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Formation, Structure and Properties of Polymer Networks: Theory and Modelling

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Summary: The application of a Monte-Carlo (MC) algorithm to account fully for loop formation in RA_2 + $R'B_3$ and RA_2 + $R'B_4$ polymerisations is described. The resulting interpretation of experimental elastic moduli of polyurethane networks prepared at different dilutions shows it is essential to account for elastic losses in loop structures of all sizes. An important parameter, x, is introduced, namely the average fractional loss of elasticity per larger loop structure relative to the loss per smallest loop structure. Values of x vary between 0.50 and 0.60, depending on junction point functionality, reactant or network chain stiffness and number of skeletal bonds per smallest loop structure. Application of the MC calculations to the formation and resulting structure of poly(dimethyl siloxane) networks again predicts significant reductions in modulus due to loop structures. However, comparison with experimental modulus data shows that the reductions in modulus due to loops are outweighed by increases due to chain entanglements.

Introduction

Relationships between concentrations of chains and junction points that assume perfect network structures are often used when interpreting elastic properties of endlinked networks[1]. The assumption is rarely true and deviations from perfect network structures may be due to topological entanglements and chain interactions[2-4], to side reactions, incomplete reaction in endlinking polymerisations (giving loose ends)[5,6] and, more fundamentally and generally, inelastic chain or loop formation due to the intramolecular reaction of pairs of groups[4,7]. Hence, to understand and predict elastomeric properties, it is important to be able to model, statistically, the molecular growth leading to network formation. Further, by considering RA_{fa} + $R'B_{fb}$ polymerisations at various dilutions of reactive groups, it is possible to evaluate the effects of loop formation resulting from intramolecular reaction.

Intramolecular Reaction

A useful measure of the propensity of a system at a given ratio of reactants for intramolecular reaction is λ_{a0}, where

$$\lambda_{a0} = P_{ab} / c_{a0} \qquad (1)$$

c_{a0} is the initial concentration of A-groups, representing the concentration of groups for intermolecular reaction, and P_{ab} characterises intramolecular reaction[7].

$$P_{ab} = (3/2\pi < r^2 >)^{3/2} / N_{Av}. \qquad (2)$$

It is the mutual concentration of A- and B-groups at the ends of the shortest sub-chain, of root-mean-square end-to-end distance $<r^2>^{1/2}$, that can react intramolecularly, assuming that the end-to-end distance distribution can be represented by a Gaussian function. The units of P_{ab} are moles per unit volume. It can be seen that, for a given ratio of reactive groups, λ_{a0} captures the combined effects of reactant structures and reactive-group concentrations on intramolecular reaction.

Monte-Carlo Polymerisation Algorithm

Theories to predict the modulus of a polymer network material must begin by constructing a realistic model of the network structure. Detailed characterisation of the connectivity, or topology, by experimental means is impossible. In order to investigate the effects of network topology on elastomeric properties one must use numerical simulations of the network-forming nonlinear polymerisations. In such simulations, it is important to account correctly for the formation of loop-structures of various sizes resulting from intramolecular reaction, correctly weighted according to their probabilities of formation. To these ends, a Monte-Carlo (MC) nonlinear polymerisation algorithm has been developed[8-10] to simulate self-polymerisations (RA_f), and two-monomer polymerisations of the general type RA_{fa} + $R'B_{fb}$. All the connections are recorded as a function of extent of reaction of A- or B-groups, along with the calculated sol and gel fractions, and average degrees of polymerisation. Ring-size distributions have been evaluated and have been found to be very broad[8-10].

Correlation of Model Network Topologies with Measured Network Moduli[8-10]

For a trifunctional network, each smallest loop structure renders three chains inelastic and larger loops are subject only to partial losses in elasticity. These considerations lead to the expression for the modulus, relative to that of the perfect network structure,

$$G^o / G = M_c / M_c^o = 1/(1 - 6p_{re,1} - x \cdot 6p_{re,i>1}), \tag{3}$$

where G^0 is the modulus of the (unswollen) perfect network, G is that of the actual network, M_c is the average molar mass of elastically active chains connecting pairs of junction points in the actual network and M_c^o is that in the perfect network. $p_{re,1}$ is the extent of reaction (at complete reaction) leading to smallest loops, and $p_{re,i>1}$ is the extent of reaction leading to larger loops. x is the fractional loss of elasticity for chains in loop structures larger than the smallest. A similar expression can be derived for tetrafunctional network structures. They lose only 2 elastic chains per smallest loop and

$$G^o / G = M_c / M_c^o = 1/(1 - 4p_{re,1} - x \cdot 4p_{re,i>1}). \tag{4}$$

Polyurethane Networks

In the absence of theoretical evaluations of entropy reductions in loop structures, estimates of x can be made using experimentally determined values of M_c / M_c^o. This has been done for polyurethane (PU) networks based on hexamethylene diisocyanate (HDI) reacting with polyoxypropylene (POP) triols and tetrols. The results, for six series of networks prepared in bulk and at various dilutions in solvent, are shown in Figure 1. The theoretical curves have been fitted by choosing least-squares values of the ring forming parameter, P_{ab} and x in conjunction with eqs 1 and 2. In this respect, it should be noted that, because $p_{re,1}$ and $p_{re>1}$ depend on λ_{a0}, which is directly proportional to P_{ab} (eq 1), M_c / M_c^o depends on P_{ab} as well as on x.

