Theoretical and experimental studies of network formation and properties

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A survey of recent work on pre-gel intramolecular reaction and gelation in oxypropylene–triol and tetrol-based polyester and polyurethane network-forming systems is presented, and relationships between the properties of the networks formed at complete reaction and the product of extents of reaction at gelation (α_c) are discussed. In contrast to that in corresponding linear reaction systems, the amount of pre-gel intramolecular reaction in the triol-based polyurethanes is never negligible, even in bulk. Kilb's model of $RA_2 + RB_f$ type gelling systems has been reanalysed and a more accurate condition for gelation evaluated. The shear moduli and T_gs of dry networks are found to increase as α_c increases, indicating that these properties are strongly dependent on the amount of pre-gel loop formation. Extrapolated values of the shear moduli indicate that perfect, affine rather than phantom networks would be formed by reaction systems having the ideal gel point $[\alpha_c = (f - 1)^{-1}]$.

INTRODUCTION

The properties of a polymer network depend not only on the chain structures, molecular weights, and amounts of reactants used to prepare the network but also on the conditions (concentration and temperature) of preparation. In the Gaussian sense, the perfect network can never be obtained in practice, but, through random polymerizations of polyfunctional and difunctional monomers and prepolymers. networks with quantifiable degrees of imperfections can be prepared, and the importance of such imperfections on network properties can be ascertained. In this context, the use of well-characterized random polymerizations for network preparation may be contrasted with the more traditional method of crosslinking polymer chains. With the latter, uncertainties with regard to the distribution of primary chain lengths, chain lengths between junction points, loose ends, and entanglements often exist.

The present paper presents a survey of recent work carried out into correlations between network properties and reactant structures and reaction conditions. The reaction systems used have been generally oxypropylene triols or tetrols of various molecular weights reacting irreversibly with diisocyanates (to give polyurethanes) or diacid chlorides (to give polyesters), with like functional groups having equal reactivities. Emphasis has been placed on the extent to which pre-gel intramolecular reaction defines the physical properties of the networks formed at complete reaction.

PRE-GEL INTRAMOLECULAR REACTION

Previous studies[1] have shown how ring fractions formed during an irreversible linear random polymerization may be measured. The results obtained may be correlated successfully in terms of a kinetic analysis[2], cascade theory[3], or rate theory[4]. The important quantities in such correlations are

$$Pab = \left(\frac{3}{2\pi\nu b^2}\right)^{3/2} \text{(functional groups/unit volume)} \quad (1)$$

and the initial concentrations of reactive groups (c_{a0} and c_{b0}). In equation (1), ν is the number of bonds in the smallest ring that can form, and b is the effective bond length ($\nu b^2 = \langle r^2\rangle$) of the chain forming that ring. The effects of reactant molecular weight on ring formation enter through ν, and those of chain structure, temperature, and solvent through b. The ratio of Pab to some function of c_{a0} and c_{b0} defines a parameter characterizing the competition between intramolecular and intermolecular reaction, and the various theories[2–4] provide frameworks describing how ring and chain species form as a polymerization progresses. The same quantities are important in descriptions of non-linear polymerizations and gelation[5].

In non-linear polymerizations recently studied[6,7], using oxypropylene triols and hexamethylene diisocyanate (HDI), it was found that the fraction of ring structures (N_r) was always significant, even in bulk reactions. *Figure 1* shows results obtained[6] in benzene solution and in bulk at 70° for stoichiometric amounts ($r = 1$) and $\nu = 115$. The product of the extents of reaction at gelation (α_c) were also measured, and theoretical correlations in terms of rate theory[8] and cascade theory[9] show that the measured values of both N_r and α_c can be separately explained, but that for each theory different values of b are required for the two quantities. These inconsistencies indicate that further theoretical developments are needed before quantitative descriptions of intramolecular reaction from zero reaction through to the gel point can be achieved. Comparisons with the results for linear systems show that N_r, at a given value of p and with the same values of Pab, c_{a0} and c_{b0}, will be about an order of magnitude higher for triol as compared diol.

