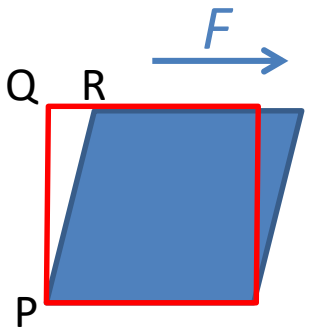
# Generalities on networks

Giuseppe Marrucci, Emeritus
University Federico II
Napoli, Italy

# Basic mechanical property of networks is shear modulus *G*

*G* controls deformability of the network




$$\text{Shear deformation} = \gamma = \frac{\mathrm{QR}}{\mathrm{PQ}}$$

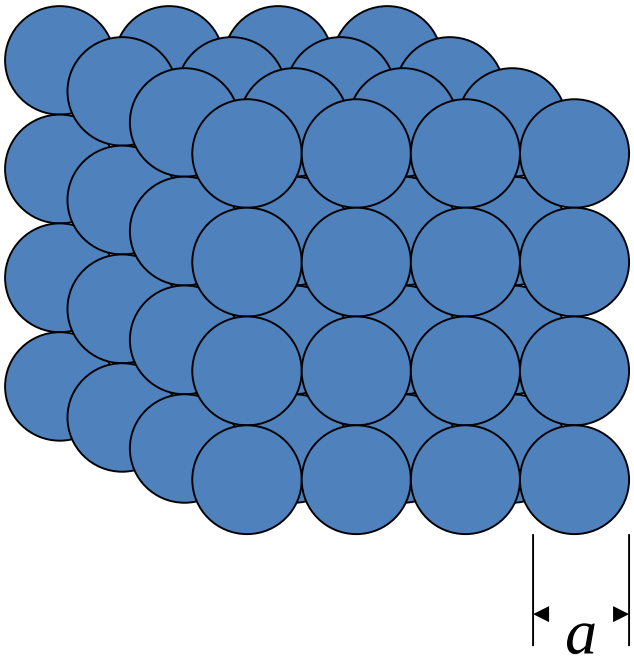
$$\text{Shear stress} = \sigma = \frac{F}{A}$$

$$\text{Shear modulus} = G = \frac{\sigma}{\gamma}$$ (independent of $\gamma$ as long as $\gamma$ is small)

Since $\gamma$ is dimensionless, dimensions of *G* are: force/area
or equivalently: energy/volume

Hence, for a generic material, *G* can be interpreted as the energy per unit volume that binds one to another the constitutive elements of the material.

Let's digress briefly, and consider a crystalline material:




The particles (blue balls in the figure) can be small atoms or molecules, but they can also be much larger objects, like polystyrene microspheres, for example.

Let's take a volume $V = a^3$ containing a single particle. The energy that binds that particle to the others can be estimated by considering that, at some sufficiently high temperature $T$, the crystal melts (or decomposes), and such event occurs because the thermal energy $k_B T$ of the particle overcomes the binding energy. Hence:

$$G = \frac{E}{V} \approx \frac{k_B T_{melting}}{a^3}$$

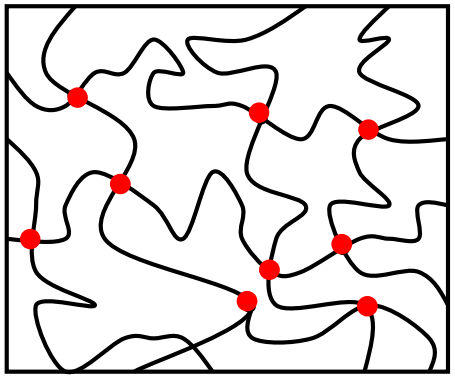
Now, while the melting (or decomposition) temperature is not too much different for different materials (1 order of magnitude, or 2 at most), $a^3$ can differ by as many as 9 orders of magnitudes from the case of atoms or molecules ($a \approx 10^{-9}$m) to that of microparticles ($a \approx 10^{-6}$m).

