Study of three-dimensional polystyrene networks containing linear chains:
2. Relaxation spectrum of linear chains

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A study of the relaxation phenomenon in polystyrene networks containing linear polystyrene chains of high molecular weight has been carried out using measurements in methylcyclohexane and in the dry state by dynamic sinusoidal deformation and static stress relaxation. It is shown that the relaxation of the free chains contained in the network is (i) proportional to $(1 - v_2^2)$ where v_2 is the volume fraction of the crosslinked network in the dry state, and (ii) depends very little on their concentration in the network. The distribution of relaxation time shows a peak related to the glass transition of the networks and a second peak corresponding to the spectrum of the linear chains of high molecular weight.

INTRODUCTION

Model polystyrene networks containing varying proportions of linear polystyrene chains of high molecular weight have been prepared in order to demonstrate and study the relaxation of free chains contained in a similar environment.

In the first part of this study, we showed from swelling ratios and modulus measurements that the calculated number of elastic active chains and mean functionality shows that a non-negligible number of pendant chains appears during polymerization.

Having studied these networks, it seemed of interest to complete the studies already undertaken by measuring mechanical properties at low swelling rate and in the dry state. Experiments of this kind make it possible to show the relaxation of crosslinked chains, and the influence of entanglements or pendant chains.

The networks were obtained by anionic polymerization of styrene and divinylbenzene (DVB), with the molecular weight between crosslinks varying between 15 000 and 20 000. Free polystyrene chains of molecular weight $\overline{M}_n$ = 810 000 are retained inside the network at the crosslinking stage. Their proportion varied between 0 and 12.5%: 0, 2.5, 5, 7.5, 10, 12.5% for gels 1912, 1112, 2711, 612, 412 and 1712 respectively.

MEASUREMENTS IN METHYLCYCLOHEXANE

The study of the relaxation phenomenon of polystyrene networks in the dry state requires high temperatures and long times. For this reason it is interesting to reduce relaxation times by swelling the networks in a poor solvent.

In benzene and cyclohexane, the volume fraction of the network is less than 0.25, and so the relaxation times are very short and unattainable. On the other hand, we can study the chain relaxation in methylcyclohexane where the volume fraction of the polymer is around 0.5. Measurements consist of enforcing deformation on a sample, and measuring the stress necessary to maintain constant deformation over the time period. The stress relaxation for the networks studied is shown in *Figure 1*; it becomes negligible after about 3 h. The modulus and the corresponding number of network elastic chains are given in *Table 1.*

The number of elastic chains calculated is equal to that already found in benzene and cyclohexane (see Part 1). This confirms that equilibrium was indeed obtained after 3 h.

The stress relaxation observed is the sum of three effects: (i) the relaxation of the network; (ii) the relaxation of free chains and (iii) the swelling effect of the network under stress.

We have therefore shown in *Figure 2* the difference $G(t) - G_e$ which represents the difference of the stress

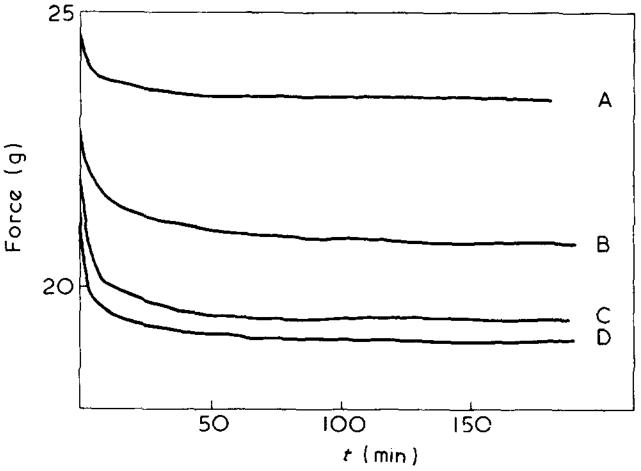

Figure 1 Stress relaxation for samples 1912 (A), 2711 (B), 412 (C), 1712 (D), containing 0, 5, 10 and 12.5% of linear chains respectively

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Table 1

Gel	Linear chains (wt %)	$G \times 10^{-6}$ at $t = 10^4$ sec (dynes/cm^2)	$\nu_e^* \times 10^5$ (mole/cm^3)
1912	0	0.127	4.95
1112	2.5	0.094	3.68
2711	5	0.163	6.37
612	7.5	0.125	4.90
412	10	0.129	4.91
1712	12.5	0.143	5.41

