# Comparative study of stress relaxation of radical and anionic gels

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A comparative study of the physicochemical properties of radical and anionic polystyrene gels was undertaken to show the distinctive features of these two kinds of networks. In the condensed phase, the measurements of viscoelasticity gave evidence of considerably shorter relaxation times than for anionic gels, linked to the high degree of entanglement in radical networks. This influence is also seen in the value of the elasticity modulus, as the number of active chains is notably higher in the dry phase than in the swollen state.

## INTRODUCTION

The object is to show the distinctive features of radical and anionic polystyrene gels, by studying the physicochemical properties in the swollen and condensed state.

In the swollen state, the high polydispersity in molecular weight of radical gels acts preferentially on the structural parameters of the networks (the mean functionality of the crosslinks and the number of elastic active chains). This leads us to define the network by a two phase model made up of the elastic active chains and of nodules whose crosslinking density is high[1].

The use of this model makes the values of the structural parameters, which control the physicochemical behaviour in the swollen state, more coherent. This leads us to define the parameters $Q_{va}$, $Q_{vr}$, $\bar{M}_c$, $\bar{M}'_c$, in which $Q_{va}$ and $\bar{M}_c$ represent the apparent swelling ratio and molecular weight, $Q_{vr}$ and $\bar{M}'_c$ the same parameters, but taking into account the contribution of the elastic active chains in the network only[1].

Continuing this comparative study, we undertook measurements of viscoelasticity so as to show the role of entanglements, given the high concentration at the crosslinking stage (30 and 50%) compared with that for ideal networks (7.5%).

## EXPERIMENTAL

The viscoelasticity study of radical gels was carried out on 6 samples of varying porosity or molecular weight, prepared with polymer concentrations of 30 and 50%.

The dynamic measurements were taken with a Rheovibron model DDV II–B, which gives loss and conservation moduli against frequency and temperature. We used 6 frequencies: 0.035; 0.11; 0.35; 3.5; 11 and 35 Hz, the temperature being varied each time between 80° and 200°C. Temperature measurement was carried out with a constantan–copper thermocouple placed near the sample and linked to a digital voltmeter. Temperature stability was assumed to be within ±1/10°C. Circulation of nitrogen made it possible to avoid any oxidative degradation of the network. The experimental results are plotted in *Table 1*.

## ELASTIC MODULUS OF RELAXED NETWORKS

In *Figures 1, 2* and *3* we have plotted the master curves reduced to $T = 150°C$, relative to the elastic modulus, $G'$, for anionic gels and radical gels prepared at concentrations of 30 and 50%.

For radical and anionic gels, we have carried forward in *Table 1*, the value of Young's modulus, defined from the

*Table 1*

| Gel number | Concentration $q_c^{-1}$ (%) | $\bar{M}'_c$ (ref 1) | $E$, (dynes/cm$^2$) (viscoelasticity measurements) | $3GQ_{va}^{1/3} \times \frac{\rho T}{\rho_0 T_0}$ (dyne/cm$^{-2}$) (Modulus measurement in swollen state[1]) | $3GQ_{vr}^{1/3} \times \frac{\rho T}{\rho_0 T_0}$ (dyne/cm$^{-2}$) |
|---|---|---|---|---|---|
| 2511 | 30 | 11400 | $4.55 \times 10^6$ | $2.49 \times 10^6$ | $2.63 \times 10^6$ |
| 112 | 30 | 40660 | $2.86 \times 10^6$ | $4.43 \times 10^5$ | $5.40 \times 10^5$ |
| 312 | 30 | 6600 | $5.85 \times 10^6$ | $4.72 \times 10^6$ | $5.10 \times 10^6$ |
| 812 | 50 | 14000 | $7.9 \times 10^6$ | $2.69 \times 10^6$ | $2.94 \times 10^6$ |
| 1012 | 50 | 25000 | $6.1 \times 10^6$ | $1.32 \times 10^6$ | $1.46 \times 10^6$ |
| 512 | 50 | 64400 | $4.5 \times 10^6$ | $3.75 \times 10^6$ | $4.7 \times 10^5$ |
| 343 | Anionic gels | 10000 | $1.6 \times 10^6$ | $1.23 \times 10^6$ | $1.23 \times 10^6$ |
| 743 | | 20000 | | $5.74 \times 10^5$ | $5.74 \times 10^5$ |
| 2743 | | 30000 | | $3.80 \times 10^5$ | $3.80 \times 10^5$ |
| 1912 | | 20000 | $6.0 \times 10^5$ | $5.7 \times 10^5$ | $5.7 \times 10^5$ |