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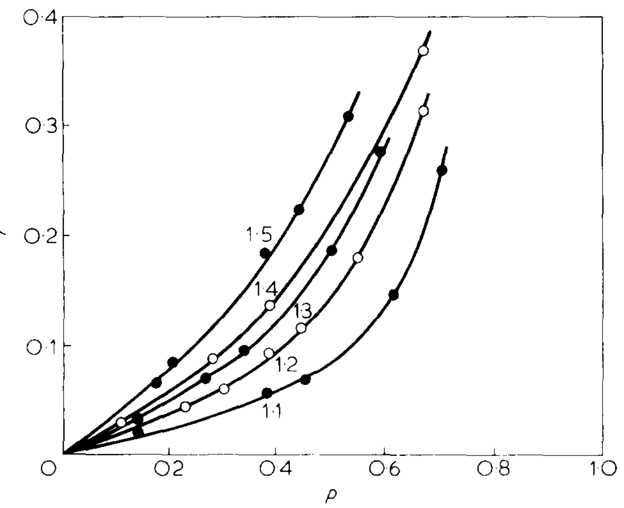

Figure 1 Number fraction of ring structures, N_r, *versus* extent of reaction, *p*, for $r = 1$. Reaction system: oxypropylene triol + HDI ($\nu = 115$)/benzene/70°C. ●, Expt 1.1 – bulk; ○, expt 1.2 – 70% monomers; ●, expt 1.3 – 50% monomers; ○, expt 1.4 – 40% monomers; ●, expt. 1.5 – 30% monomers. [Reproduced with permission from *Br. Polym. J.* 1977, **9**, 124 ©]

GELATION

It has been shown[5], that values of α_c measured for reactions at different initial dilutions can be correlated by means of approximate theories of gelation due to Frisch[10], and to Kilb[11], at least for reactions with $r = 1$. The use of analytical expressions for α_c derived from such approximate theories of gelation avoids the numerical calculations necessary with the more complete cascade and rate theories, and such expressions at present provide an equally satisfactory means for interpreting gel point data.

Recently, the Kilb model for a gelling system has been analysed in more detail[12] and a more accurate condition for gelation in an $RA_2 + RB_f$ type random polymerization derived, namely:

$$\alpha_c(f-1)(1-\lambda)^2 = 1 \tag{2}$$

α_c is the product of extents of reaction of A and B groups ($pa{\cdot}pb$) at gelation, f is the junction point functionality, and λ is a ring forming parameter, with:

$$\lambda = \frac{(f-2)Pab\,\phi(1,3/2)/N}{(f-2)Pab\,\phi(1,3/2)/N + (c_a' + c_b')} \tag{3}$$

$\phi(1,3/2)$ is the Truesdell function[5], N is Avogadro's number, and $(c_a' + c_b')$ is some average concentration of the reactive groups external to a given molecule. $(c_a' + c_b')$ may most simply be equated to the total initial or gel concentrations, $(c_{ao} + c_{bo})$ or $(c_{ac} + c_{bc})$, respectively[5]. Equation (2) reduces to Kilb's expression

$$\alpha_c(f-1)(1-\lambda_K) = 1 \tag{4}$$

for small λ, with $\lambda = \lambda_K/2$.

The analysis of gel point data is made by using experimental values of α_c to evaluate λ according to equation (2), and then plotting $\lambda/(1-\lambda)$ *versus* $(c_a' + c_b')^{-1}$, and evaluating *Pab*, and hence *b*, through equations (1) and (3), from the slope of the line so obtained. This analysis is now preferred to that based on Frisch's theory[5]. Compared with the Frisch analysis, the values of *b* so obtained show the same variation with the structure of the chain (of ν bonds) which forms the smallest ring, the absolute values of *b* are in better accord with values expected from solution properties, and the analysis is not subject to the condition that $\lambda \ll 1$.

Recent work on gel points includes studies of the effects of temperature on α_c in triol-based polyester systems[7], the study of triol/diol-based polyester systems[7], and of tetrol-based polyurethane systems[13].

