Theory of the variation of relaxational properties of polymers during network formation

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Recent work on the change of mechanical and dielectric relaxational properties accompanying the formation of a polymer network from reactive oligomers is reviewed. The theoretical considerations cover the essential features of the behaviour observed in different polymer systems. The theory offers new possibilities for obtaining information about the chemical kinetics, physical structure, and structure formation during crosslinking, by means of relaxation studies. Analysis of the theory of the kinetics of structure formation suggests the following picture of the process of crosslinking. Shortly before the gel point, there appears a state of 'kinetic entanglement', which is completed at gel; chemical crosslinks then start to form. Beyond the gel point the contribution of entanglements to the mechanical behaviour is insignificant. However, fluctuation restrictions on crosslinks, and the topological restrictions on network chains play an important role in the reduction of the front-factor and in the increase of the Mooney—Rivlin C_2-term during network formation.

INTRODUCTION

There exist different techniques for the preparation of rubber-like networks[1]. Networks may be prepared from polymers of very high molecular weight by the introduction of crosslinks at segments distributed randomly along the chain. Alternatively, networks are prepared by end-linking of branched oligomers or, more generally, by end-linking of a mixture of branched and linear oligomers.

This paper concerns only the second method of network formation which provides better control of the crosslinking process and of the structure of the resulting networks. For the sake of simplicity we shall start with the special case of three-functional oligomers (with groups A) reacting with small two-functional molecules (with groups B). It will be shown later that the assumption of sizes of the three-functional and two-functional units is not important. The condition for the functionality, f, of the oligomers is not necessary and the results are also valid for f-values higher, or lower, than three.

In our simple model, however, we shall consider *three-functional oligomers*, which, from the point of view of network formation, are *monomers;* when the reaction starts, we obtain dimers, trimers, etc. In general, we deal with *x-mers.*

Beyond the gel point, in addition to branched units, we obtain crosslinked units, which provide elastically effective network chains. The progress of the reaction is controlled by the conversion parameter, α, i.e. the fraction of groups A, which have reacted with groups B. For $\alpha = 0$ only monomers are present, and for $\alpha = 1$ a complete network without a sol-fraction is obtained. In the absence of cyclization, the gel point is reached at the critical conversion $\alpha = 1/(2)^{1/2}$.

Experimental studies of the mechanical and dielectric relaxation at various stages of the network formation give a characteristic picture of the variation of shear modulus, G, and the dielectric constant ϵ.

Mechanical relaxation experiments (*Figure 1*) show beyond the gel point a steep increase of the real modulus, G' and a very broad maximum of the imaginary modulus, G''; both these components increase with increasing frequency ω. In the example shown in *Figure 1* the gel point is reached at a time of 80 min.

The dielectric behaviour (*Figure 2*) shows a monotonic decrease of ϵ' and ϵ'' during network formation. Unlike the mechanical case, dielectric relaxation exhibits a continuous transition near the gel point.

A molecular statistical theory of the variation of the mechanical and dielectric behaviour during network formation does not exist. The following investigations provide an attempt to build a theory covering the experimental results observed in different polymer systems.

ASSUMPTIONS

The starting point for the theoretical considerations consists of the following assumptions.

(i) The distribution function of x-mers is given by the Flory and Stockmayer[2] equation, originally derived for polycondensation of f-functional units.

(ii) The statistics of formation of crosslinked units is given by the theory of the 'graph-like state of matter' by Gordon[3].

(iii) The monomers are represented by a modified subchain model[4], which allows the treatment of chains with orthogonal dipole moments.

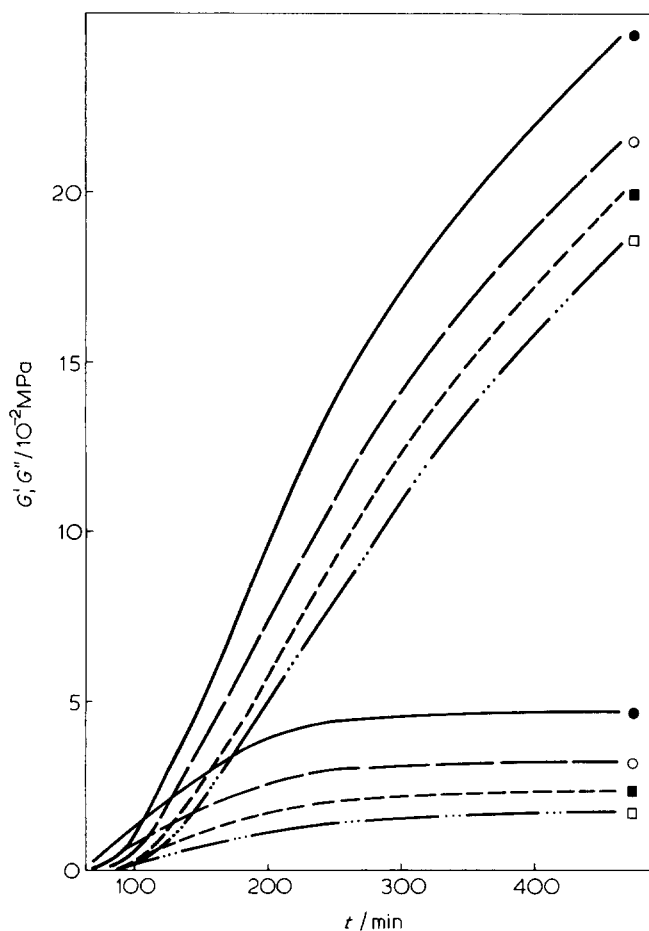(iv) During the formation of a network, the free volume

Figure 1 Dependence of G' and G'' on the time, t, of the reaction of an oligomeric triol with a diisocyanate. Frequency ω(Hz): $\square$, 22; $\blacksquare$, 69.1; $\bigcirc$, 220; $\bullet$, 691

decreases; this follows from the molecular-statistical generalization of the WLF relation[5,6].