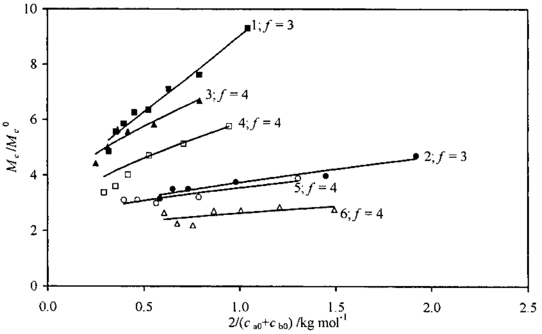


Figure 1. Experimental and calculated values of M_c / M_c^o at complete reaction as functions of the average initial dilution of reactive groups, $2/(c_{a0}+c_{b0})$, for six series of PU networks from stoichiometric reaction mixtures. 1,2: trifunctional networks from polyoxpropylene (POP) triols of different molar masses and hexamethylene diisocyanate (HDI). 3-6: tetrafunctional networks from POP tetrols and HDI.

The effect of assuming $x = 0$, no entropy reduction or elastic loss in ring structures larger than the smallest, is illustrated in Figure 2. It is impossible to account for experimental reductions in modulus with $x = 0$. Hence, joining the ends of the elastic subchains of networks together into ring structures always causes a reduction in entropy compared with that of the independent chains, whatever the size of the structure. It is expected that x will decrease as overall size of the ring structure increases. The value of x used here for each system is the average over all sizes of ring structure.

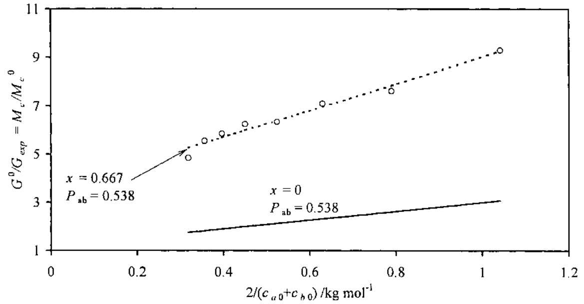


Figure 2. Illustrating the effect of assuming $x = 0$ using the results and calculations for system 1 of Figure 1. If $x = 0$ the reductions in modulus are greatly underestimated.

Poly(dimethyl siloxane) Networks

The values of x deduced for the six reaction systems of Figure 1 are plotted in Figure 3 versus P_{ab}. Because both chain entropy and P_{ab} are related directly to $<r^2>$, it is assumed that x versus P_{ab} is a universal function for given functionalities of reactants. Thus, the plots in Figure 3 can be used to predict reductions in modulus for networks formed from other stoichiometric $RA_2 + R'B_3$ and $RA_2 + R'B_4$ systems.

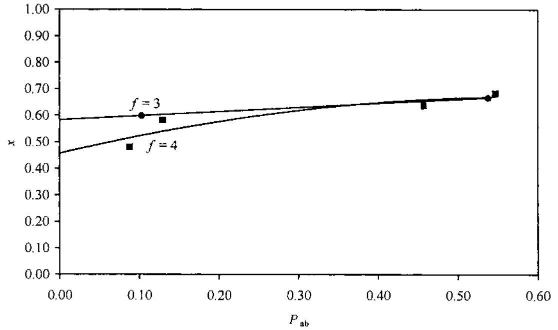


Figure 3. x versus P_{ab}, corresponding to the theoretical curves in Figure 1.

The present work now considers networks formed from linear PDMS chains of various molar masses using a trifunctional and a tetrafunctional endlinker. The systems chosen first have been used previously for a gel-point investigation[12]. From the known molar masses, endlinker functionality and chain statistics of a pair of reactants, P_{ab} can be calculated and the appropriate value of x found from Figure 3. Values of $p_{re,i}$ and $p_{re,i>1}$ are known as universal functions of λ_{a0}. Hence, curves of $G^o / G = M_c / M_c^o$ versus λ_{a0} can be constructed using eqs 3 and 4, as shown in Figure 4. It can be seen that the predicted reductions in modulus are large and must be accounted for when interpreting measured moduli. Significantly, the trifunctional and tetrafunctional systems give distinct curves. Amongst the tetrafunctional systems, there is little sensitivity to reactant molar masses or P_{ab}, showing that x does not vary much over the systems chosen.