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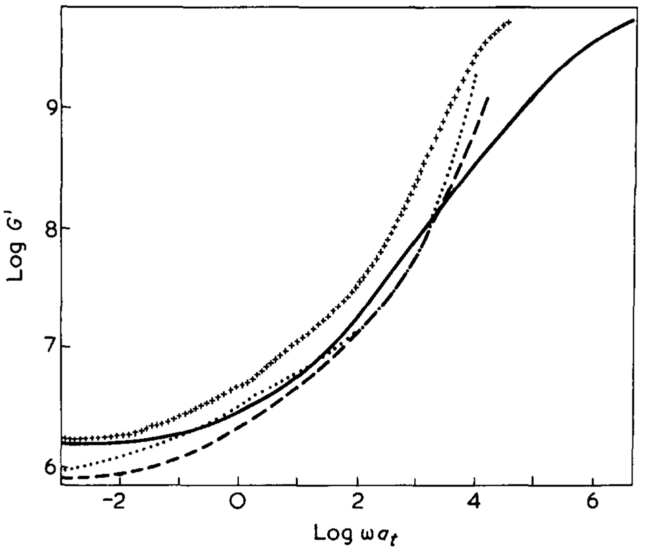

*Figure 1* Master curves log $G'$ *versus* log $\omega a_t$ for four anionic samples at different molecular weights, $G'$ reduced to 150°C. ———, 343, $\bar{M}_n = 10\,000$; – – –, 743, $\bar{M}_n = 20\,000$; · · · ·, 2743, $\bar{M}_n = 30\,000$; + + + +, 553, $\bar{M}_n = 75\,000$

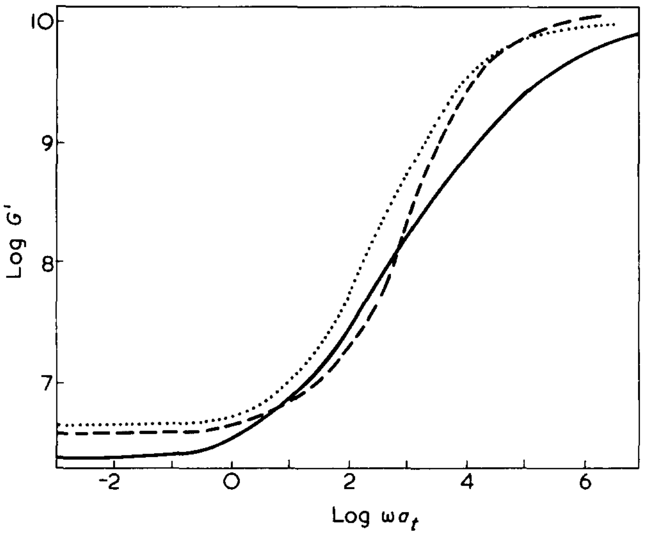

*Figure 2* Master curves log $G'$ *versus* log $\omega a_t$ for three radical gels at $q_c = 30\%$. Radical gels ($c = 30\%$): · · · ·, 312 ($\bar{M}'_c = 6600$); – – – –, 2511 ($\bar{M}'_c = 11\,400$); ———, 112 ($\bar{M}'_c = 40\,700$)

elastic level of the master curve reduced to $T = 150°C$. For the sake of comparison, we have also given the corresponding value of Young's modulus determined with crosslinks at swelling equilibrium in benzene and in cyclohexane, taking into account some corrections in temperature and density[1]. For this correction we took into account either the apparent swelling ratio $Q_{va}$ of the crosslink, or the real swelling ratio determined by the two phase model[1].