(v) The influence of cyclization reactions, contributing to a small increase in the critical conversion at the gel point, is eliminated using the procedure of Gordon and Roberts[7].

We have to distinguish between the real conversion, β, and the theoretical conversion, α, related by the equation:

$$\beta/\beta_c = \alpha/\alpha_c \tag{1}$$

where the subscript c indicates critical conversion at the gel point; $\alpha_c = 1/(2)^{1/2}$. In addition to α, another parameter is applied for the characterization of the degree of conversion, as defined in the equation:

$$Z = \beta/\beta_c - 1 = \alpha/\alpha_c - 1 \tag{2}$$

A critically branched state near the gel point is characterized by low values of Z. It is also assumed that network formation is homogeneous, and there is no specific interaction between the oligomers.

Having discussed the assumptions of the theory, we will move to the main problem concerning the mechanical case. We shall start with the formula for the complex shear modulus:

$$G = G_0 + \Delta G \int \frac{i\omega/s}{1 + i\omega/s} H(s) d\ln s \tag{3}$$

which includes, as its most important characteristic, the relaxation time spectrum H, which is dependent on the relaxation frequency, s. G_0 is the equilibrium modulus for low frequencies, and ΔG is the intensity of the spectrum. Both G_0 and the relaxation spectrum H are functions of the conversion, α:

$$G_0 = G_0(\alpha) \quad [\alpha \leqslant \alpha_c; G_0 = 0] \tag{4}$$

$$H(s) = H(\alpha, S/S_m) \tag{5}$$

The spectrum includes a parameter S_m, which is also a function of the conversion. S_m is the maximum frequency of the spectrum, equal to the maximum frequency, ω_m, of the imaginary modulus G''. The dependence of S_m on α is given by the relation:

$$S_m = S_{mi} \exp[-B(1/f - 1/f_i)] \tag{6}$$

The subscript i indicates the initial state of reaction, B is a constant close to unity, and f is the relative free volume[8–10], linearly decreasing with an increase of the conversion:

$$f = f_i - \alpha \Delta f \tag{7}$$

The shear modulus (3) consists of two parts corresponding to the sol and gel fractions respectively. The main problem is the calculation of the sol spectrum, determined by the sum of the spectra of all x-mers. It should be mentioned here that x-mers may have different configurations. This is illustrated in *Figure 3* for $x = 10$. In *Figures 3a* and *3c* two limiting configurations are shown, *viz.* the star-like and the linear arrangements; an intermediate structure is shown in *Figure 3b*. It is important to note that *different configurations yield different spectra*, and a simple calculation of the relaxation spectrum is possible only for the limiting configurations; in a more general case one has to solve a very difficult eigenvalue problem. *Figure 4* shows the wedge-shaped spectrum of an x-mer in a log–log plot. The part of the
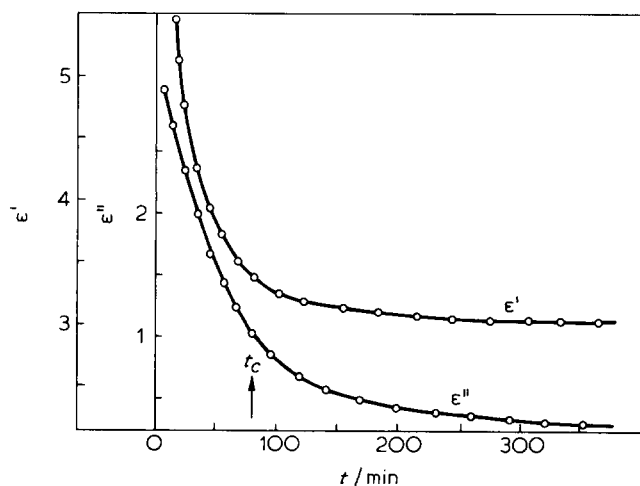

Figure 2 Dependence of ϵ' and ϵ'' on the time, t, of the reaction of an oligomeric triol with a diisocyanate. ($\omega = 6.3 \times 10^3$ Hz)
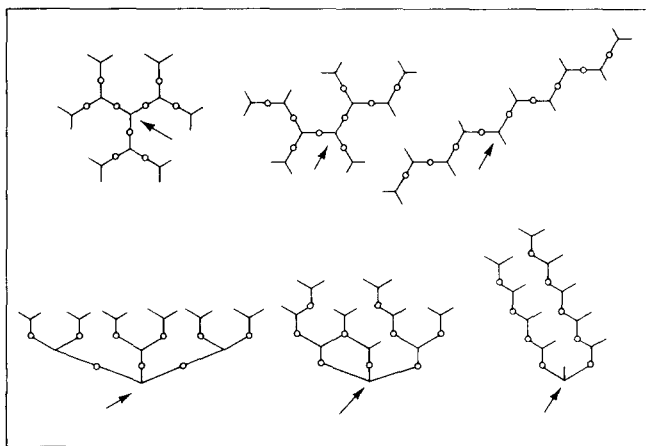
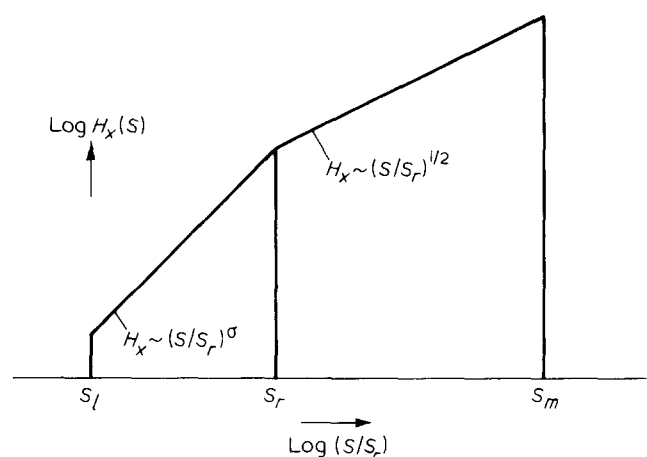**Figure 3** Example configurations of an *x*-mer (*x* = 10)