NETWORK PROPERTIES AND GELATION

The results of the preceding studies of ring formation and gelation show how the gel point is related to reactant structures and to reaction conditions. The present work indicates how the physical properties of the networks formed at complete reaction are to a large extent determined by the experimental values of α_c, and hence, by the amount of pre-gel loop formation.

Oxypropylene triol- and tetrol-based polyester and polyurethane networks have been formed, principally from reaction systems at various initial dilutions and with $r = 1$, and values of α_c have been determined en route to complete reaction. SHear moduli have been determined from uniaxial compression[14–16] and torsion pendulum experiments[17–19] and the latter have also been used to determine loss moduli and T_g. Creep behaviour has also been studied[16]. A brief selection of the results is presented here.

For the reaction systems used, the value of M_c^0, the molecular weight between junction points for the perfect network, is always known at complete reaction. It is closely related to ν, and is defined by the structures of reactants, as illustrated in *Figure 2* with respect to the reaction of a polyoxypropylene tetrol, based on pentaerythritol, and HDI. The shear moduli (G) determined experimentally on dry and swollen networks can be analysed through Gaussian theory to give apparent values of M_c according to equation (5):

$$G = ART\rho\phi_2^{1/3}(V_u/V_F)^{2/3}/M_c \tag{5}$$

ρ is the density of the dry network, ϕ_2 is the volume fraction of solvent present in the swollen network, V_u is the volume of the dry, unstrained network and V_F is the volume of the network at formation. A has the value of $(1 - 2/f)$ for phantom networks and the value of 1 for affine networks[20].

Figure 3 shows values of M_c/AM_c^0 *versus* α_c for oxypropylene tetrol/HDI polyurethanes[15]. P1 and P2 refer to two tetrol prepolymers with different values of M_c^0. The variation

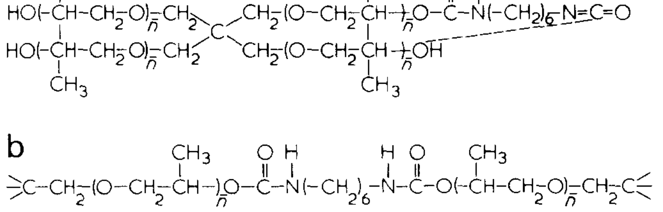

Figure 2 Parts of chain structure used in defining (a) ν – the number of bonds in the chain forming the smallest ring, and (b) M_c^0 – the molecular weight between junction points in the perfect network. Illustrated with reference to an oxypropylene tetrol, based on pentaerythritol, reacting with HDI

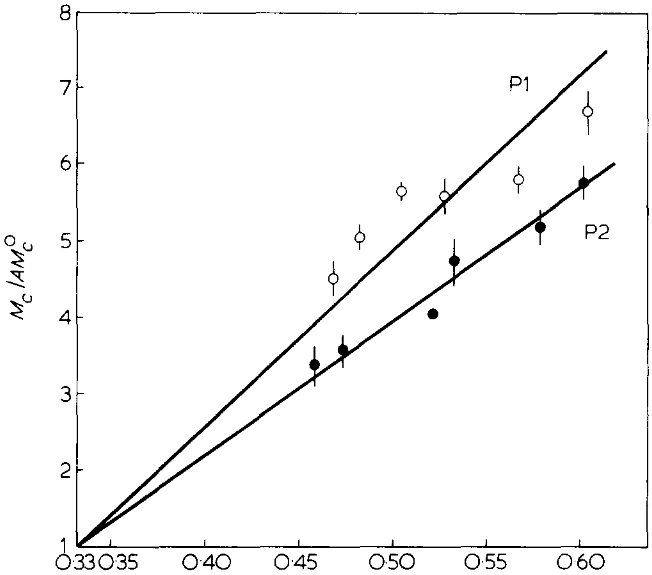

Figure 3 M_c/AM_c^0 *versus* α_c for two tetrafunctional polyurethane network systems. Reaction systems: oxypropylene, pentaerythritol-based tetrol + HDI/nitrobenzene/80°C. P1 – $M_c^0 = 500$, P2 – $M_c^0 = 586$