### *Anionic gels*

In most cases of dynamic measurements of relaxation we were not able to show the elastic equilibrium except for gels 343 and 1912, of molecular weights 10 000 and 20 000. In these cases and within the limit of experimental errors, the number $v_e^*$ of elastic active chains (per unit volume of dry polymer) is the same in the dry and swollen state; this is in agreement with the Gaussian theory of rubber elasticity.
It also signifies that the rate of entanglement which could appear in the condensed phase is negligible (in relation to the effect of high dilution at the crosslinking stage).

### *Radical gels*

*Figures 2* and *3* represent the master curves reduced to 150°C for radical gels at 30 and 50% concentration. We can see that these kinds of network have much quicker relaxation times than anionic gels (*Figure 1*), whatever the molecular weight $\bar{M}'_c$ of their elastic chains (elastic level).

For radical gels, the elastic level is very rapidly attained (a few minutes at 150°C), making it possible to compare the equilibrium modulus with the modulus which was characterized in the diluted phase, taking into account normalization in temperature, swelling ratio and density. The values in *Table 1* show that whatever the swelling ratio chosen, $Q_{va}$ or $Q_{vr}$, the extrapolated moduli are considerably inferior to Young's moduli, and this all the more so as the molecular weight $\bar{M}'_c$ is high. Thus the influence of network defects (polydispersity of chain links, pendant chains, entanglements) is of greatest importance in the condensed phase and contributes to a great extent in underlining the distinctive characteristics of radical networks.

So as to define the structural parameters which differentiate radical and anionic gels, we have plotted in *Figure 4*, the values of the Young modulus, $E$, against $\bar{M}_c^{-1}$ and $\bar{M}_c'^{-1}$, in accordance with the Gaussian description of rubber elasticity. The slope of the straight line obtained in this way is linked to the 'memory terms' $q_0$ as follows:

$$q_0^{-2/3} = q_c^{-2/3} \frac{\langle r_c^2 \rangle}{\langle r_{0s}^2 \rangle}$$

in which $\langle r_{0s}^2 \rangle$ and $\langle r_c^2 \rangle$ represents the mean square end-to-end distance of network chains in the swollen reference state and after crosslinking, respectively. We can note that, whatever the model used, the results obtained show the preponderant influence of the concentration of polymeric chains at crosslinking ($q_c^{-1}$).

On the one hand, the original ordinate, zero for anionic gels, is a growing function of this parameter. However,we know that when $q_c^{-1}$ is less than 10%[2-5], the entanglement ratio must be very low, which explains the behaviour of ideal networks in the condensed phase[2]. For radical gels prepared

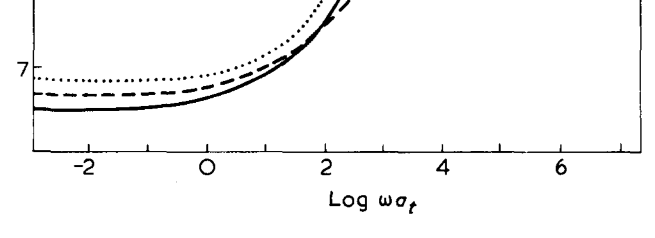

*Figure 3* Master curves log $G'$ *versus* log $\omega a_t$ for three radical gels at $q_c = 50\%$. Radical gels ($c = 50\%$): . . . . , 812 ($\bar{M}'_c = 14\,000$); – – –, 1012 ($M'_c = 25\,000$); ———, 512 ($\bar{M}'_c = 64\,400$)