Figure 4 Wedge-shaped spectrum of an *x*-mer

affected by two factors. First, the change in the geometrical conditions leads to the broadening of the spectrum up to the gel point; beyond the gel point it becomes narrower again. Second, the reduction of the free volume causes a monotonic shift of the spectrum to lower values of S. *Figure 5* shows an example of such a change. At the gel point the spectrum exhibits its maximal width and extends from $S = 0$ to S_m. The change of the spectrum in the high frequency range for high values of α is caused by the fluctuation of the free volume; this effect does not influence the gel process, however, and will not be discussed here.

Now we shall discuss the behaviour of the shear modulus G, which depends on the relaxation spectra, as well as on the frequency ω. *Figure 6* presents classification of the behaviour of G''. The spectra of the initial state (monomers) and the final state (the complete network) are labelled with the subscripts i and f, respectively. A rough classification is

Table 1 Steepness parameter σ, and limiting frequency, S_l, of the different configurations of an *x*-mer

Configuration	σ	S_l/S_r
Star-like	1	$1/\pi^2\,x$
Linear	1/2	$1/x^2$
General case	1/2—1	$1/\gamma(x)^{1/\sigma}$

spectrum important for the process of network formation is the left wedge: the limiting frequency $S_l \cdot S_r$ is the reference frequency, and S_m is the maximum frequency, introduced earlier.

The steepness parameter σ of the left wedge can be calculated for star-like, and linear configurations, but not for more general cases. As an approximation, we shall assume that (as in the limiting cases) the sum of all configurations of an *x*-mer yields a spectrum with a constant σ value; this must lie between 1/2 and 1. It will be shown later that the range below 2/3 is favoured. *Table 1* gives a survey of the steepness parameter, σ, and the limiting frequency S_l; the 'general case' corresponds to the sum of all different configurations.

It should be mentioned that the resulting sol spectrum of all *x*-mers is also wedge-shaped with a steepness parameter $(3/2)\,\sigma$.

RESULTS

Special cases

The mathematical background to the theory is discussed elsewhere[11]. In this paper, we will report only the results of the calculated relaxation behaviour of polymers during network formation. We shall start with the mechanical case. To obtain a general survey we shall first consider the relaxation spectrum. The calculation shows that the spectrum is
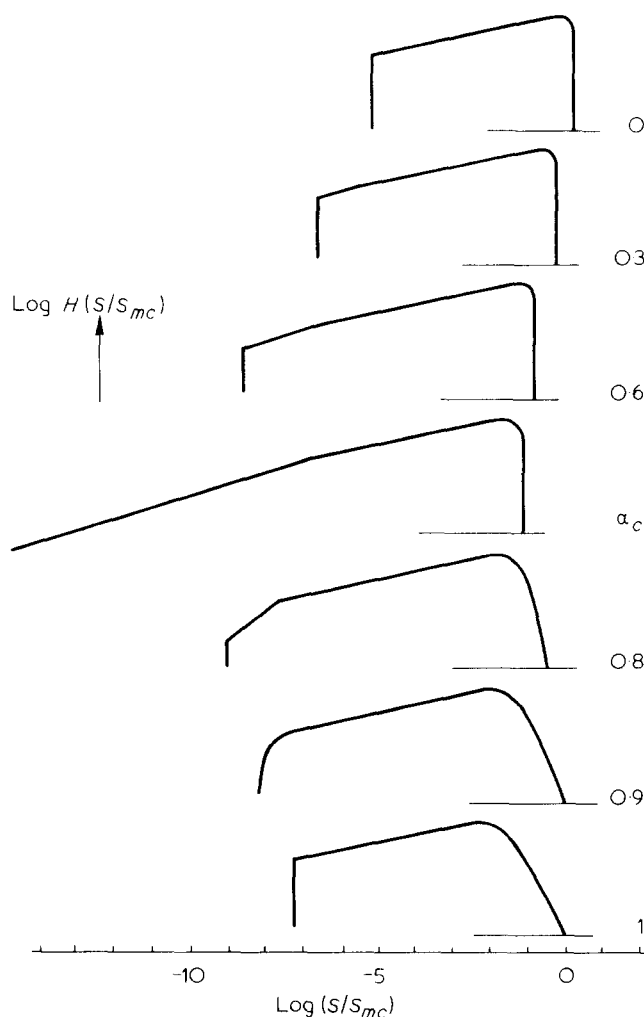

