Effect of chain length on the network modulus and entanglement

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The viscoelasticity of a series of monodisperse molten polystyrenes was investigated over a wide molecular weight range (9200 to 756 300). The plateau modulus was determined as the value of G' at the minimum of $\tan \delta$ in the rubbery zone, because this point defines a gel-like viscoelastic behaviour. A possible dependence of the entanglement density on chain length was explored, as a recent model predicts such an effect. The experimental indication is that the onset of the entanglement network occurs rather abruptly around M_e and that the entanglement density is constant for $M > M_e$.

(Keywords: entanglement; plateau modulus; melt viscoelasticity; polystyrene)

INTRODUCTION

Despite extensive experimental and theoretical work in the past decades, polymer melt viscoelasticity is still a challenging topic. Even the physical nature of the stress originating from a strain (or from a strain rate) applied to a polymeric liquid is a matter of controversy. In the generally accepted framework the stress arises mainly from the intramolecular force due to the orientation of the bond vectors of the chain (entropic origin)[1]. However, in a recent series of papers[2–5] many viscoelastic properties, both below and above T_g, were modelled in terms of intermolecular (enthalpic) dielectric interactions. Among other things, the entanglement concept is often discussed and revised in the literature, as it is one of the most typical features of chain molecules and a key factor controlling the melt rheology[1,6] and the solid-state deformation mechanisms[7,8].

It is frequently useful to think of entanglements as defined contact points between chains acting like pseudo-crosslinks; however, it is more correct to represent entanglements by a rather 'delocalized' picture[6]. In the reptation theory[1], for instance, an entanglement spacing is not specified; however, the tube diameter proves to be an equivalent parameter.

The molecular weight between entanglements, M_e, is usually determined from the rubbery plateau modulus G_N^0 through an equation derived from the theory of rubber elasticity:

$$M_e = \frac{\rho RT}{G_N^0} \tag{1}$$

where ρ is the density of the polymer, R the gas constant and T the absolute temperature.

In the literature there are many models which describe the entanglement network of polymer melts[5,9–17], and sometimes they are quite different. Relevant for this paper is the model recently proposed by Kavassalis and Noolandi[15–17], in which the entanglement spacing is considered as a quantity representing an averaged topological parameter. They imagined a test chain divided into a number of blobs, each containing N_e segments, where the number of segments between entanglements is initially an arbitrary parameter. They calculated the number of tail segments in the blob and the number of segments threading the blob without a tail, and considered only the latter as effective for topological constraining. Within this framework, M_e was found to be independent of chain length and determined by intrinsic properties only for quite high molecular weights; conversely, as the molecular weight decreased (being still above the entanglement spacing), a marked increase of M_e was predicted.

In the present work the melt viscoelasticity of a series of monodisperse polystyrenes was investigated, to seek a possible dependence of G_N^0 on molecular weight. A comparison was made between different methods of G_N^0 assessment in order to determine it carefully over a wide molecular weight range.

EXPERIMENTAL

Materials

A series of narrow-distribution polystyrenes (PS), normally used as calibration standards for g.p.c. instruments, was investigated. Their molecular data, as attested by the supplier (Polymer Laboratories), are reported in *Table 1*. It can be seen that the molecular weights span almost two decades. The smallest chain length investigated (sample PS-9) is well below the entanglement spacing of PS, which is approximately in the molecular weight range ≈17 000–21 000[6,7,18–20]. Sample PS-8 has a molecular weight similar to M_e and sample PS-7 has a molecular weight similar to or slightly lower than M_c, where M_c is the critical molecular weight for the transition from $\eta_0 \propto M$ to $\eta_0 \propto M^{3.4}$, where η_0 is the zero shear viscosity.