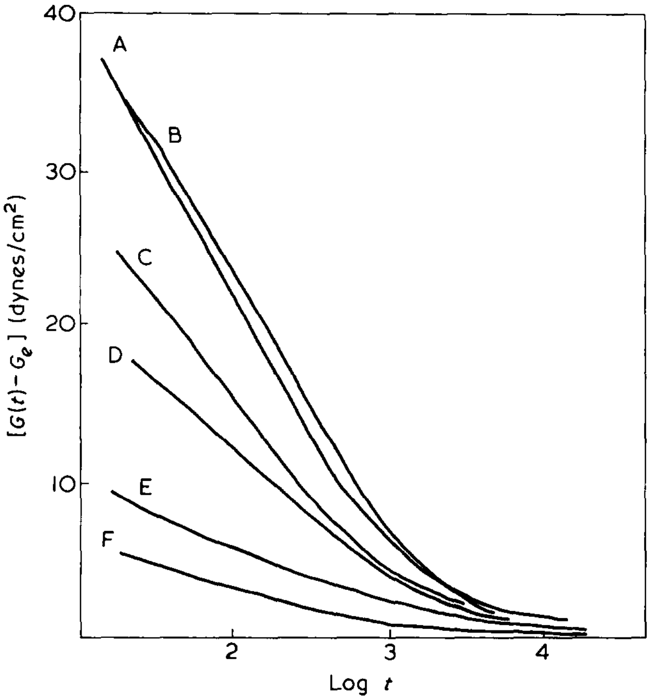

Figure 2 The contribution of free chains stress relaxation ($G(t)-G_e$) *versus* log t. A, 1712; B, 412; C, 612; D, 2711; E, 1112; F, 1912

relaxation modulus at time t from that at stress equilibrium. We can see that it becomes higher as the network contains more free chains. To calculate the contribution of the free chains to the stress relaxation modulus, we must subtract from $[G(t)-G_e]$ the stress relaxation modulus of the network without free chains. This quantity can be calculated from sample 1912 since this sample does not contain free chains.

If we suppose that relaxation is the same for all samples (the same $\bar{M}_n$ between crosslinks), we can calculate the modulus of free chains as follows:

$$G_{CL}(t) = |G(t)-G_e| - |G_0(t)-G_{0e}|$$

where $G(t)$ and G_e are the moduli of the network containing free chains at time t and at stress equilibrium respectively; $G_0(t)$ and G_{0e} are the same for sample 1912 without free chains.

The advantage of this method is that it is independent of the influence of swelling. These moduli are normalized at unit swelling ratio. To compare our results with those obtained by other researchers[1], we shall use Young's modulus:

$$G(t) = \frac{3f(t)}{S_0}\frac{1}{(\Lambda - \Lambda^{-2})}$$

where $f(t)$ is the force at time t, S_0 is the initial cross-section, and Λ is the stressed length/initial length.

Figure 3a represents the function $\log G_{CL}(t) = f(\log t)$. We can see that the value of the modulus depends on the number of free chains.

Ferry and coworkers[2] showed that for the copolymer ethylene–propylene, the relaxation of the free chains contained in networks of the same nature is proportional to $(1 - \nu_2^2)$, where ν_2 is the volume fraction of the cross-linked network in the dry state.

In *Figure 3b* we have plotted the curve: $\log G_{CL}/(1 - \nu_2^2) = f(\log t)$ at 17°C.

The curves are identical if we take into consideration the horizontal translation due to differences in relaxation times caused by different dilutions. This relaxation corresponds to the terminal zone as the modulus falls from the elastic plateau right down to the zero value. The modulus of free chains for low time scale must then correspond to the modulus at the elastic plateau for linear chains. The value of this modulus is independent of the molecular weight of linear chains and for polystyrene is equal to $G_{eN}^0 =$