In conclusion: $a \approx 1$ nanometer $\rightarrow$ rigid matter (G very large)

$a \approx 1$ micrometer $\rightarrow$ soft matter (G very small)

This result also applies to amorphous materials. For example: ordinary glass is rigid, while rubber is a well known example of soft matter.

The structure of rubber is one of a 3D network of polymer chains. In vulcanized rubber, the nodes of the network are chemical crosslinks between chains (red dots in the figure). Polymer chains can be thought of as highly flexible filaments (for reasons to be explained later on). Hence, locally, the thermal motion of the chains is similar to that in a liquid. Globally, however, because of the crosslinks, the behavior is one of a solid.



It will be shown that the shear modulus of vulcanized rubber is (to a good approximation) given by:

$$G = \nu k_B T$$

where $T$ is the sample temperature, and $\nu$ is the number density of chains (strands between crosslinks).

This formula is the same of the previous slide, except for the fact that $T$ is the actual temperature, not that of rubber decomposition. Indeed, $1/\nu$ is the volume occupied by a single chain.

Thus, to obtain a more rigid rubber we need to increase the number of crosslinks (and hence of chains). More generally, the material becomes harder by increasing the number of connections per unit volume, which can also be obtained by using fillers (carbon black, silica particles, etc.) that stick to the polymer chains.

Conversely, to obtain a softer material we need to dilute the connectivity. This is exactly what takes place in gels, which are polymeric networks containing a large proportion of a solvent.

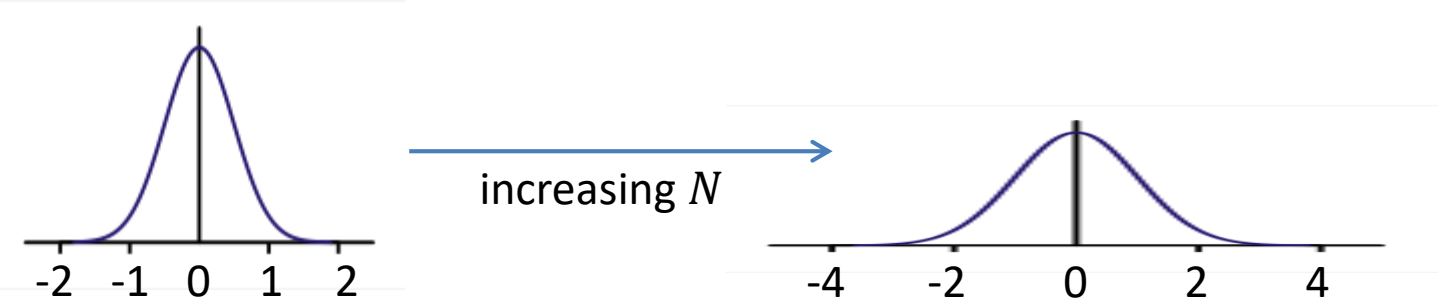
# To calculate the modulus *G* of rubber we need a brief digression on random walks

Consider a random walk along a line: at each step you decide with a 50% probability to move forward or backward. After taking a large number $N$ of steps, where along the line will you find yourself?

The probability of finding yourself at the location $x$ is given (to a good approximation) by the Gaussian function:

$$p(x) = Cexp\left(-\frac{1}{2}\frac{x^2}{Nb^2}\right)$$

where $b$ is the step length, and $C = 1/\left(b\sqrt{2\pi N}\right)$ is the normalization factor.

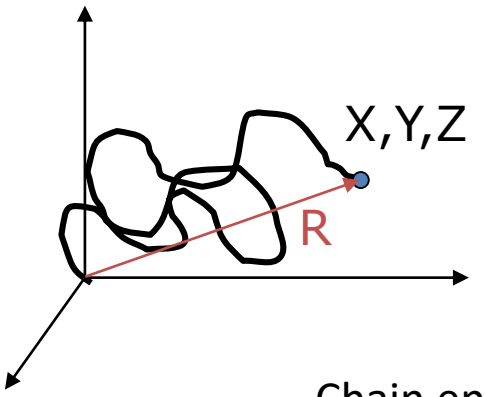



The average square distance from the origin is $\langle x^2 \rangle = Nb^2$.