Rheological characterization

The materials were compression-moulded to form discs subsequently used for the melt viscoelasticity character-

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Table 1 Molecular parameters and network moduli of the monodisperse polystyrenes used in this study

Sample	M_w	M_w/M_n	G' at tan δ minimum (10^5 Pa)
PS-1	756300	1.04	2.06
PS-2	326600	1.03	2.09
PS-3	222200	1.03	2.06
PS-4	94300	1.04	2.06
PS-5	66400	1.03	1.95
PS-6	50800	1.03	1.99
PS-7	30200	1.03	2.03
PS-8	18900	1.05	2.35
PS-9	9200	1.03	3.80

ization: this was carried out with a Rheometrics mechanical spectrometer RMS-800. Sinusoidal strain was imposed, with a small-oscillation amplitude to stay within the linear viscoelasticity limits of the materials. Frequency sweeps at different temperatures were performed. For each material both the rubbery plateau and the terminal region were explored. As the molecular weight affects the relaxation time and the glass transition temperature too, different temperature ranges were investigated: for PS-9 the range was 120–150°C, whereas for PS-1 it was 150–260°C.

For all the polystyrenes the viscoelastic quantities of interest for this work (G', G'', tan δ) were superimposed at the reference temperature of 150°C by means of a suitable software (Rhecurve, supplied by Rheometrics).

RESULTS

Plateau modulus from integration of the loss modulus

As long as equation (1) is used to estimate entanglement spacing, the most crucial point is the determination of the plateau modulus. One method is the integration of the loss modulus G'' in the terminal zone[6,9,20–23]. However, as pointed out by Ferry[6], some guesswork is needed to separate the contribution of the terminal zone from the rest of the relaxation spectrum. A practical method of doing this is to integrate the G'' vs ω dispersion from $-\infty$ to the frequency $\omega_{\max}$ at which G'' has a maximum and to double the result; thus the plateau modulus is given by[9,20–23]

$$G_N^0 = (4/\pi)\cdot\int_{-\infty}^{\omega_{\max}} G''\,\mathrm{d}(\ln\omega) \qquad (2)$$

The determination of the plateau modulus by integration of the loss modulus terminal zone is sometimes questionable. For instance, Masuda *et al.*[22] found with PMMA samples that M_e increased with molecular weight, a trend which appears unrealistic and very difficult to account for. Furthermore, if the molecular weight is not high enough or if there is polydispersity, the maximum in the G'' vs ln ω dispersion becomes rather indefinite. *Figures 1* and *2* show the G'' master curves split into two groups for clarity. The G'' maximum is weak for sample PS-3 with molecular weight 222000 and becomes a vague shoulder at lower molecular weights. This is consistent with the work of Onogi *et al.*[20], in which equation (2) was applied only to PS samples with a molecular weight above 215000.

Even when the maximum is well defined, a closer inspection of the experimental data shows some degree of uncertainty: *Figure 3* shows the master curve of G'' for the PS-1 material; the arrows mark a possible range for the upper integration limit of equation (2). Consequently the plateau modulus estimation varies from 135 to 173 kPa. Thus the error which can be introduced in the calculation is quite high; in this case also, the mean value appears to be underestimated. For lower molecular weights the uncertainty in defining the upper integration limit is even more severe.

Plateau modulus from G' at the tan δ minimum

If entanglements are thought of as localized points, it is well known[24] that they have to be considered, at least instantaneously, as fixed points like crosslinks, in order to apply the kinetic theory of rubber elasticity. Also, in a more 'delocalized' picture of entanglements, Graessley

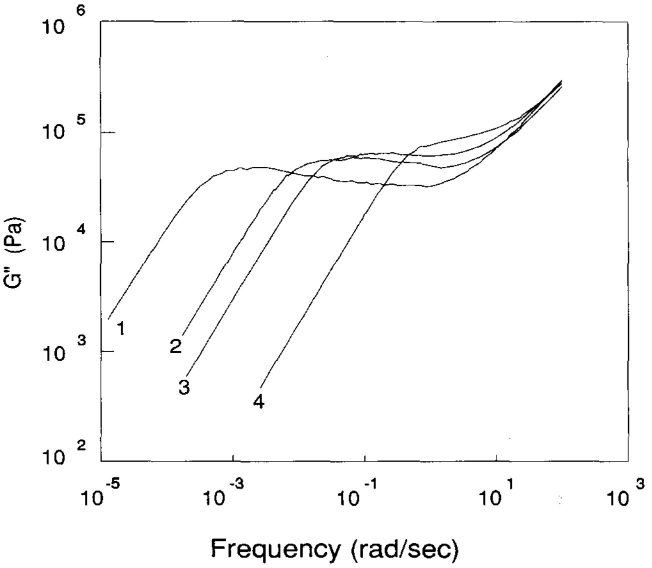

Figure 1 Double-logarithmic plots of G'' vs ω at 150°C for medium–high molecular weight monodisperse polystyrenes. Labels refer to sample numbers in *Table 1*

