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Influence of the final extent of reaction on the structure of model polydimethylsiloxane networks obtained by the end-linking hydrosilation reaction

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Summary

Model silicone networks obtained by hydrosilation of vinyl terminated polydimethylsiloxane chains have been used extensively to verify molecular theories of rubber elasticity. In these networks, the maximum extent of reaction obtained during cross linking considerably affects their final structure. The degree of completion of the hydrosilation reaction depends on the concentration of reactive groups. A recursive approach and kinetic data from the literature are used to show that, for this particular reaction, perfect networks, i.e. those with high concentration of elastically active network chains, are only obtained when a relatively high concentration of reactive groups is present in the system. This critical concentration corresponds in a bulk reaction to polydimethylsiloxane chains with a number average molecular weight lower than 10,000.

Introduction

Well-characterized model networks have been extensively used for the study of structure-property relations (1-5). These networks are mainly prepared by synthetic procedures that link long telechelic chains of a given linear polymer by their ends. In particular, ideal or model networks have been obtained by end-linking vinyl terminated difunctional polydimethylsiloxane chains with cross linking agents bearing silane groups, as is shown in Figure 1 (4-7).

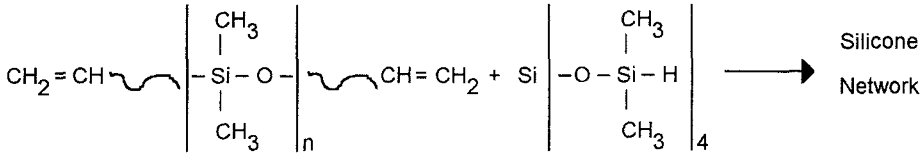

Figure 1. Cross linking reaction between a bifunctional pre-polymer B_2 and a tetra functional silane A_4.

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An ideal or model network is obtained when every pre-polymer chain end effectively reacts with different cross linker molecules. The average chain length between cross linking points is then equal to the length of the bifunctional molecules used to prepare the network. On the other hand, thanks to living polymerization procedures, today is possible to build model networks with chains of narrow molecular weight distribution.

However it has been reported that for stoichiometrically balanced systems, the maximum extent of reaction reached by hydrosilation depends on the concentration of reactive groups (8-10). Chaumont et al. studied the reaction between monofunctional vinyl-terminated polystyrenes and model molecules containing silane groups. Vallés et al. prepared model silicone networks cured in bulk and in solution. In every case a relationship was found between the concentration of reactive groups and the maximum extent of reaction attained by the system. Complete reaction is not attained at low concentration of vinyl-end groups, and pendant chains and extractables are present. In this case the length of the elastically active chains is larger than that of the pre-polymer used to build the network and the concentration of these chains is lower than expected.

This implies that some of the silicone networks prepared in the past assuming ideal reactions are not model networks. In order to understand the correlation between network structure and properties, it is necessary to calculate in every case the final structure obtained by hydrosilation. The present work evaluates some of the necessary conditions to obtain model networks. The recursive method by Miller and Macosko (10-12), has been used to estimate the structure of the networks. A derivation made by Bibbó and Vallés (13) with some extensions (14) is also used to estimate the average molecular properties of imperfect networks.

Results and discussion

Figure 2 shows the results from kinetic measurements of the maximum extent of reaction, (p_{inf}), achievable by hydrosilation between vinyl and silane groups as a function of its initial concentration (expressed as the inverse of the normality (N^{-1})). They correspond to different results obtained by Chaumont et al. (8) and Vallés et al. (9) from stoichiometrically balanced reactions in bulk and in solution.