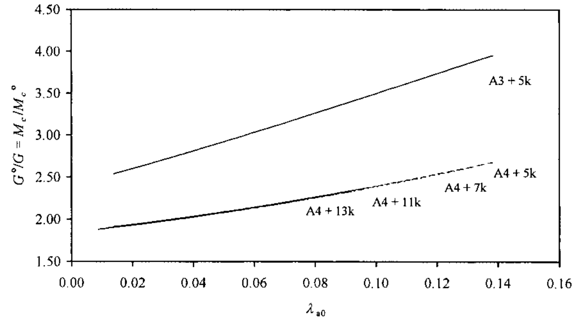


Figure 4. Predicted reductions in modulus as a function of ring-forming parameter λ_{a0}. Networks prepared from linear PDMS fractions 5k, 7k, 11k, 13k (of nominal molar masses 5000 g mol^{-1}, 7000 g mol^{-1}, 11000 g mol^{-1} and 13000 g mol^{-1}) reacting with a trifunctional endlinker (A3) and a tetrafunctional endlinker (A4). Details of the reactants are given in reference 12.

The present calculations can also be used to reconcile the measurements of Llorente and Mark[13] for the moduli of stoichiometric PDMS networks prepared at different volume fractions of diluent (D) with the occurrence of entanglements in PDMS melts as characterised, for example, by Fetters *et al.*[14]. Through eq 1 and knowledge of c_{a0}, the axis in λ_{a0} may be transformed to one in reactant molar mass, for polymerisations in bulk, or to one in dilution (c_{a0}^{-1}) for reactions diluted with solvent. For linear reactant RA_2 reacting with endlinker $R'B_f$ the equation is

$$\lambda_{a0} = \left(\frac{M_{A2}}{2} + \frac{M_{Bf}}{f}\right)\frac{P_{ab}}{\rho}\cdot\frac{1}{1-D} \qquad (5)$$

where ρ is the assumed uniform density of the reactants. Figures 5(a) and 5(b) show essentially constant values of M_c/M_c^o over a range of dilutions. As can be seen in Figure 6, the plots in Figure 4 also transform into nearly horizontal plots with D as

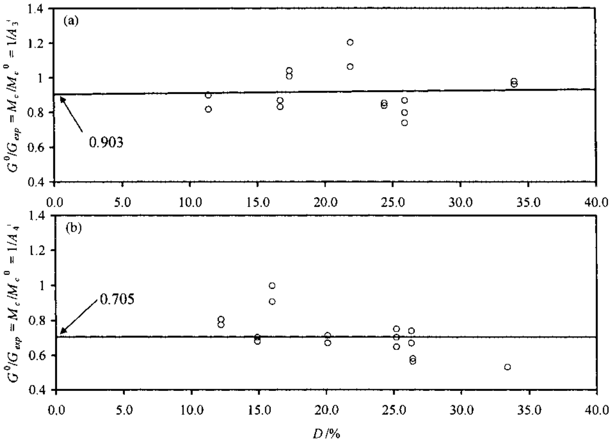


Figure 5. $G^o/G = M_c/M_c^o = 1/A'_f$ versus dilution of preparation (*D*) for PDMS networks from stoichiometric polymerisation using a siloxane diluent. Data of Llorente and Mark[13]. (a) $RA_2 + R'B_3$ and (b) $RA_2 + R'B_4$ polymerisations. For an explanation of the symbols A'_3 and A'_4 see reference 13.

abscissa. However, because of entanglements, in contrast to the results in Figure 1, the experimental values of M_c/M_c^o of 0.903 for *f* = 3 and 0.705 for *f* = 4 from Figure 5 are less than the predicted values that account for loops.

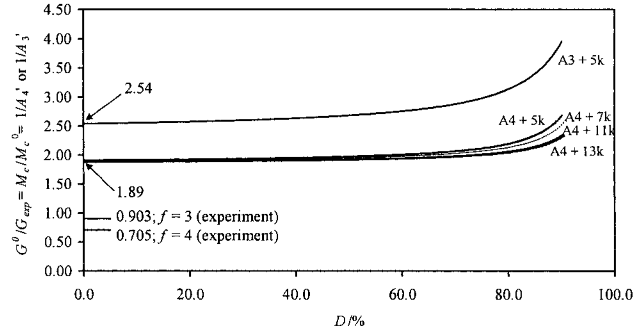
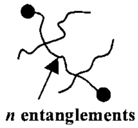


Figure 6. Predicted (from Figure 4) and experimental modulus reductions for PDMS networks.