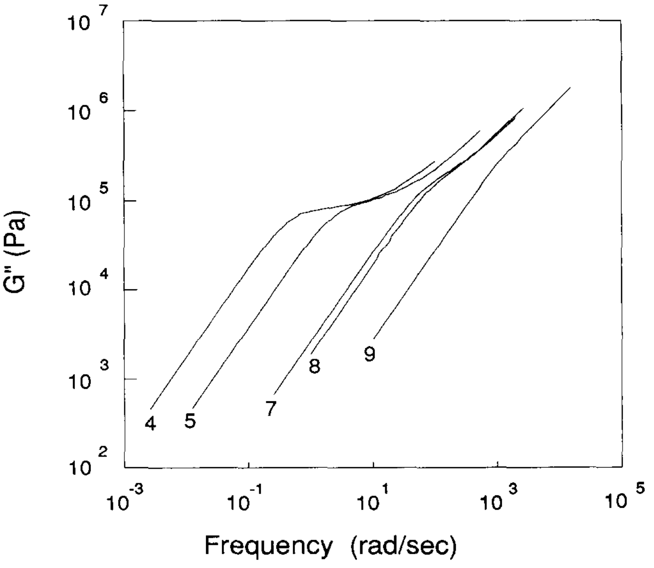

Figure 2 Double-logarithmic plots of G'' vs ω at 150°C for medium–low molecular weight monodisperse polystyrenes. Labels refer to sample numbers in *Table 1*

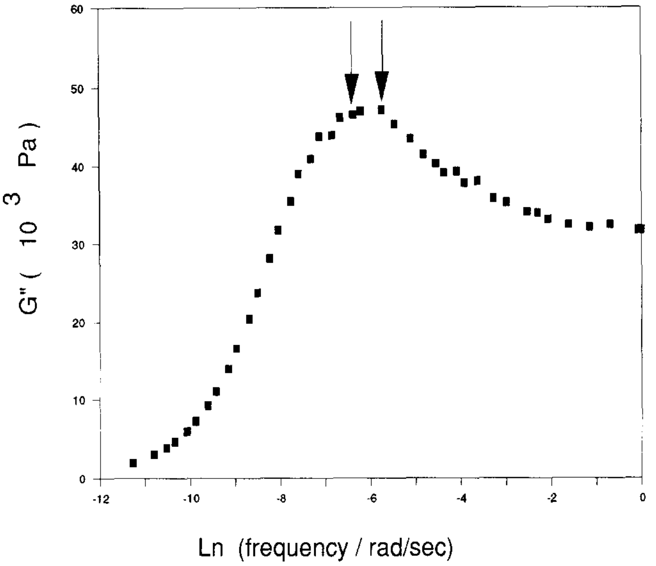

Figure 3 G'' vs $\ln \omega$ at 150°C for PS-1. The arrows mark a possible range for the upper integration limit of equation (2)

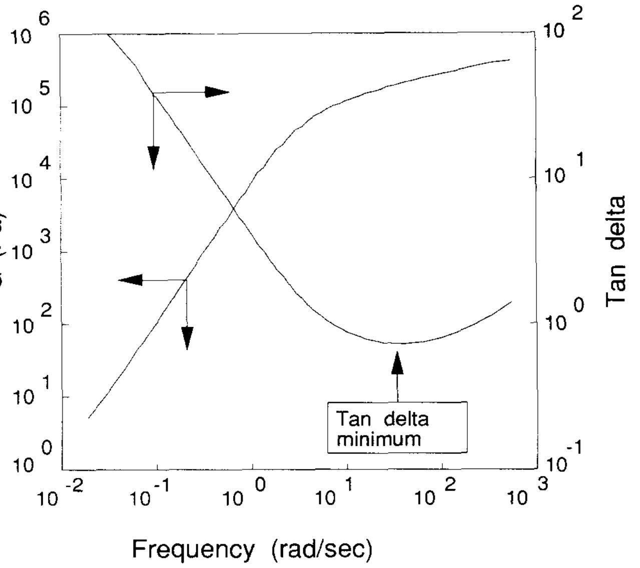

Figure 4 G' and $\tan \delta$ master curves at 150°C for PS-5. The $\tan \delta$ minimum in the rubbery plateau region is marked

and Edwards[13] pointed out that G_N^0 is an instantaneous modulus. Therefore it is conceivable that the plateau modulus can be characterized by a single point in the modulus–time (modulus–frequency) curve.