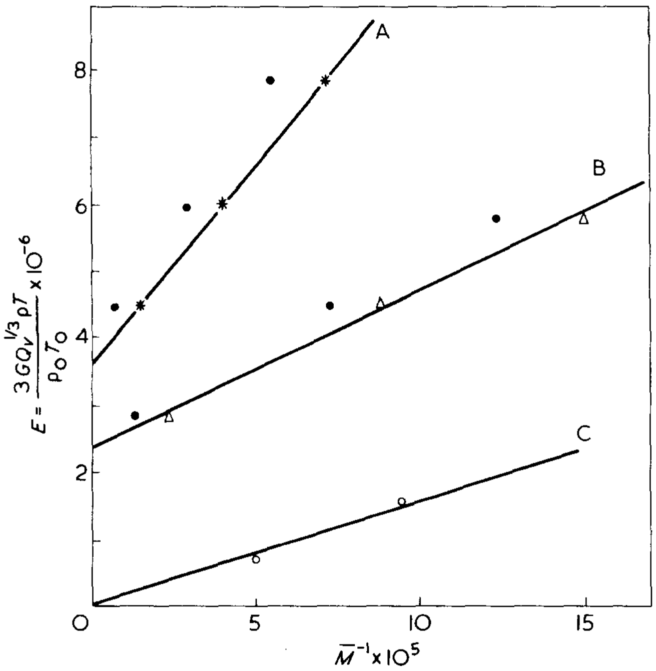

*Figure 4* $3GQ_v{}^{1/3}\rho T\rho_0^{-1}T_0{}^{-1}$ *versus* $\bar{M}^{-1}$ for anionic and radical samples without molecular weight correction (●, $\bar{M}_c$) and with the two phases correction (*$M'_c$). Radical gels: A, 50%, $\langle r_c\rangle/\langle r_{0s}^2\rangle = 1.46$; B, 30%, $\langle r_c^2\rangle/\langle r_{0s}^2\rangle = 0.8$; Anionic gels: C, $\langle r_c^2\rangle/\langle r_{0s}^2\rangle = 0.95$

at concentration $q_c{}^{-1}$ at 30 and 50%, however, the influence of entanglements is very marked (the original ordinate not being zero), which partly explains the high value of the moduli in the dry state.

On the other hand, the relationship $\langle r_c^2\rangle/\langle r_{0s}^2\rangle$ must, according to its definition, represent values linked only to the experimental parameters at the crosslinking stage, independent of the nature of the tests made later. It is clear that this feature of ideality, credible in the diluted phase, becomes less so in the condensed phase, given the complex topology of a polymeric network and of the intensity of the resulting intermolecular contacts. At a concentration of 30%, the ratio $\langle r_c^2\rangle/\langle r_{0s}^2\rangle$, equal to 0.8 gives evidence of a behaviour similar to that of anionic gels, except for the high proportion of entanglements in the network, the proportion of which remains quite independent of crosslinking density, in the region of molecular weight examined. On the contrary, for samples prepared at $q_c^{-1}$ = 50% this ratio is considerably higher, which contradicts its definition, as $\langle r_c^2\rangle$ cannot be greater than $\langle r_{0s}^2\rangle$. Paradoxically, for these crosslinks, the rate of entanglement seems to increase rapidly when the molecular weight decreases, and this contrary to the behaviour of linear chains in a solution. But it is possible that this contradication is only apparent and that it is necessary to reason in terms of topology, rather than crosslinking density. It is indeed reasonable to assume that structural defects (polydispersity, pendant chains, entanglements) increase as does the concentration $q_c^{-1}$. Up to a value of 30%, the influence of entanglements seems to be more marked than that of pendant chains, whereas, at 50%, the latter is important as it contributes actively in creating permanent entanglements.

## SPECTRUM OF RELAXATION

$H(\tau) = f(\log\tau)$. Using the Williams and Ferry approximation[6,7], we have plotted the relaxation spectrum $H(\tau)$ against $\log(\tau)$ in *Figure 5* for radical samples (812, 112) and anionic samples (343, 1912, 553). We can establish that for short times, no distinctive feature appears to separate these two types of networks as their glass transition temperatures are sufficiently close for all the samples examined. But, for longer times, the differences are much more important. Radical networks are the ones which have the shortest relaxation times; this is certainly attributable to the high degree of entanglement of polymeric chains.

With anionic networks, the elastic equilibrium appears only for static measurements at long time[2]. The influence of polydispersity hardly counts then in the measurement of relaxation spectra, whereas we could expect a much wider spectrum in the case of radical gels.