Similar formulae apply to random walks in 2D and 3D.

# Polymer chains are like 3D random walks

The monomer (Khun segment) length is b, and N is number of monomers




Probability $p$ of end-to-end vector **R** is the 3D Gaussian

$$p(\mathbf{R}) = Cexp\left(-\frac{3}{2}\frac{R^2}{Nb^2}\right)$$

Chain entropy: $S(\mathbf{R}) = k_B \ln p(\mathbf{R}) = -\frac{3}{2}k_B\frac{R^2}{Nb^2} + k_B \ln C$

Free Energy: $A(\mathbf{R}) = -TS(\mathbf{R}) = \frac{3}{2}k_B T\frac{R^2}{Nb^2} - k_B T \ln C$

Force **F** needed to maintain chain end-to-end fixed at **R** is:

$$\mathbf{F}(\mathbf{R}) = -\frac{dA}{d\mathbf{R}} = -\frac{3k_B T}{Nb^2}\mathbf{R}$$

# Free energy of a rubber network

## (a sum over chains)

$$a = \frac{3}{2} k_B T \sum_{i=1}^{i=\nu} \frac{{R_i}^2}{N_i b^2} = \frac{3}{2} \nu k_B T \left\langle \frac{R^2}{Nb^2} \right\rangle$$

$\nu$ is number of chains/volume

For an arbitrary deformation of the sample let $x$,$y$,$z$ be the principal directions, and $\lambda_1$, $\lambda_2$, $\lambda_3$ the principal stretch ratios. Because volume does not change it is: $\lambda_1 \lambda_2 \lambda_3 = 1$.

Let's decompose $R^2$ along principal directions: $R^2 = X^2 + Y^2 + Z^2$. By assuming that all crosslinks move affinely with the macroscopic deformation, $X, Y, Z$ are given by:

$$X = \lambda_1 X_0, \quad Y = \lambda_2 Y_0, \quad Z = \lambda_3 Z_0$$

where $X_0$, $Y_0$, $Z_0$ are before deformation. Hence:

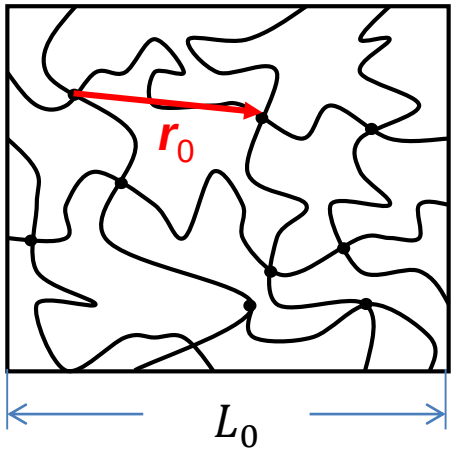
$$R^2 = (\lambda_1 X_0)^2 + (\lambda_2 Y_0)^2 + (\lambda_3 Z_0)^2, \qquad a = \frac{3}{2} \nu k_B T \left( {\lambda_1}^2 \left\langle \frac{{X_0}^2}{Nb^2} \right\rangle + {\lambda_2}^2 \left\langle \frac{{Y_0}^2}{Nb^2} \right\rangle + {\lambda_3}^2 \left\langle \frac{{Z_0}^2}{Nb^2} \right\rangle \right)$$