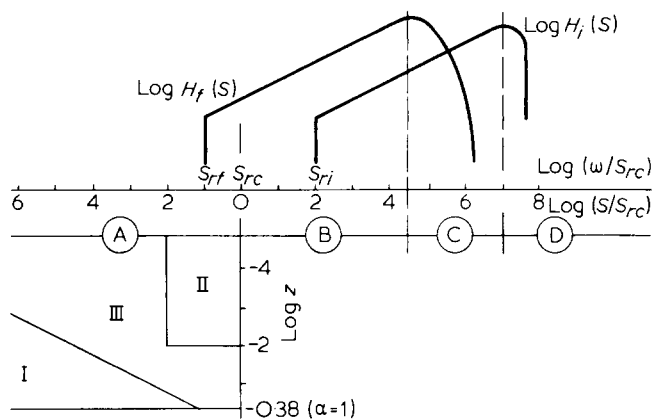**Figure 5** The change of the spectrum $H(s)$ with conversion, α

Figure 6 Classification of the behaviour of G'' vs. frequency ω, dependent on the conversion parameter Z

given by the ω ranges, A, B, C and D. These ranges are determined by the reference frequency at the gel point, S_{rc}. This frequency and its shift can be calculated; to a first approximation they are functions only of the glass transition temperature, crosslink density of the final network and the temperature. Measurements performed in the range A and C yield a maximum of G'' vs. conversion (or time). In range B one finds only a monotonic increase and in the range D, only very small variations of G''. In range C, the gelation process is accompanied by glass transition. Range A has a special significance for network structure. Only this range will be discussed below, taking three parts, where the conversion parameter, Z, plays an important role.

The region I is marked by low values of tan δ and lies beyond the maximum of G''. On the other hand, region II is characterized by low values of Z and a negligible shift of the spectrum. It lies before the maximum of G''. In the region III we always observe a maximum in G''. A simple theoretical evaluation of experimental results is possible only in the regions I and II.

In the region I the theory yields:

$$G' = G_0 + 2aW_g(\omega/S_r)^{2/3} \tag{8}$$

$$G'' = aW_g(\omega/S_r) \tag{9}$$

where a is a constant and W_g is gel fraction. From these equations we obtain a simple relation for the equilibrium modulus G_0:

$$G_0 = G' - 2G''/(3aW_g) \tag{10}$$

In region II the theory yields:

$$G' = G_0 + b(\omega/S_{rc})^{3\sigma/2}\omega s(3\pi\sigma/4) + cZ(\omega/S_{rc})^{1/2} \tag{11}$$

$$G'' = b(\omega/S_{rc})^{3\sigma/2}\sin(3\pi\sigma/4) + cZ(\omega/S_{rc})^{1/2} \tag{12}$$

where b and c are constants. To obtain the equilibrium modulus G_0, it is convenient to consider the difference $G' - G''$:

$$G' - G'' = G_0 - \Delta G' \tag{13}$$

where

$$\Delta G' = b[\sin(3\pi\sigma/4) - \cos(3\pi\sigma/4)](\omega/S_{rc})^{3\sigma/2} \tag{14}$$

is a constant for fixed ω. The relation (13) suggests that we plot the difference $G' - G''$ as a function of time t. The following information (illustrated in *Figure 7*) can be obtained from such a plot:

(1) we can find the point t_h, corresponding to a horizontal tangent. This is the gel point;

(2) the intercept $\Delta G'$ yields the steepness parameter, σ;

(3) the vertical shift of $G' - G''$ yields the equilibrium modulus G_0 according to the equation:

$$G_0 = G' - G'' + \Delta G' \tag{15}$$

It should be noted here that σ can also be calculated from the plot of G'', after the gel point is determined from equation (1). *Figure 8* shows an example of the difference $G' -$
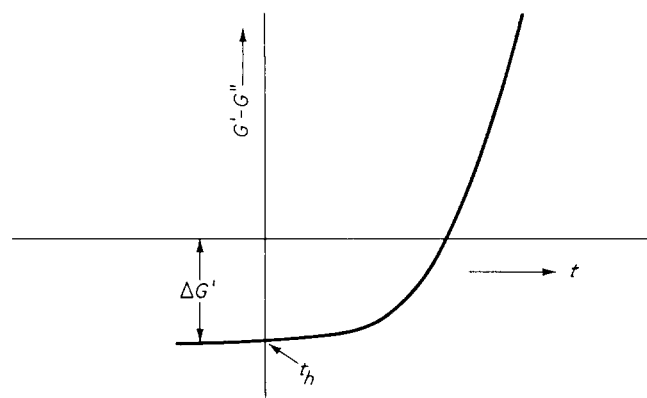

Figure 7 Illustration of the evaluation of the parameters in the region II
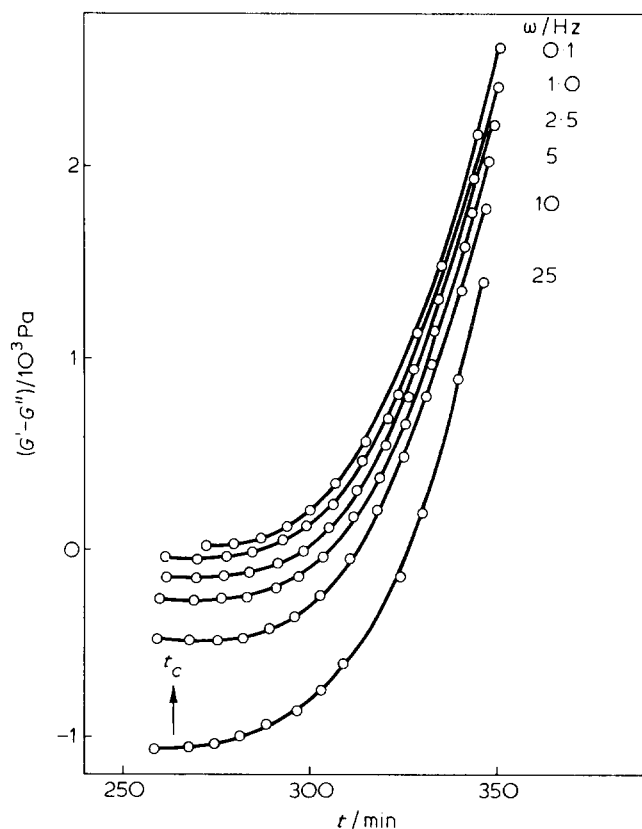