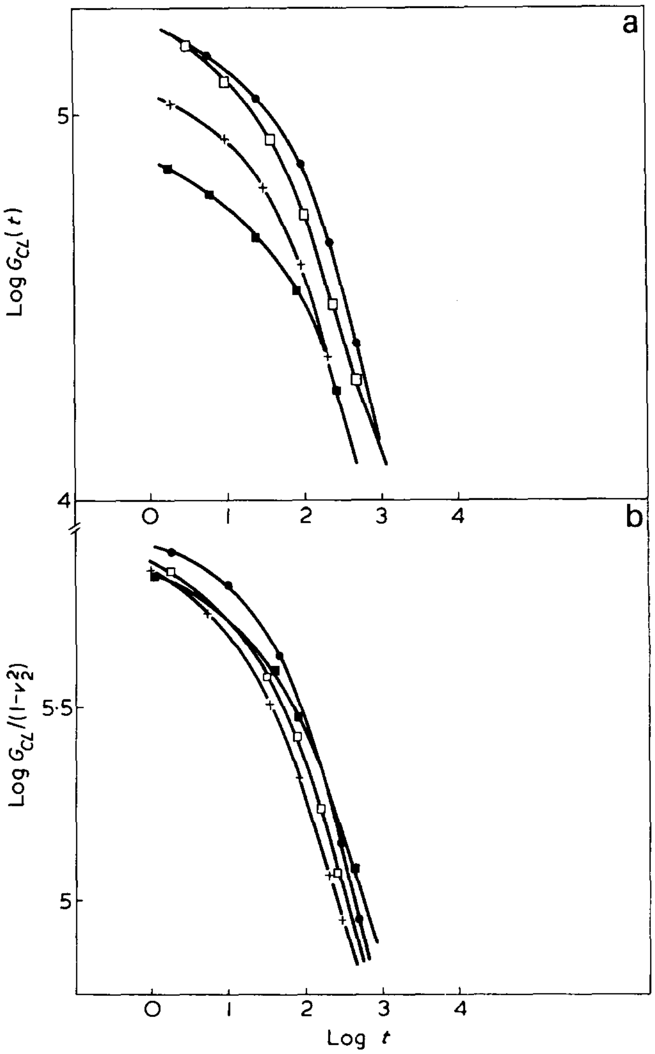

Figure 3 (a) Log $G_{CL}(t)$ *versus* log t; (b) log $G_{CL}/(1 - \nu_2^2)$ *versus* log t. ■, 2711; +, 612; ●, 412; □, 1712

Table 2

Gel	Linear chains (wt %)	$G^0_{eN} \times 10^{-6}$ at 160°C (dynes/cm^2)
2711	5	1.21
612	7.5	1.25
412	10	1.34
1712	12.5	1.11

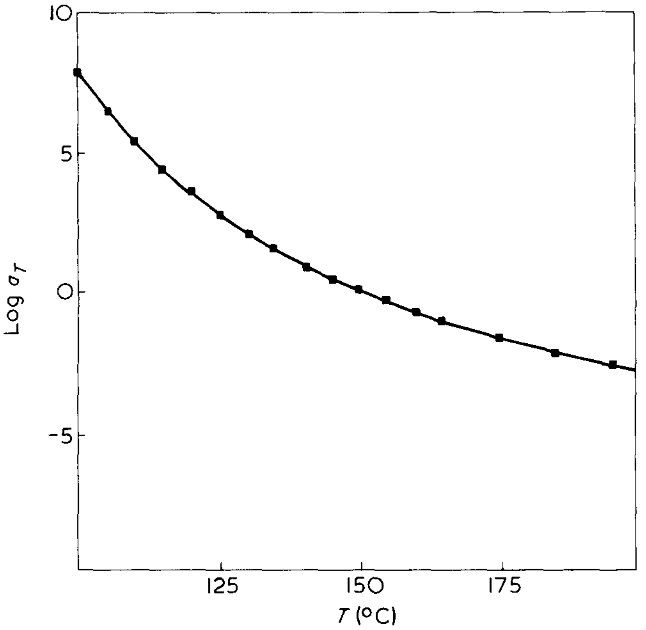

Figure 4 WLF equation. Log a_T *versus* T(°C) reduced to T_0 = 150°C. Loga_T = −8.55 ($T-T_0$)/104 + $T-T_0$

2 x 10^6 dynes/cm^2 at T = 160°C. (G^0_{eN} corresponds to the instantaneous force $f(t)$ measured after deformation.) In *Table 2* we present values of the modulus at the elastic level.

It is probable, however, that we can only see the end relaxation of free chains; some of the relaxation times are too short to be observed with the method used, and this leads to an underestimation of G^0_{eN}.