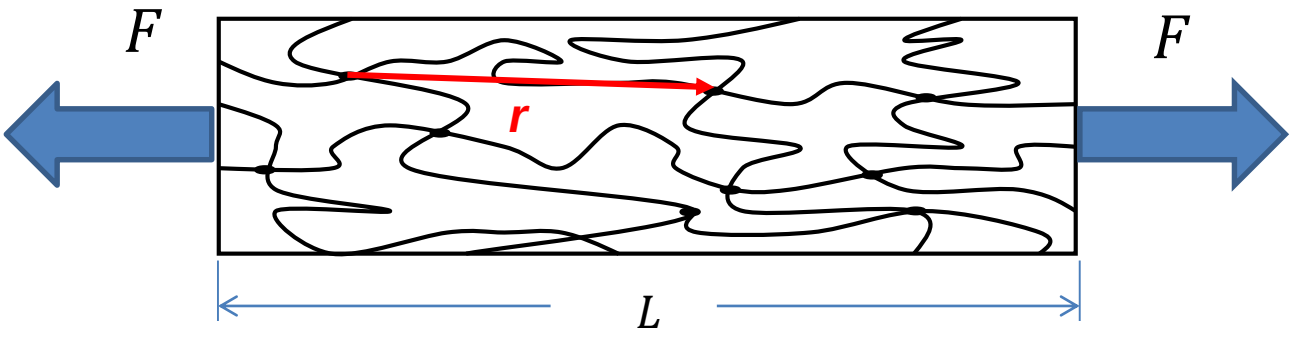
Since before deformation rubber is isotropic, each of the three averages is equal to $1/3$, so that finally:

$$\boxed{a = \frac{1}{2} \nu k_B T \left( {\lambda_1}^2 + {\lambda_2}^2 + {\lambda_3}^2 \right)}$$

$$\boxed{A = aV}$$

# A simple example: Uniaxial stretch (or compression)



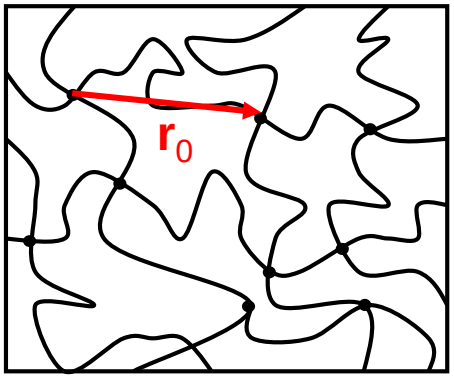

$$\lambda_1 = \frac{L}{L_0} = \lambda\,, \qquad \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}\,, \qquad (\lambda_1\lambda_2\lambda_3 = 1)$$

$$A = \frac{1}{2}V\nu k_B T\left(\lambda^2 + \frac{2}{\lambda}\right), \qquad F = \frac{dA}{dL} = \frac{1}{L_0}\frac{dA}{d\lambda} = \frac{V}{L_0}\nu k_B T\left(\lambda - \frac{1}{\lambda^2}\right)$$

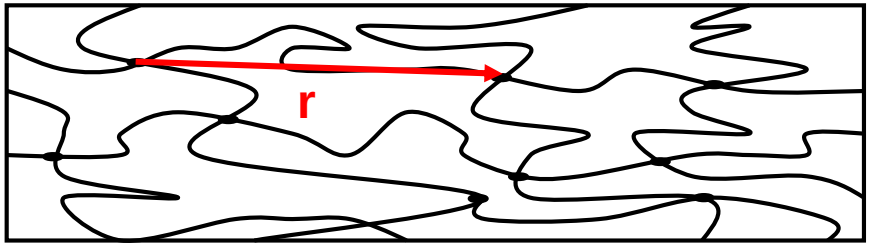
$$\frac{F}{S_0} = \sigma_{eng} = \nu k_B T\left(\lambda - \frac{1}{\lambda^2}\right) = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

Modulus: $G = \nu k_B T$

# In summary




Rubber network

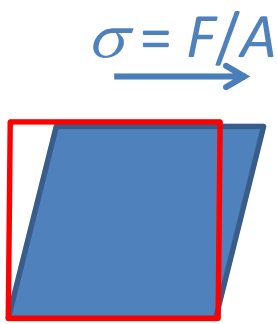



Deformed network

When chains are stretched, their entropy decreases and hence free energy increases.