The reconciliation of experimental and predicted values of M_c/M_c^o is straightforward. M_c^o = 18500 g mol^{-1} for the systems studied by Llorente and Mark. Hence, $M_{c,experiment}$/g mol^{-1} = 0.903 × 18500 = 16706 for *f* = 3 networks and $M_{c,experiment}$/g mol^{-1} = 0.705 × 18500 = 13043 for *f* = 4 networks. Both of these values are somewhat greater than the value of 12000 g mol^{-1} for the entanglement molar mass (M_e) in linear PDMS[14].

However, accounting for loop structures, without entanglements one would expect $M_{c,chemical} = 2.54 \times 18500 = 46990$ for $f = 3$ networks and $M_{c,chemical} = 1.89 \times 18500 = 34965$ for $f = 4$ networks. Thus, $M_{c,chemical} / M_{c,experiment} = 46990/16706 = 2.54/0.903 = 2.81$ for $f = 3$ networks defines the factor by which $M_{c,chemical}$ is reduced due to entanglements. For $f = 4$ networks $M_{c,chemical}/ M_{c,experiment} = 34965/13043 = 1.89/0.705 = 2.68$. Alternatively, as illustrated in Figure 7, one may consider that the average number of entanglements per equivalent linear chain between junctions of the actual networks is 2.81 - 1 = 1.81 for $f = 3$ networks and 2.68 - 1 = 1.68 for $f = 4$ networks.



$$M_c \to \frac{M_c}{n+1}$$

Figure 7. Illustrating the relationship between M_c and the average number of entanglements per equivalent linear chain in PDMS networks.

Conclusions

The present paper shows the importance of accounting fully for loop formation when interpreting the absolute values of the moduli of networks. Even for reactants of high molar mass, the effects of loops on elastic modulus are significant. Model networks are *not* perfect networks and the effects of loops have to be considered, alongside those of loose ends and entanglements, when interpreting modulus. For PU networks based on HDI and POP polyols, the effects of loops are dominant. For PDMS networks, using a linear reactant of molar mass greater than M_e, the reductions in modulus due to loops are significant, but are outweighed by those due to entanglements.

Acknowledgements

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References

[1] J.E. Mark, B. Erman, in *Polymer Networks – Principles of Their Formation, Structure and Properties*, R.F.T. Stepto, ed., Blackie Academic & Professional, London,1998, Chap. 7.

[2] W.W. Graessley, *Adv. Polymer Sci.*, **1974**, *16*.

[3] O. Kramer, in *Elastomeric Polymer Networks*, J.E. Mark, B. Erman, eds., Prentice Hall, Englewood

Cliffs, NJ, 1992, Chap. 17.

[4] R.F.T. Stepto, B.E. Eichinger, in *Elastomeric Polymer Networks*, J.E. Mark, B. Erman, eds., Prentice Hall, Englewood Cliffs, New Jersey, 1992, chap. 18.

[5] M. Gottlieb, C.W. Macosko, G.S. Benjamin, K.O. Meyers, E.W. Merrill, *Macromolecules*, **1981**, *14*, 1039.

[6] C.W. Macosko, J.C. Saam, *Polymer. Prepr., Div. Polymer Chem., Amer. Chem. Soc.*,**1985**, *26*, 48.

[7] R.F.T. Stepto, in *Polymer Networks – Principles of Their Formation, Structure and Properties*, R.F.T. Stepto, ed., Blackie Academic & Professional, London, 1998, Chap. 2.

[8] R.F.T. Stepto, D.J.R. Taylor, in *Cyclic Polymers 2 nd edition*, J.A. Semlyen, ed., Kluwer Acadenic Publishers, Dordrecht, 2000, Chap.15.

[9] S. Dutton, R.F.T. Stepto, D.J.R. Taylor, *Angew. Makromol. Chem.* **1996**, *240*, 39.

[10] R.F.T. Stepto, J.I. Cail, D.J.R. Taylor, *Polimery* **2000**, *XLV*, 455.

[11] R.F.T. Stepto, *Polym. Bull. (Berlin)*, **1990**, *24*, 53.

[12] R.F.T. Stepto, D.J.R. Taylor, T. Partchuk, M. Gottlieb, in *ACS Symposium Series 729, Silicones and Silicone-Modified Materials*, S.J. Clarson, J.J. Fitzgerald M.J. Owen, M.D.Smith, eds., Amer. Chem. Soc., Washington DC 2000, Chap. 12.

[13] M.A. Llorente, J.E. Mark, *J. Chem. Phys.* **1979**, *71*, 682

[14] L.J. Fetters, D.J. Lohse, S.T. Milner, W.W. Graessley, *Macromolecules* **1999**, *32*, 6847