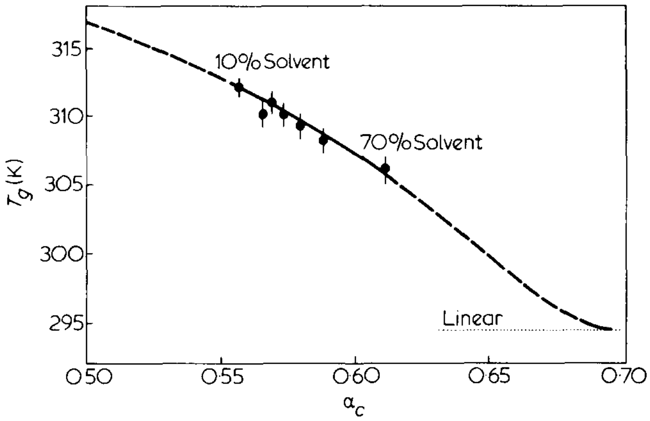

Figure 4 T_g *versus* α_c for trifunctional polyurethane networks (●). Reaction system: oxypropylene triol + PMDI/nitrobenzene/80°C. $M_c^0 = 710$. ●, Oxypropylene diol + PMDI, $M_{\text{repeat}} = M_c^0$

in α_c results from the use of reaction mixtures of different initial dilutions. The lines through the experimental points have been extrapolated to $M_c/AM_c^0 = 1$ at the ideal gel point ($\alpha_c = 1/3$), consistent with $A = 1$ (affine behaviour) and $M_c = M_c^0$. For both P1 and P2 systems, the points at the smallest values of α_c refer to bulk reactions.

The behaviour exemplified in *Figure 3* is typical of that shown by the other polyester and polyurethane systems studied. M_c/AM_c^0 is always greater than unity, and increases with the initial dilution of the reaction system by an amount larger than that which can be accounted for by a transition from affine to phantom behaviour. In general, the results indicate that in the limit of the ideal gel point ($\alpha_c = (f-1)^{-1}$) a perfect, affine, rather than phantom, network is formed. Entanglements are apparently of negligible importance and the behaviour observed is consistent with the presence of elastically ineffective loops, and with the number of these increasing with pre-gel intramolecular reaction. The range of M_c/AM_c^0 values shown in *Figure 3* indicates that such defects can lead to a reduction in modulus by a factor of about 7. This range of values is typical of that found for other systems. In addition, larger proportions of the loops formed by the systems with the smaller value of M_c^0 appear to be elastically ineffective. This follows from the relative positions of the two lines in *Figure 3*, and such a comparative behaviour is also found for other network forming systems[12,14].

Figure 4 shows the variation of T_g with α_c for polyoxypropylene triol/phenylmethane diisocynanate (PMDI) polyurethanes[18]. These systems have an M_c/AM_c^0 *versus* α_c behaviour similar to that shown in *Figure 3*. Thus, *Figure 4* indicates that T_g is a decreasing function of α_c or M_c.

The horizontal line refers to a linear PMDI/oxypropylene polymer having a repeat unit of molecular weight equal to M_c^0. In general, the variation of T_g with α_c (or M_c) is a reflection of the influence of elastic junction-point density on the freedom of segmental motion, and the maximum range of T_g values shown (295–317K) reflects, possibly, the maximum influence for the triol system considered.

CONCLUSIONS

The properties of the networks formed at complete reaction in random polymerizations have been shown to be strongly dependent on the amount of pre-gel intramolecular reaction which has occurred. Even with bulk reactions, it is not possible to obtain perfect networks. However, in the limit of no pre-gel intramolecular reaction, perfect, affine rather than phantom networks are predicted. Present theoretical development allows only the semiquantitative correlation of the amount of intramolecular reaction and the extents of reaction at gelation with reactant structures and reaction conditions. In addition, the properties of perfect networks are not unambiguously defined[20]. In spite of these shortcomings, the present results show how network properties (as exemplified by M_c and T_g) may be related, through α_c, to reactant and reaction variables.

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