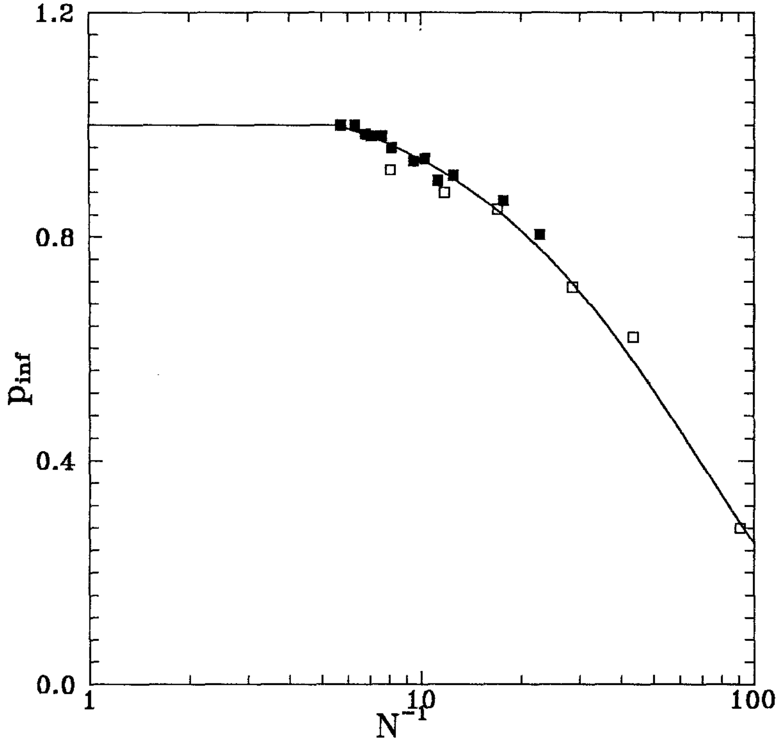

Figure 2: Maximum extent of reaction reached by hydrosilation (p_{inf}) as a function of concentration of reactive groups present in the initial mixture expressed as the inverse of normality (N^{-1}). Symbols: (■) Vallés et al. (9),and (□) Chaumont et al. (8). The curve represents the least square fit of the experimental data.

The least square fit of p_{inf} as a function of N^{-1} for all the data points gives the following function:

$$p_{inf} \begin{cases} 1 & \text{if } N^{-1} \leq 5.615 \\ 1.084915 \exp\left(-0.01415\, N^{-1}\right) & \text{if } N^{-1} > 5.615 \end{cases}$$

Experimental results indicate that even in bulk, since the concentration of reactive groups depends on the length of the pre-polymer chains, the maximum extent of reaction will be a strong function of the molecular weight of the pre-polymer used. Complete reaction is not achieved for concentrations of reactive groups below 0.175 mol/l which corresponds to a number average molecular weight of the pre-polymer chain in the order of 11,000.

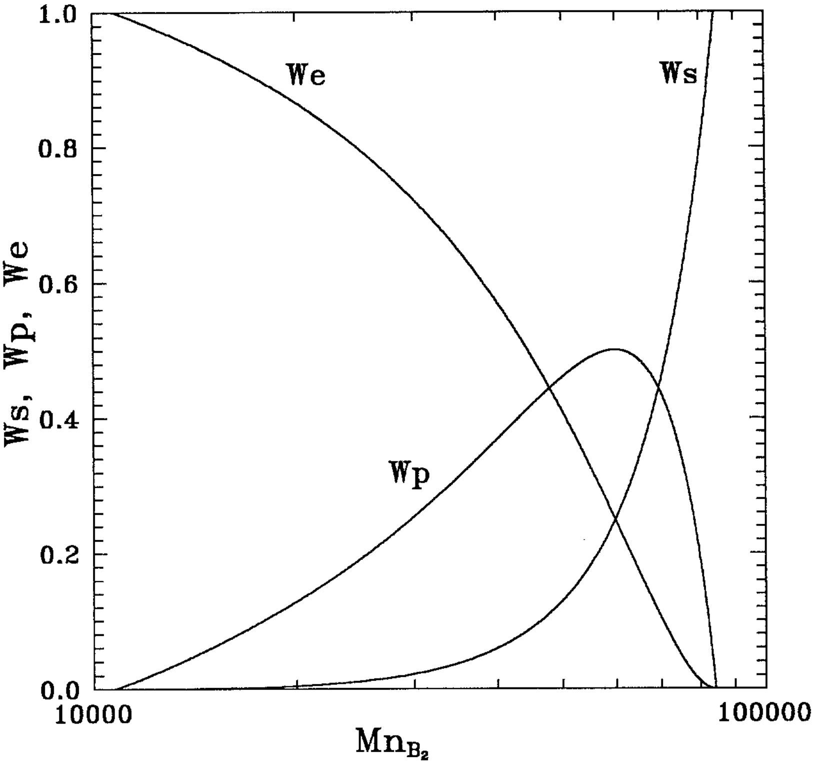

Figure 3: Weight fraction of solubles (W_s), pendant chains (W_p), and elastic material (W_e) for stoichiometrically balanced networks ($r = 1$) at maximum extent of reaction reached by the hydrosilation reaction (p_{inf}) as a function of molecular weight of difunctional chains (Mn_{B_2}), system A_4+B_2 ($M_{A_4} = 328$).