Recently the following criterion for the determination of G_N^0 has been used:

$$G_N^0 = (G')_{\tan \delta \to \text{minimum}} \qquad (3)$$

where the plateau modulus is taken to coincide with the storage modulus at the minimum of $\tan \delta$ in the rubbery plateau region of the material. This method has been applied to homopolymers[9], random copolymers[18] and miscible polymer blends[25–27].

In *Figure 4* the G' and $\tan \delta$ vs ω master curves at 150°C of PS-5 ($M_w = 66400$) are plotted. It can be noticed that the minimum of $\tan \delta$ in the rubbery plateau region for this material is well defined, whereas its G'' terminal zone appears only as a weak shoulder (*Figure 2*).

If one restricts the analysis of the viscoelastic functions very locally around the frequency at which the $\tan \delta$ minimum occurs, it is interesting that a viscoelastic model of a gel-like situation can be adopted. Winter *et al.*[28,29] modelled the viscoelastic functions both for chemical and for physical gelation processes. At the gel point the following scaling law is observed:

$$G'(\omega) \propto G''(\omega) \propto \omega^n \qquad (4)$$

and thus $\tan \delta$ has a constant value $\tan \delta_c$ as a function of the frequency. Assuming that the power law of G' and G'' holds over the entire frequency axis, and applying Kramers–Kronig relationships, the $\tan \delta_c$ value is given by

$$\tan \delta_c = \tan\left(n \frac{\pi}{2}\right) \qquad (5)$$

As a minimum in $\tan \delta$ means a zero first derivative, it can be assumed in the present case as a first-order approximation that $\tan \delta$ is constant and thus a gel-like situation holds. Of course this point holds only locally on the frequency axis.

The density of experimental points was increased, for some materials, just around the $\tan \delta$ minimum. *Figure 5* shows the results for PS-2 at 160°C: the rate range is between 9 and 10.8 rad s^{-1} and $\tan \delta$ is nearly constant with a minimum of 0.2318 and a maximum of 0.2322. The G' and G'' points scale with the frequency as follows:

$$G' \propto \omega^{0.135 \pm 0.001}$$

$$G'' \propto \omega^{0.137 \pm 0.003}$$

whereas $\tan \delta_c$ estimated from equation (5) is 0.217, compared with the experimental value of ≈ 0.232.

The same approach is given in *Figure 6* for PS-7 at 130°C: the rate here ranges from 9.4 to 14.2 rad s^{-1} and $\tan \delta$ from 1.384 to 1.396. The fit in this case is

$$G' \propto \omega^{0.497 \pm 0.003}$$

$$G'' \propto \omega^{0.504 \pm 0.004}$$

and $\tan \delta_c$ is 1 from equation (5), compared with the experimental value of ≈ 1.39.

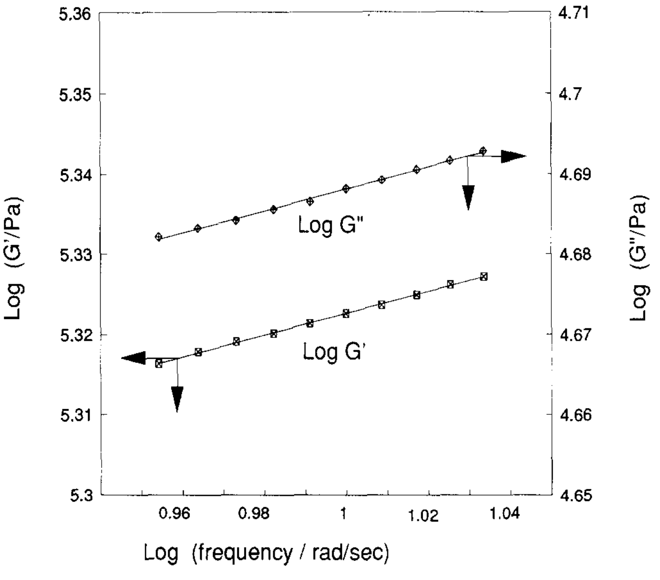

Figure 5 G' and G'' vs ω around the $\tan \delta$ minimum at 160°C for PS-2. The symbols are experimental data, the lines are fitted to equation (4)