In the light of these results, the contribution of free chains to the modulus seems to be proportional to $(1 - \nu_2^{\frac{2}{3}})$. According to Ferry[2] this proportionality shows that we are dealing with a phenomenon which on the one hand, joins up temporary entanglements of free chains among themselves, and on the other hand, joins up free chains with the network.

MEASUREMENTS IN THE DRY STATE

Until now we have studied the behaviour of samples in the swollen state which, on the one hand, leads to a decrease in relaxation times and on the other implies polymer solvent interactions. In order to study the relaxation of the network and of the free chains that they contain, without taking into account any interactions other than those between polymer chains, we have taken the measurements in the dry state.

We measured the modulus using two techniques, which made it possible to plot master curves for a very wide range of frequencies and so calculate the relaxation spectra of the different samples.

Dynamic measurements

The Rheovibron enables the measurement of the complex modulus and the loss tangent δ. We can then calculate the storage modulus $G' = G^* \cos\delta$ and the loss modulus $G'' = G^* \sin\delta$. From these values at different frequencies and temperatures and after vertical shift corrections $\rho_0 T_0/\rho T$ (where ρ_0 and ρ are densities at reference temperature T_0 and at temperature T) we were able to calculate the coefficients of the WLF equation and so to plot the master curves (*Figures 4, 5* and *6*). However these measurements enable us to know the modulus only in the case of high frequencies over 10^{-3} radian/sec. We therefore had to complete them with measurements of stress relaxation.

Stress relaxation

We measured the variation of the modulus in static relaxation at three temperatures: 150°, 160° and 170°C. For each of these temperatures, we measured the stress at constant elongation. The deformation imposed on the sample varied from 5 to 15% according to the gel and the temperature.

The curves $G(t) = f(t)$ for different elongations are superimposable, which shows that for low deformations the modulus is independent of Λ. The curves $\log G(t) = f(\log t)$ at different temperatures are reduced to 150°C by applying a translation $\log a_T$. We obtain good superposition over a precision of about 5%. The master curves $\log G(t) = f(\log t a_T)$ are plotted in *Figure 7*.

So as to associate the measurements of static and dynamic relaxation, we calculated $G'(\omega)$ and $G''(\omega)$ from $G(t)$

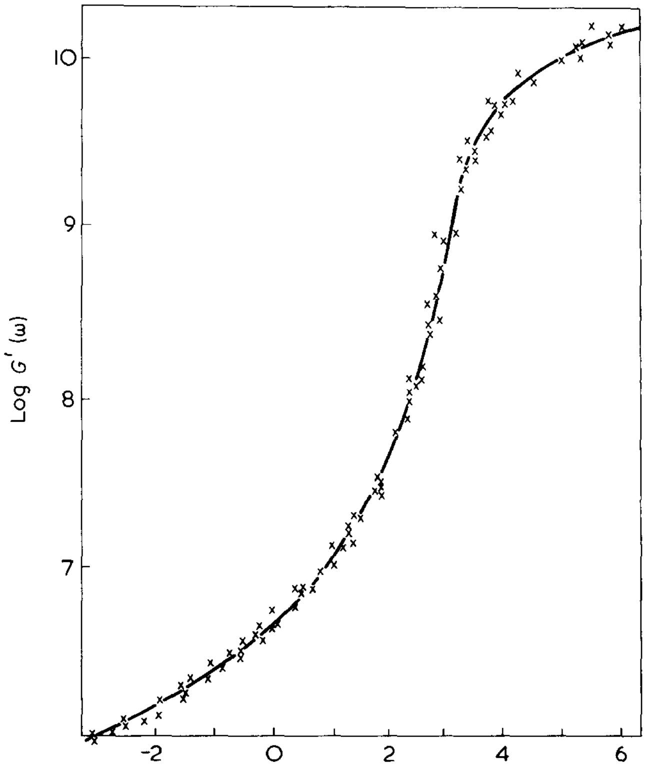

Figure 5 Master curve $\log G'(\omega) = f(\log \omega a_T)$ for the storage modulus G' reduced to T_0 = 150°C