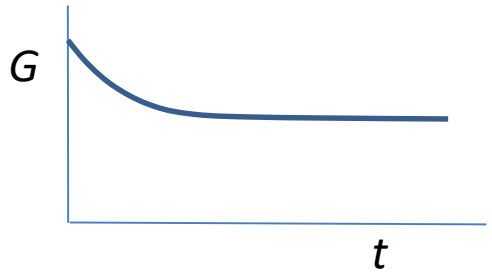
Increase in free energy implies the work of an elastic force that pulls back the rubber band.

The modulus of a network is proportional to the concentration of crosslinks (degree of connectivity).

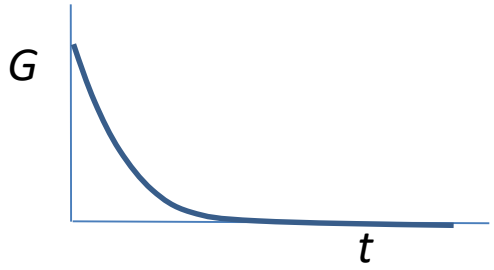



So far we have tacitly assumed that time effects are absent. In other words, we have assumed that, after a deformation has been applied at time $t = 0$, and maintained therefrom, the stress $\sigma$ remains constant in time. Such a behavior is observed only for materials that are purely elastic, and for them the modulus $G$ is independent of time. Many materials, however, are more complex than that: they are viscoelastic. For them $G$ is a decreasing function of time.

Two quite distinct situations are envisaged, depicted in the two graphs below:




Viscoelastic solid




Viscoelastic liquid

As shown in the left graph, the modulus asymptotically approaches a nonzero value, characterizing a solid state. In the right graph, conversely, the stress relaxes down to zero, characterizing a liquid-like behavior.

Because we have learnt that the modulus reflects the number density of connections between the elements of the material, a decreasing function $G(t)$ implies that at least some of the connections are not permanent. For a viscoelastic liquid, all connections are impermanent. $G(t)$ is called relaxation modulus.

Viscoelasticity also introduces a new material parameter, the relaxation time $\tau$, which tells us how long it takes to reach equilibrium after the initial deformation (milliseconds, seconds, hours, …). Strictly speaking, the relaxation time is generally not uniquely defined, except for the special case where $G(t)$ is described by a simple negative exponential:

$$G(t) = G(0)\exp(-t/\tau) \qquad \text{liquid}$$

$$G(t) = G(\infty) + [G(0) - G(\infty)]\exp(-t/\tau) \qquad \text{solid}$$

Generally, a viscoelastic material exhibits a spectrum of relaxation times, i.e., some of the connections relax sooner, others later on. A relaxation time can nevertheless be defined, as shown below for the case of a liquid.

For a viscoelastic liquid, the integral over time of the relaxation modulus defines a very important property: the viscosity $\eta$. Next, another integral defines the relaxation time $\tau$:

$$\eta = \int_0^\infty G(t)dt\,, \qquad \tau = \frac{1}{\eta}\int_0^\infty t\,G(t)dt$$

If $G(t) = G\exp(-t/\tau)$, then the integral for the viscosity gives: $\eta = G\tau$.

Hence, another important message: A liquid is more viscous the more impermanent connections there are (measured by $G$), and/or the longer they last (measured by $\tau$).