Figure 8 Dependence of the difference $G'-G''$ on reaction time, t, for the autocatalytic polyesterification. (Run 23, Gordon and Roberts[12])
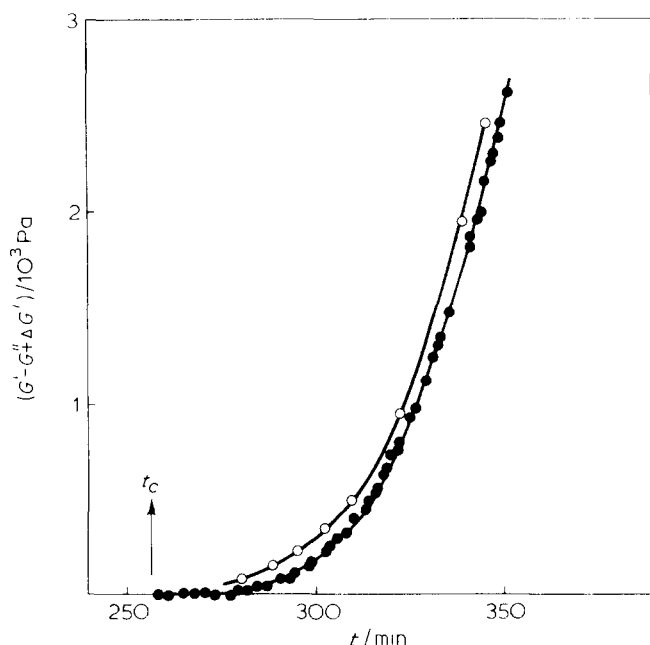
Figure 9 Dependence of the equilibrium modulus G_0 on time t for the autocatalytic polyesterification. (Run 23, Gordon and Roberts[12])

G'' plotted vs. reaction time, t, and *Figure 9* shows the resulting equilibrium modulus G_0 (equation 15) obtained from the shift procedure. In agreement with the theoretical predictions, one observes a transition to the range with a horizontal tangent and negative limiting values of $\Delta G'$. The curve for G_0 is also consistent with the theory, independent of frequency, ω. It should be noted at this point that the deviation observed at 25 Hz indicates that this frequency is too high and lies in range B.

For the same reaction as discussed above, *Figure 10* shows the dependence of the modulus G'' on the conversion parameter Z. We find a linear increase with Z, in agreement with theory with the slope proportional to $\omega^{1/2}$.

Now we wish to present the results of the theory for dielectric relaxation, which, contrary to the mechanical case, are very simple. This is caused by the fact that the dielectric relaxation spectrum does not show a broadening effect in the range of low values of S. For S_0 in the range A, the real component, ϵ', is independent of frequency, ω, but depends linearly on the conversion, α, because each act of chemical linking is accompanied by a change of the dipole moment. Furthermore, it is important that there is always anionic conductivity, which controls the imaginary component, ϵ''. This conductivity depends on the free volume in a similar way as relaxation frequencies in the mechanical case discussed above.

Introducing the conversion difference

$$y = \alpha - \alpha_c \tag{16}$$

the theory yields:

$$\epsilon' = \epsilon_c'' - y(\epsilon_c' - \epsilon_f')/(1 - \alpha_c) \tag{17}$$

$$\epsilon'' = \epsilon_c'' \exp[-B'(1/f - 1/f_c)] \tag{18}$$

where the subscript f indicates the final state, B' is a constant and the relative free volume f is given by the formula:

$$f = f_c - y\Delta f \tag{19}$$

Equations (17–19) can be tested by the use of the linear plot:

$$y/[\ln(\epsilon_c''/\epsilon'')] = a' - b'y \tag{20}$$

with the constants a' and b':

$$a' = f_c^2/B'\Delta f \tag{21}$$

$$b' = f_c/B' \tag{22}$$

For the reaction of an oligomeric triol with a diisocyanate (see the example shown in *Figure 2*), our measurements of ϵ' and ϵ'' when plotted according to equation (20) show a straight line beyond the gel point. So, in this range, the experiment is consistent with the theory.

More general results

It has been assumed that network formation is homogenous, and no specific interactions between the oligomers occur. Now, we should ask what happens, if this assumption is not satisfied. However, discussion of this problem must be limited to the special case: how to choose experimental conditions suitable for obtaining information about the influence of the deviation from the normal (homogeneous) case.

We shall define an *inhomogeneous network formation* as one in which the resulting sample includes domains with different degrees of conversion. As a simple model we can imagine spheres with a conversion $\alpha + \Delta\alpha$, embedded in a matrix with conversion, α.

