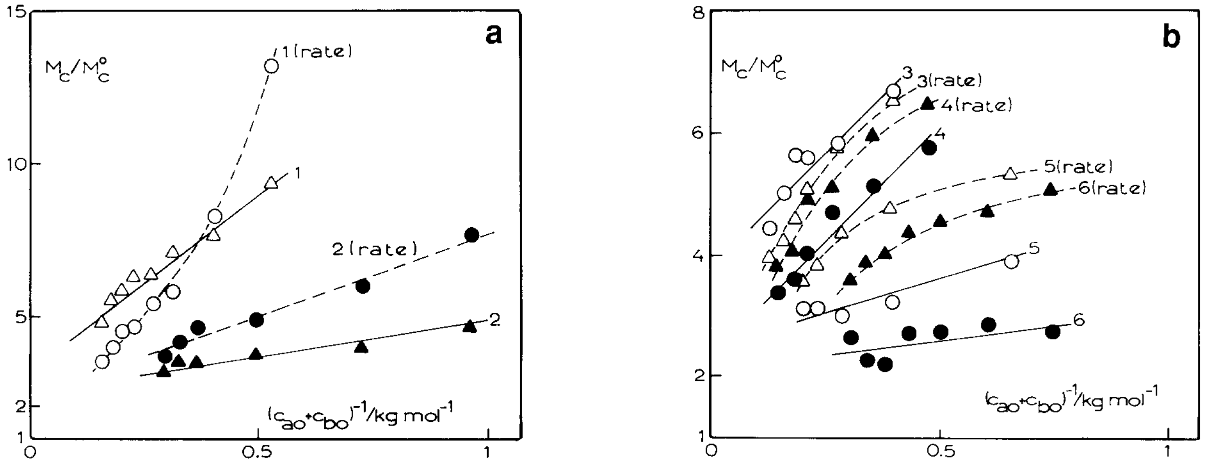

Figure 7 M_c/M_c^0 *versus* initial dilution $[(c_{a0}+c_{b0})^{-1}]$: (a) $f=3$, systems 1 and 2; (b) $f=4$, systems 3–6. (——) Experiment; (– – –) rate theory using values of λ_{a0} to fit experimental gel points (see ref. 10 for details)

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