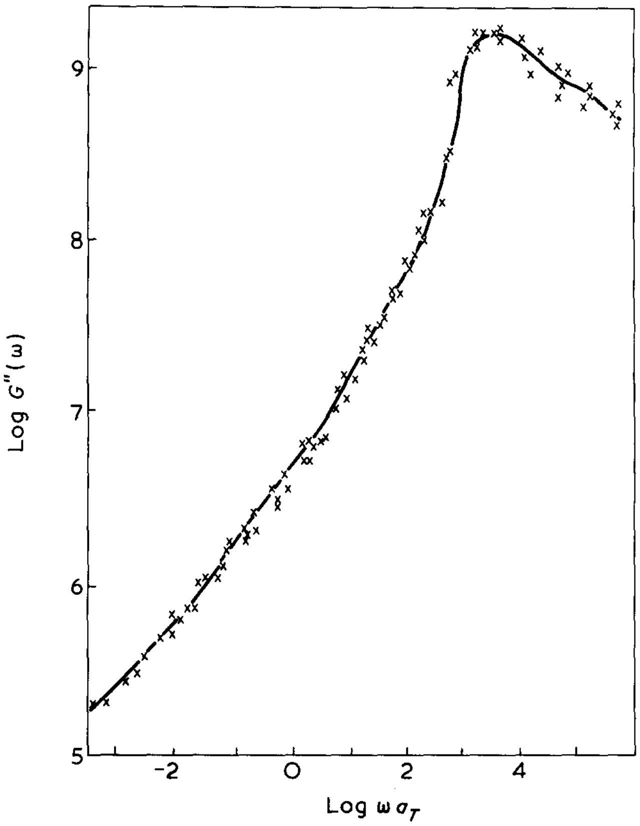

Figure 6 Master curve log $G''(\omega) = f(\log \omega a_T)$ for the loss modulus G'' reduced to $T_0 = 150°C$

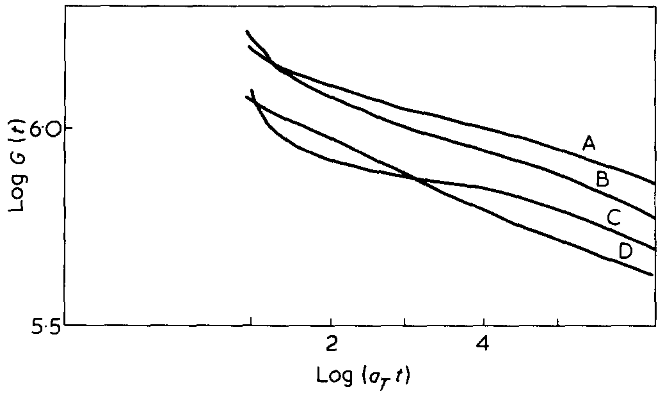

Figure 7 Master curves for static relaxation log $G(t) = f(\log a_T t)$ reduced to $T_0 = 150°C$. A, 2711; B, 1712; C, 1912; D, 412

using Schwarzl's approximation[3]. We are able to make the dynamic and the static measurements coincide to within a few percent. *Figure 8* represents the loss modulus and the storage modulus of the different samples.

We can see that for log $\omega < -3$, the decrease of the loss modulus $G''(\omega)$ is greater for networks containing free chains than for those with no free chains. The slope $|\mathrm{d} \log G''(\omega)/\mathrm{d} \log (\omega)|$ shows a trend to decrease with increasing 'free chains' (*Table 1*). In fact the elastic component of the system 'free chains–network' is equal to the sum of the storage modulus of the network and of the free chains. However at the terminal zone, the storage modulus of the free chains is reduced to zero, and the total elastic component decreases. It is clear that the more free chains in the network, the greater the drop.

On the other hand, the time required by the storage modulus of the free chains to cancel itself out must be porportional to their molecular weight as well as to the obstacles which they meet, and consequently on the nature of the network. As the networks are more or less identical, we can suppose that the kinetics of the relaxation of free chains will be the same for all our networks, which leads to an increase in the slope d log $G(\omega)$/d log ω against the quantity of free chains in the network. Also, when the relaxation of the free chains is complete, i.e. when the storage modulus and the static modulus of the free chains is zero, the variation of the observed modulus is then that of the network itself.

The curves which give the modulus of the different samples are parallel for log $\omega < -5$ (*Figure 7*) and so show that the relaxation of free chains is over. The flow of free chains also causes an increase in the viscous component and so in the loss modulus, which gives the latter a higher value for gels containing free chains (*Figure 8*). We can therefore consider that for log $\omega < -5$, the modulus is that of the network itself; this makes it possible to calculate the modulus of the free chains.