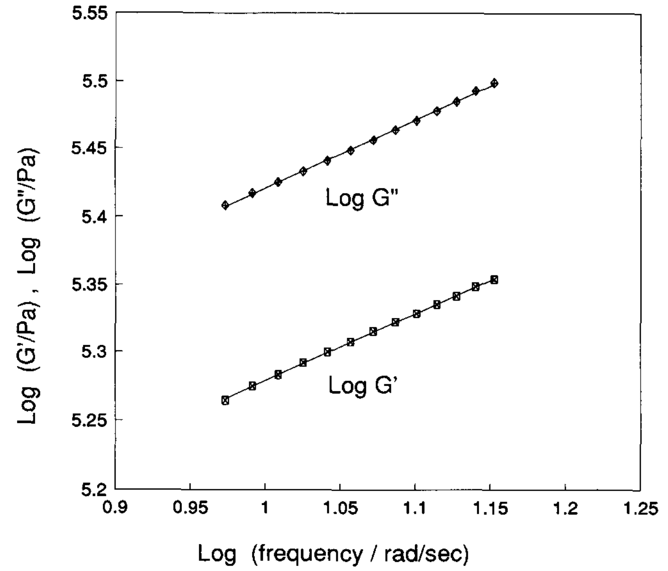

Figure 6 G' and G'' vs ω around the tan δ minimum at 130°C for PS-7. The symbols are experimental data, the lines are fitted to equation (4)

Thus experimentally the gel equation (4) is satisfied, as is reasonably expected (see the Appendix). Less agreement is observed for equation (5); this could stem from the fact that Winter's model assumes the power-law behaviour (equation (4)) over the entire frequency spectrum, while in the present case this occurs only locally around the frequency of the tan δ minimum.

Of course, the comparison between the melt network and the physical gelation process should be considered just as an analogy and not as a strict similarity. For example, it is not obvious to depict the transition in frequency through the tan δ minimum as a transition from a pre-gel situation to a post-gel one. However, the fact the scaling law equation (4) is satisfied seems to reinforce the idea that the tan δ minimum point defines a network (gel-like) structure.

Plateau modulus and chain length

The typical dispersion curves of G' and tan δ vs frequency are reported in *Figures 7* and *8* respectively. It can be seen that a tan δ minimum exists for all the molecular weights investigated, even when they are around or below the entanglement spacing. In *Table 1* the network moduli are reported for each material. The experimental accuracy of the values obtained is in the region of 5%.

When the molecular weight is above M_e, the plateau modulus is constant for all the materials, with a value close to 200 kPa, which is generally accepted, as the experimentally determined values range from ≈ 170 to about 220 kPa[18–20,30,31].

A typical M_e of about 18 000 (depending slightly on the temperature and density values selected) is deduced from equation (1) with a plateau modulus of 200 kPa.

For the sample PS-8 (with molecular weight quite close to the entanglement spacing) a slightly higher G_N^0 is observed, while for PS-9 (molecular weight well below the entanglement spacing) G_N^0 is about twice the value measured for the $M > M_e$ polymers.

DISCUSSION

Consider first the case of chain lengths above M_e. Assuming the tan δ minimum criterion, it is evident from the experimental results that the entanglement density is a quantity which acquires its typical value quite abruptly above M_e. It is interesting at this point to make a comparison with the topological model of Kavassalis and Noolandi[15–17], as it predicts the entanglement density to be sensitive to chain length. They found the following equation:

$$\tilde{N}+1=\left(\frac{\pi\psi}{6}\right)\cdot N_e^{1/2}\cdot\left(1-\frac{N_e}{N}\right) \qquad (6)$$

where $\tilde{N}+1$ is a universal constant (average value about 9.1) called the coordination parameter, and N and N_e are the number of skeletal bonds of the chain and between