We introduce the concept of 'kinetic entanglements' to allow for interactions between chain segments in the sol fraction. These entanglements do not contribute to the equilibrium modulus G_0. Kinetic entanglements are important for the viscoelastic behaviour of linear polymers.
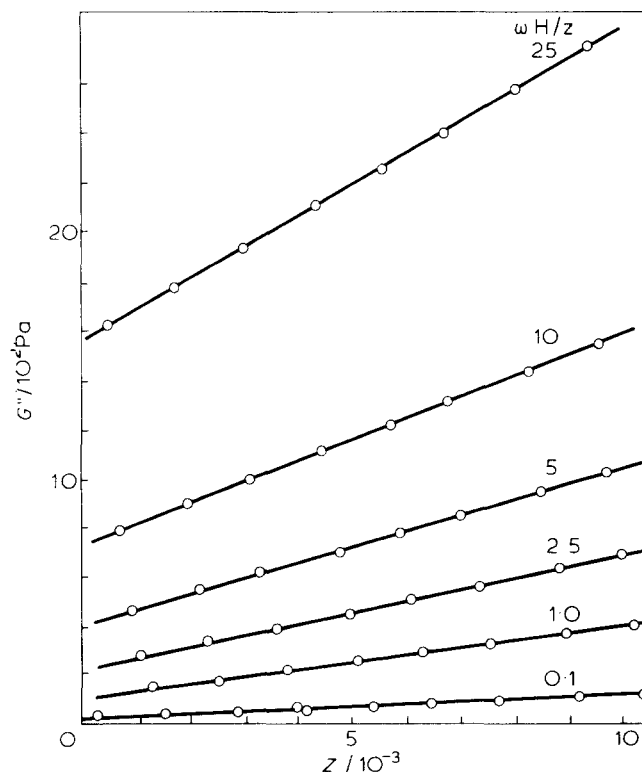

Figure 10 Dependence of G'' on the conversion parameter Z for the autocatalytic polyesterification. (Run 23, Gordon and Roberts[12])
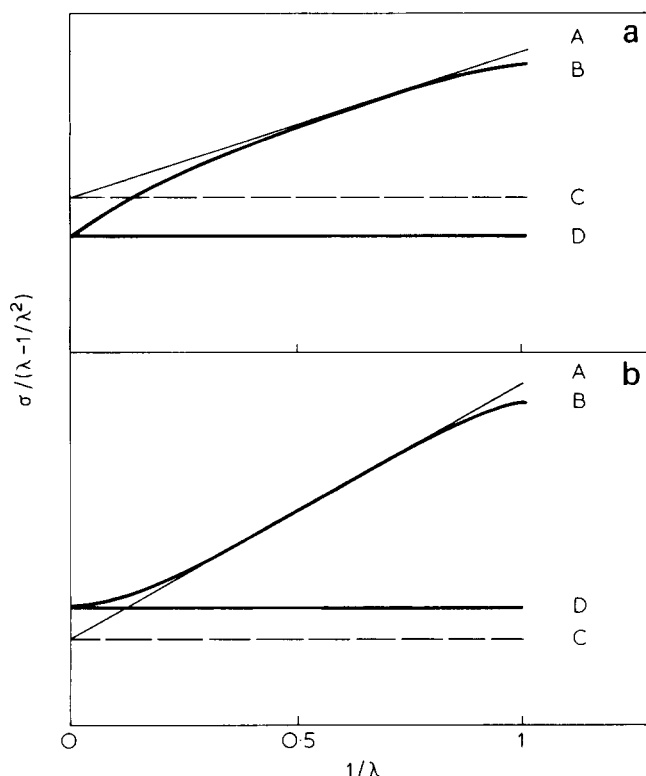
Figure 11 Evaluation of the Mooney—Rivlin plot (schematic). A, $C_1^* + C_2^*$; B, G_0; C, C_1^*; D, $gvkT$

Furthermore we shall introduce *network chain interactions*, which yield the so-called C_2 effect in the stress—strain relations. There exist many different theories which purport to explain the nature of such interactions. These theories emphasize various factors as being possibly responsible for the C_2 effect: intermolecular energy[13], bundle structure[14,15], short-chain effects[16], chain volume[17-19] chain statistics[20], loop effects[21], short range order[22], trapped entanglements[23-25], topological restrictions of network chains[26-32] and fluctuation restriction of crosslinks[33-35].

Here we shall discuss whether the study of relaxational behaviour during the formation of a network can contribute to the understanding of the network chain interaction. Several remarks should be made in this context.

Among the factors mentioned, fluctuation restrictions have a special significance, because not only do they contribute to the C_2 term, but also affect the front factor g. The theory of fluctuation restrictions is not yet complete, as will be discussed elsewhere[36]. However, the following statements seem to be true. When the fluctuation amplitude is large compared with the mean junction distance, we obtain the front factor:

$$g = 1 - 2/\phi \qquad (23)$$

where ϕ is the functionality of crosslinks. Equation (23) corresponds to the classical theory of rubber elasticity of James and Guth[37]. When the fluctuation amplitude is small as compared with the mean distance between junctions, the relation:

$$g = 1 \qquad (24)$$

holds true, which corresponds to the theory of Wall and Flory[38]. For these two limiting cases, equations (23) and

(24), the fluctuations do not contribute to the C_2 term. Alternatively a maximum contribution is reached at the intermediate state:

$$g = 1 - 1/\phi \qquad (25)$$

Generally, network chain interactions increase with increasing density of network chains. If we reduce the density, e.g. by swelling, the interactions can be eliminated. In the critically-branched state, the density of network chains is very low, and therefore the interactions of network chains become negligible.