Figure 3 shows the kind of structures that are obtained at p_{inf} for networks prepared in bulk from pre-polymers of different molecular weights cross linked with a tetra functional silane of low molecular weight (A_4+B_2 type of reaction). In all cases a balanced stoichiometry was assumed. As the molecular weight of the pre polymer (Mn_{B_2}) increases from 10^4 to 10^5 the concentration of reactive groups decreases. This gives rise to incomplete reactions. As a consequence, the weight fraction of elastically active chains in the final network decreases steadily from one to zero indicating that imperfect networks are formed for molecular weights $Mn_{B_2} > 11,000$. For lower molecular weights, networks are composed almost exclusively by elastic chains. As the molecular weight of the pre-polymer used to build the network is raised, an increasing amount of pendant chains and soluble material begins to appear as revealed by the evolution of the weight fraction of pendant chains (Wp) and the weight fraction of solubles (Ws). In the extreme of high molecular weight (Mn_{B_2} close to 10^5) very imperfect networks are formed with few elastic and pendant chains and considerable amounts of soluble material.

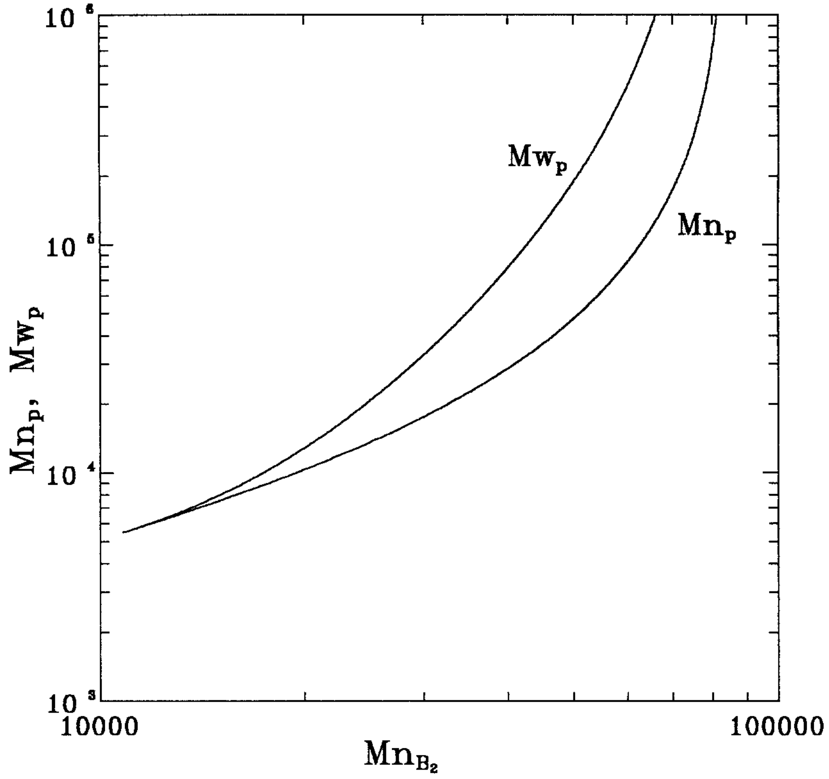

Figure 4: Number and weight average molecular weight of pendant chains (Mn_p,Mw_p) for stoichiometrically balanced networks ($r = 1$) at maximum extent of reaction reached by the hydrosilation reaction (p_{inf}) as a function of molecular weight of difunctional chains (Mn_{B_2}). System A_4+B_2 ($M_{A4} = 328$).

The complexity of the final network structure also increases when low concentration of reactive end-groups is employed. For example the polydispersity and the degree of branching of the pendant chains increases steadily with the molecular weight of the difunctional chains. Figure 4 illustrates how the molecular weight of the pendant chains changes with Mn_{B_2}. For molecular weights of the B_2 chains lower than 11,000, the amount of pendant chains and soluble material is negligible. When siloxanes of higher molecular weights are employed in the reaction the molecular weight and the polydispersity increase very rapidly. This is due to the growing complexity of the branched structures of the pendant chains. The same effect is obtained when the cross linking reaction is carried in solution since dilution of the pre-polymer chains also affects the reactivity of the cross linking reaction.

Conclusions

We have analyzed the behavior of network molecular structure as a function of the molecular weight of the pre-polymers in networks obtained by hydrosilation. The maximum extent of reaction reached depends on the concentration of reactive groups present in the mixture. As the degree of completion of the reaction affects the concentration of loose chain ends, the degree of perfection of the network depends on the molecular weights of the dimethylsiloxane pre-polymers employed.

Even for relatively low molecular weight chains, the resulting networks are not perfect. For a typical system, considerable amounts of pendant and soluble chains are obtained if the molecular weight of B_2 chains is higher than 30,000. Under these conditions branched pendant chains and soluble structures are present. IT is therefore usually very difficult to understand the contribution of different parts of the network in respect to its final properties.

Acknowledgments

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