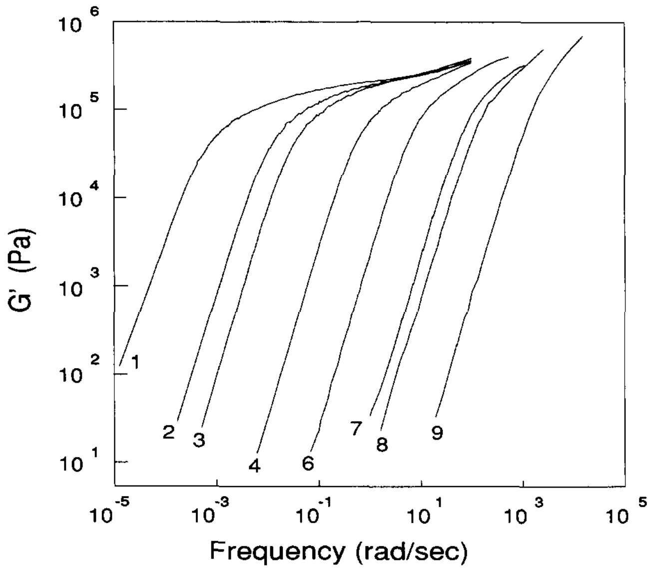

Figure 7 Double-logarithmic plots of G' vs ω at 150°C for monodisperse polystyrenes. Labels refer to sample numbers in *Table 1*

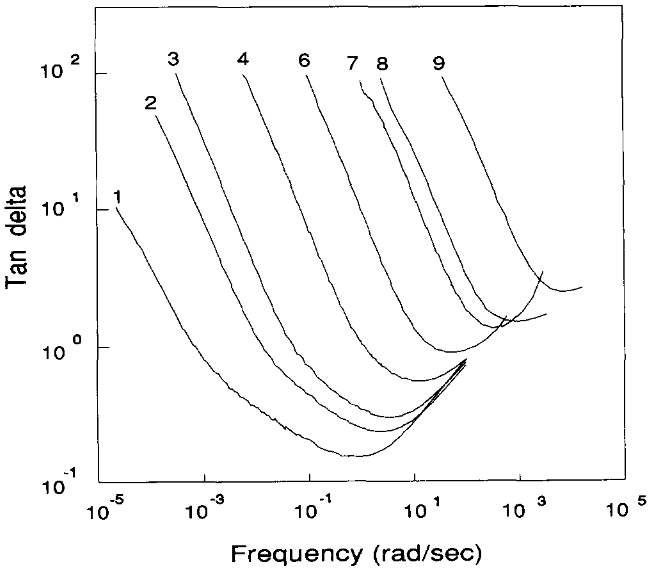

Figure 8 Double-logarithmic plots of tan δ vs ω at 150°C for monodisperse polystyrenes. Labels refer to sample numbers in *Table 1*

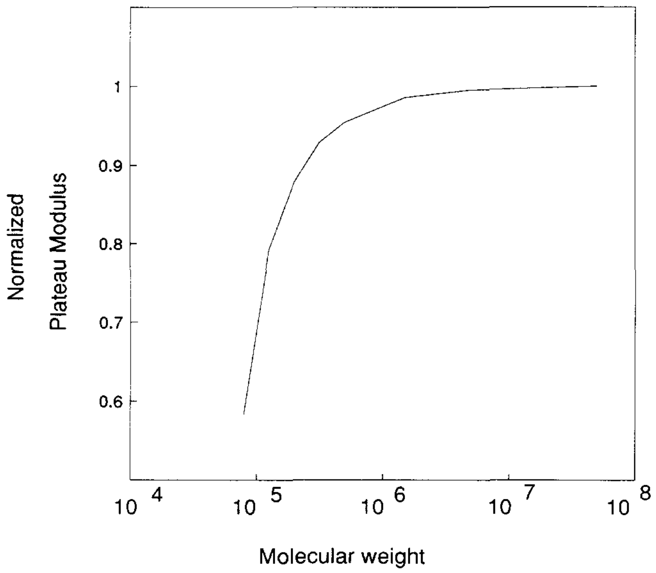

Figure 9 Normalized plateau modulus as a function of molecular weight for polystyrene as estimated from the Kavassalis–Noolandi model (equation (6)) ($\psi = 1.2$, $\tilde{N} + 1 = 9.1$)

entanglements respectively. The constant ψ is a dimensionless parameter containing the material characteristics:

$$\psi = \frac{\rho C_\infty^{3/2} l^3}{\mu_m} \tag{7}$$

where C_∞ is the characteristic ratio, ρ the density, l the mean skeletal bond length and μ_m the monomer mass per skeletal bond. It is evident from equation (6) that N_e is independent of N only in the limit $N \rightarrow \infty$.