In the case of uniaxial deformation, molecular statistical considerations of the network chain interaction force $F(\lambda)$ yield the stress, σ, in the form:

$$\sigma = g \cdot vkT(\lambda - 1/\lambda^2) + F(\lambda) \qquad (26)$$

where v is network chain density, k is the Boltzmann constant, T is the absolute temperature and λ is the elongation ratio, l/l_i. For small deformations

$$\lambda = 1 + \epsilon \qquad (27)$$

equation (26) yields the equilibrium shear modulus G_0 in the form:

$$G_0 = gvkT + [F(\lambda)/3] \qquad (28)$$

Experimental results are usually described by the Mooney—Rivlin equation[39,40]:

$$\sigma = (\lambda - 1/\lambda^2)(C_1^* + C_2^*/\lambda) \qquad (29)$$

Comparison of the equations (26) and (27) with equation (29) suggests the equations:

$$C_1^* = gvkT \qquad (30)$$

$$C_1^* + C_2^* = G_0 \qquad (31)$$

while an extract treatment yields:

$$C_1^* = gvkT + \Delta C_1^* \qquad (32)$$

$$C_1^* + C_2^* = G_0 + \Delta C_2^* \qquad (33)$$

which is illustrated in *Figure 11*. ΔC_1^* and ΔC_2^* must be derived from the exact theory of $F(\lambda)$, but they are not known. It seems now that ΔC_2^* is always negligible. ΔC_1^* seems also to be negligible for network formation by end-linking of oligomers, i.e. in the only case discussed here. On the contrary, for the case of network formation from long polymer chains it is proposed[24] that:

$$\Delta C_1^* = C_2^* \qquad (34)$$

This suggests that the network chain interaction is different in these two crosslinking cases.

The theoretical studies lead to the following predictions about the structural effects.

(a) Inhomogeneity of network formation will affect the variation of ϵ' in such a way that instead of a monotonic decrease, a maximum will appear.

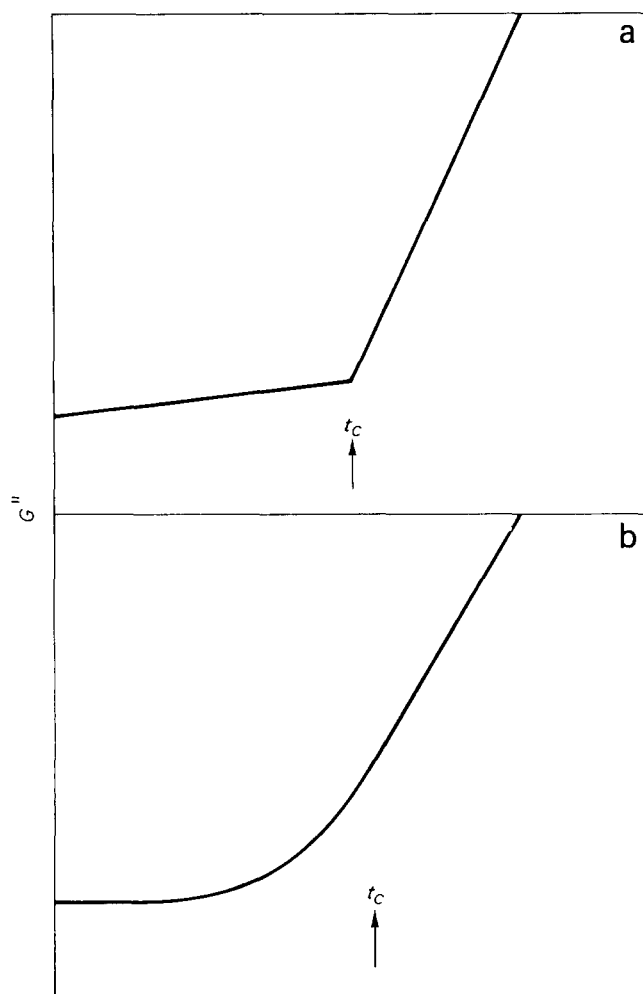(b) The 'kinetic entanglements' affect the variation of G''

Figure 12 Dependence of G'' on the 'kinetic entanglements' (a) Without entanglements; (b) with kinetic entanglements

kinetics and network structure. Besides our own experimental investigations on the polyaddition of polyurethane, the experimental results for end-linking of silicone chains[41−43], and autocatalytic polyesterification[7] will be discussed. *Table 2* shows the chemical structures of the investigated oligomers. We wish to point out that the oligomers of the polyurethane system possess a mean functionality of 2.25. The first system was measured in the frequency region range I, the second system in region II, and the third in region III.

Table 3 gives a survey of the principal possibilities of obtaining information on the chemical kinetics and network structure. It is evident that some information can be obtained only by a combination of two methods.

Tables 4–6 show the results for different systems. For the polyurethane, measured in the frequency region III, we have been able to calculate some chemical kinetic data and to find an indication of the 'kinetic entanglement state'.

For the polyester, we have calculated front factors at the critically branched state; they are close to unity, and slightly

Table 3 Survey of the possibilities to derive information from relaxational studies

Dielectric relaxation	Order of the reaction Onset of the diffusion controlled process Inhomogeneity	Reaction rate constant
Mechanical relaxation	Gel point. Characteristics M_e and τ_0 of the kinetic entanglements, front factor at the critically branched state	Kinetics of the variation of front factor, and network chain interactions
Stress—strain relations	Front factor, and network chain interactions in the final state	

Table 2 Oligomers investigated

Reacting system	M_2	M_3	M_c
Poly(dimethyl siloxane) + tri(dimethyl hydrosiloxy)silane	10 916	327	11 134
Benzene-1,3,5-triacetic acid + decamethylene glycol	174	252	306
Polyurethane triol + diol + diisocyanate	225	4 000 $f = 2.25$	11 423

in the vicinity of the gel point, as illustrated in *Figure 12*. Without entanglements the steepness of the function $G''(t)$ shows a sharp increase at the gel point. It is possible to calculate the range of conversions (or times) for which entanglements are produced, and the critical value of the molecular weight, M_e. The latter is not defined clearly yet.

(c) The front factor g can be calculated in the critically branched state.

(d) Comparison of the front factor in the critically branched state with that derived from the stress—strain measurements in the final state yield information about the kinetics of the variation of g.