## CONCLUSION

Measurements of viscoelasticity show relaxation times of radical gels considerably shorter than those of anionic gels. This particularly makes possible a precise definition of the stress equilibrium, taking into account the crosslinking den-

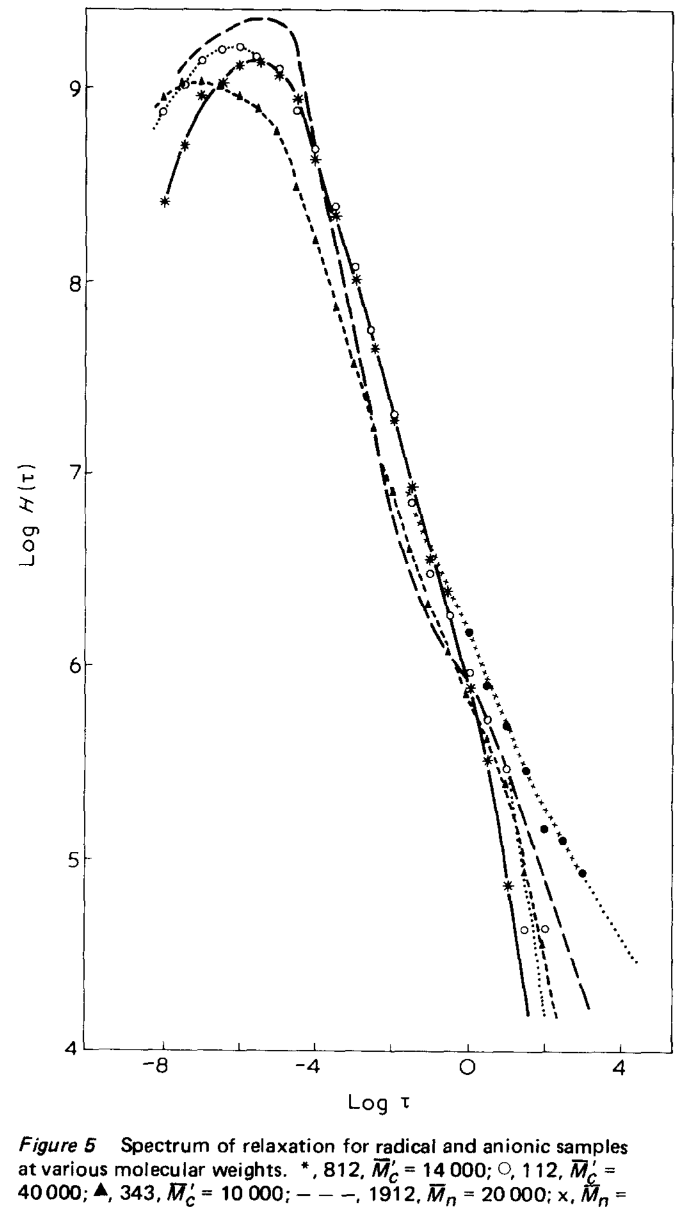

*Figure 5* Spectrum of relaxation for radical and anionic samples at various molecular weights. *, 812, $\bar{M}'_c$ = 14 000; ○, 112, $\bar{M}'_c$ = 40 000; ▲, 343, $\bar{M}'_c$ = 10 000; – – –, 1912, $\bar{M}_n$ = 20 000; x, $\bar{M}_n$ = 75 000

sity in the condensed phase. The results that we have obtained, clearly display the preponderant influence of concentration at the crosslinking stage, which causes a fair degree of entanglement and increases the apparent number of permanent physical knots. On the other hand, in the diluted phase, the mobility of polymeric chains is such that the physical knots are only temporary and the influence of concentration is then quite negligible. This high degree of entanglement consequently modifies the extent of the relaxation spectrum.

We note that all of the physicochemical results show the high proportion of structural defects which appear selectively according to the nature of the test employed. High polydispersity, which is one of the properties specific to radical gels, only appears in the characterization of the number of elastic chains in the diluted phase[1], whereas the influence of concentration is especially evident in the dry state, because of the intensity of intermolecular contacts between polymeric segments.

## REFERENCES

1 Choquet, M. and Rietsch, F. *Polymer* 1978, **19**, 519
2 Rietsch, F. and Froelich, D. *Eur. Polym. J.* submitted for publication
3 Hase, J. and Janacek, J. *J. Polym. Sci. (C)* 1967, **16**, 317
4 Janacek, J. and Hasa, J. *Collect. Czech. Chem. Comm.* 1966, **31**, 2186
5 Hasa, J., Ilasvsky, M. and Janacek, J. *Collect. Czech. Chem. Comm.* 1967, **32**, 4156
6 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1970
7 Williams, M. L. and Ferry, J. D. *J. Polym. Sci.* 1953, **11**, 169