Combining equation (6) with equation (1) leads to the calculation of the plateau modulus as a function of the molecular weight. The case of polystyrene is shown in *Figure 9*, where the plateau modulus has been divided by the asymptotic limit that it reaches for very long chains. A significant reduction in the plateau modulus (by a factor of about 0.9) is reached when the molecular weight is $\approx 240\,000$. This is in clear contrast to the present experimental findings based on the $\tan\delta$ minimum criterion. However, it is interesting to observe that the Kavassalis–Noolandi model predicts an appreciable drop in the plateau modulus in the molecular weight range 200 000–300 000, where the G'' integration criterion becomes rather indefinite (*Figures 1* and *2*). This qualitative trend is not unexpected, as both the Kavassalis–Noolandi topological model and the terminal zone relaxations depend on the whole chain length.

Thus if the entanglement network is seen as giving rise to an instantaneous network modulus, then the entanglement spacing is independent of chain length and reflects only some intrinsic material parameters such as the characteristic ratio and monomer density. If, conversely, entanglements are thought to be associated with the relaxations in the terminal zone, the whole chain topology and thus the chain length become more important. However, this last point of view appears to be difficult to assess experimentally. Furthermore some experimental facts seem in favour of the idea of the entanglement onset as a rather abrupt one with no, or quite small, dependence on the molecular weight.

For example, crazing of glassy polymers is known to be related to entanglements[7,8,32]: as the crazing stress of polystyrene is reported[33] to be appreciable and constant for molecular weights down to about 70 000, this should indicate a chain length effect certainly much weaker than that deduced from equation (6). Another indication comes from the very interesting experiments of Kotliar *et al.*[34] on the rhelogy of polymers that are at least partly in a disentangled state. Measuring the viscosity and the plateau modulus of disentangled chains, they observed no significant changes with respect to a normally entangled melt. To account for these results, they concluded that it is necessary to assume that intramolecular segments can make a significant contribution as flow obstacles. This could be another indication that large-scale features of the chain and the topology of the surrounding chains should not play a very crucial role compared with the effects determined by the local chain structure.

For $M < M_e$ the $\tan\delta$ minimum breaks down as a criterion to define G_N^0. This is reasonable, because by definition an entangled network should not exist below M_e. However, it is possible to define a network modulus even in this case.

It could be suggested that the network modulus for these materials is due to the macromolecular, Lennard-Jones-like interactions as described by Porter[2–5]. According to this author the modulus due to macromolecular interactions scales with $1/N$ (N being the polymerization index) and, below the critical molecular weight, it is larger than the rubbery plateau modulus. Of course this suggestion is highly qualitative, and further experimental and theoretical work is needed for a precise assessment of the network-like behaviour in the range $M < M_e$.

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APPENDIX

A minimum in tan δ as a function of the frequency is also a minimum in log(tan δ), so that

$$\frac{\mathrm{d}[\log(G''/G')]}{\mathrm{d}\omega} = 0 \qquad \text{(A1)}$$

and then

$$\frac{\mathrm{d}(\log G'')}{\mathrm{d}\omega} = \frac{\mathrm{d}(\log G')}{\mathrm{d}\omega} \qquad \text{(A2)}$$

If one assumes that, at least locally, the storage and loss moduli can be represented as a power law of the frequency, then

$$G' = K_1 \cdot \omega^n \qquad \text{(A3)}$$

$$G'' = K_2 \cdot \omega^m \qquad \text{(A4)}$$

where K_1, K_2, m and n are constants. Taking the logarithms of equations (A3) and (A4) leads to

$$\log(G') = \log(K_1) + n \cdot \log \omega \qquad \text{(A5)}$$

$$\log(G'') = \log(K_2) + m \cdot \log \omega \qquad \text{(A6)}$$

Combining equations (A2) with (A5) and (A6) yields immediately $n = m$, which is the expected experimental result.