(e) Subtraction of the $g \nu kT$ contribution to the modulus (see equation 31) from the characteristic $G_0(\lambda)$ yields information about the network chain interactions.

We shall now review results of the studies on the reaction

Table 4 Results for polyurethane

Order of the reaction	2
Reaction rate constant	0.12 min^{-1}
Gel point	$\alpha_c = 0.894$
Onset of the diffusion-controlled process	$\alpha = 0.969$
Kinetic entanglements are indicated	

Table 5 Results for polyester

	Front factor of the critically branched state	
	Kästner	Gordon and Roberts[7]
Run 22	1.11	1.205
Run 23	1.19	1.336

Kinetic entanglements
$$5\,\tau_0 \rightarrow \Delta Z = 10^{-2};\ \Delta t = 56 \text{ min};$$
$$M_e = 1.8 \times 10^6$$

Table 6 Results for polysiloxane

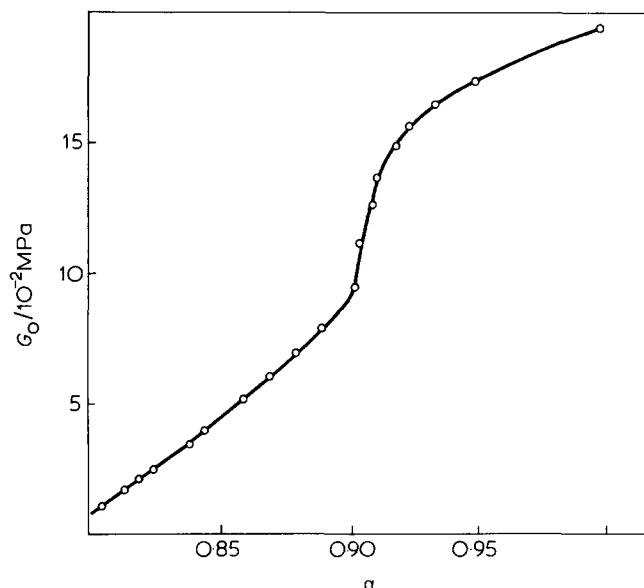| Mean value of $g(1 + C_2^*/C_1^*)$	0.98
Front factor at the critically branched state (assumed)	0.98
Front factor at the final state	0.35

Figure 13 Dependence of G_0 on the degree of conversion α for polysiloxane[41]

Figure 14 Example of an inhomogeneous network formation (ω = 6.3 x 10³ Hz)

lower, than values calculated by Gordon and Roberts[7] using another procedure. This shows that at the gel point there exists a high degree of fluctuation restrictions and the elastic behaviour corresponds to the classical theory of Wall and Flory[38]. Before the gel point, a kinetic entanglement state was found.

For a polysiloxane, the dependence of the modulus G_0 on the degree of conversion shows a peculiar, unexplained behaviour (*Figure 13*). A simple interpretation can be attempted, if we start from the experimental value of g at the final state, which lies near 1/3. We also assume that at the critical branched state the front factor is close to unity as found for the polymer system. Thus, during network formation, a transition from the model of Wall and Flory to that of James and Guth occurs. This transition is caused by the reduction of the mean length of the network chains, while the fluctuation amplitude remains nearly constant. Consequently, the ratio of the fluctuation amplitude to the mean junction distance increases, and the fluctuation restrictions decrease. Simultaneous with the reduction of fluctuation restrictions, the topological restrictions of network chains increase, and both these effects contribute to the behaviour shown in *Figure 13;* the change of steepness at a conversion of 0.9 indicates a transition.

Finally, an example of an inhomogeneous network formation is demonstrated. For this purpose, a polyurethane system containing small amounts of Aerosil was investigated. It was shown earlier using other methods[44], that Aerosil stimulates inhomogeneous network formation. *Figure 14* presents the results of dielectric measurements, exhibiting, in agreement with the theory, a maximum ε' before the gel point.

A problem still open for theoretical calculations is the exact value of the steepness parameter, σ, for the relaxation spectrum of the sol fraction. Gordon and Roberts[7] concluded from their measurements, that the value of σ was 2/3. It is supposed here, that σ should always be lower than 2/3 and should depend on the mean functionality of the oligomers. Our first estimates yield σ values equal to 0.51 and 0.55, respectively, for functionalities 2.25 and 3. This problem can be solved by further experimental investigation of the critically branched state using higher accuracy.
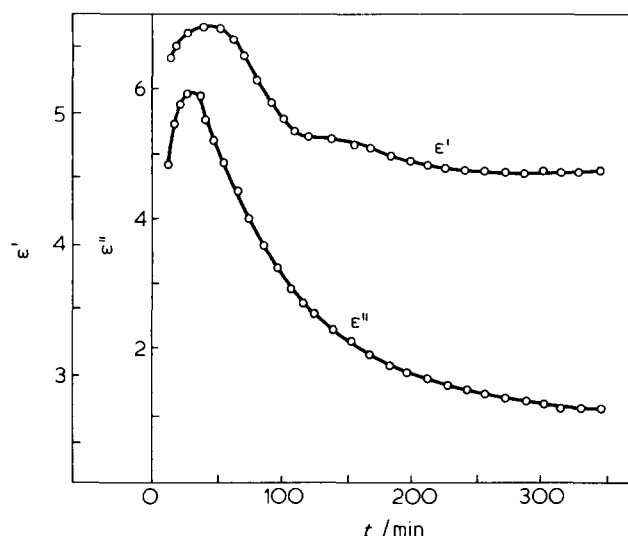
ACKNOWLEDGEMENTS

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