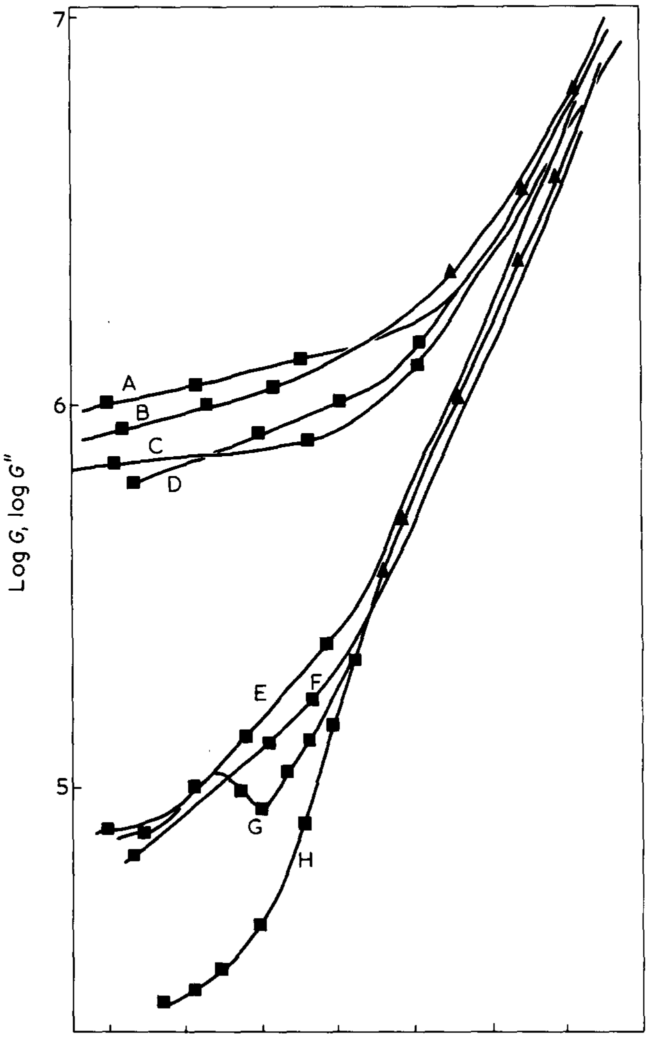

Figure 8 Log G' and log G'' *versus* log ωa_T for the storage and loss moduli of the differents samples, in dynamic ▲ and static ■ relaxation. $G'(\omega)$: A, 2711; B, 1712; C, 1912; D, 412. $G''(\omega)$: E, 1712; F, 412; G, 2711; H, 1912

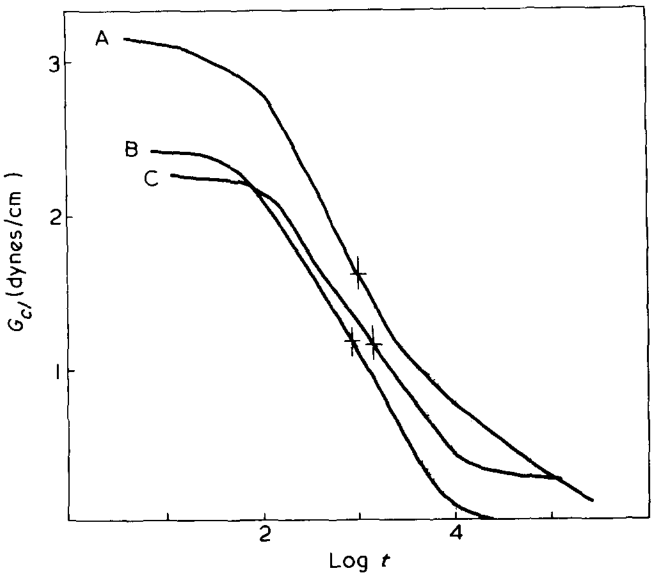

Figure 9 Modulus of the free chains G_{CL} in dynes/cm^2 *versus* log$t$ for differents samples. +, the time of half relaxation. A, 1712; B, 412; C, 2711

Following the same reasoning as for relaxation in methyl cyclohexane, the relaxation of the network and of free chains will be:

$$G(\omega) - G(\omega = 10^{-5}\ \mathrm{sec}^{-1})$$

If we subtract the relaxation of the network calculated with sample 1912 that is:

$$G_0(\omega) - G_0(\omega = 10^{-5}\ \mathrm{sec}^{-1})$$

we can obtain the modulus of the free chains:

$$G_{CL}(\omega) = |G(\omega) - G_0(\omega)| - |G(\omega) - G_0(\omega)|_{\omega = 10^{-5}\ \mathrm{sec}^{-1}}$$

Figure 9 represents the modulus of the free chains of the different samples. We cannot, on examining this Figure, establish the relationship between this modulus and the number of free chains, as we did for methyl cyclohexane. However, if we consider the half life of the relaxation, that is the time if takes for the initial value of the modulus to diminish by half, we note that this time is identical for all three concentrations, that is $t = 10^3$ sec, and deduce that the relaxation time of free chains depends very little on their concentration in the network.

Knowing the modulus for a very wide frequency range we can calculate the relaxation spectrum (from G' data of *Figure 8*) of the samples with Williams and Ferry approximation (*Figure 10*). The networks which contain free chains present a spectrum which is identical to that of the relaxation of linear polystyrene chains of high molecular weight.

We obtain a distribution of relaxation times which shows an initial peak corresponding to the glass transition and a second peak for long times. This peak does not appear in the case of a network with no free chains. We can therefore conclude, as in the case of the spectrum of linear chains, that this peak is due to the relaxation of the free chains inside the network.

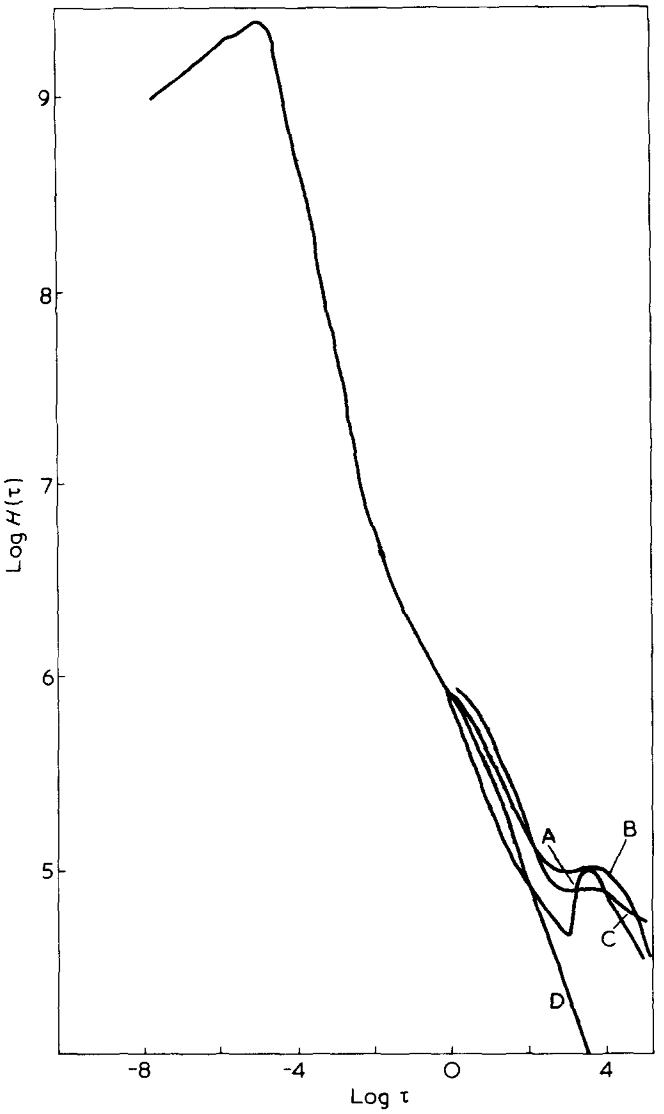

Figure 10 Relaxation spectrum $H(\tau)$ *versus* logτ for samples 1912 and 612, 412, 1712. A, 12.5%; B, 10%; C, 7.5%; D, 0%

We must note, however, that for linear chains of low molecular weight, the second peak overlaps the main peak and does not appear on the spectrum. This justifies the use of linear chains of high molecular weight which made it possible for us to separate the relaxation times of the network and of the free chains, and so measure this relaxation, and relate it to the quantity of free chains.

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