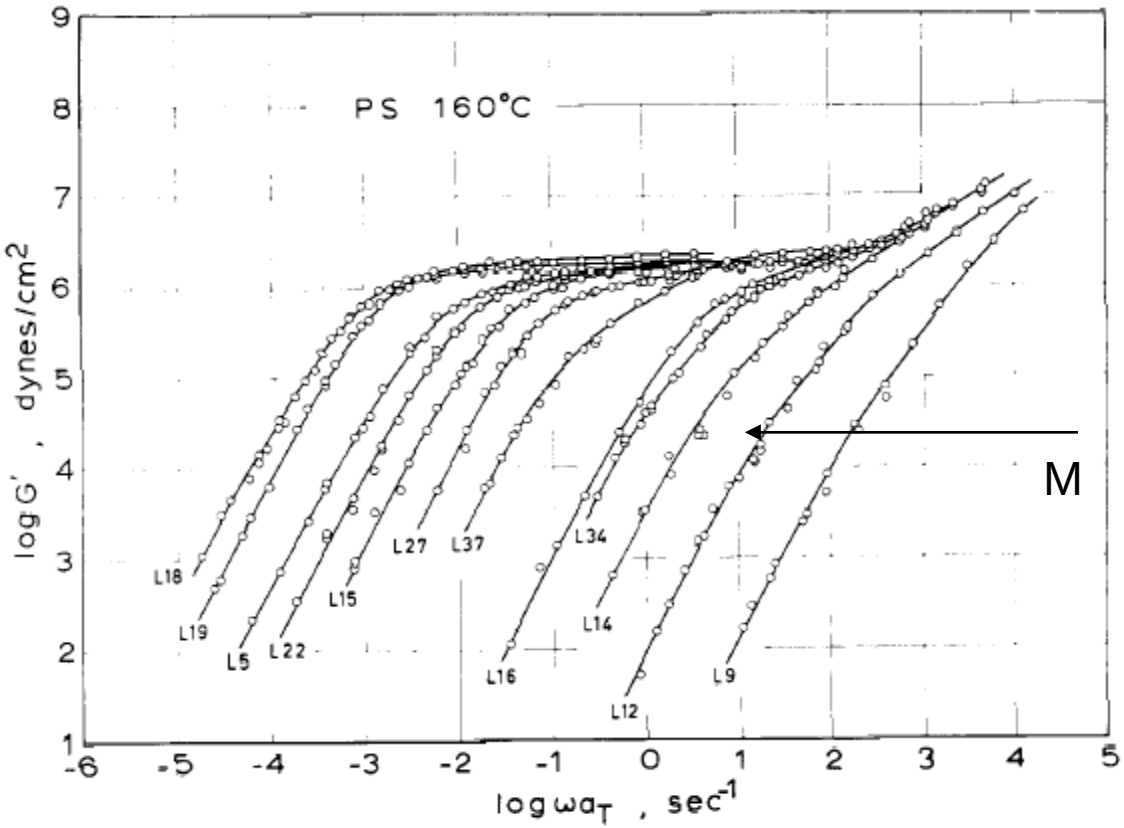
# Impermanent networks and entangled networks

Both impermanent networks and entangled networks are viscoelastic polymeric liquids.

Impermanent networks are made up of associating polymers, i.e. polymers that contain “sticky points”, either at some places along the chain, or at the chain ends (telechelic chains). The chains can therefore connect one to another at those points forming a network. The links are not permanent, however. Differently from vulcanized rubber, links among chains break and reform continuously as a consequence of thermal motion. In following slides we will show some examples of chemically different sticky points.

Entangled networks are very special impermanent networks. Indeed, they are made up of ordinary polymers that interact only through the usual Van der Waals forces. The polymer chains, however, are long enough to form “entanglements”. The latter arise from the fact that chains obviously cannot cross one another, and hence for a long chain to substantially renew its conformation (a necessary condition to fully relax stress) it is required that the chain diffuses longitudinally along itself: a very slow process (known as “reptation”).

# The plateau modulus of the entangled network




$G_{\mathrm{PS}} = 200\ \mathrm{kPa}$

Figure 2. Master curves of $G'$ for narrow-distribution polystyrenes having different molecular weights. The reference temperature is 160°.

Molecular weight ranges from $M_w = 8.9\mathrm{x}10^3$ (L9) to $M_w = 5.8\mathrm{x}10^5$ (L18). Onogi et al., *Macromolecules* **3**, 109 (1970)

# An example of associating polymers
# The HEUR telechelic molecule

Annable et al. *J. Rheol*. **37**, 695 (1993)

A long water soluble chain (PEO) with short hydrocarbon segments at both ends

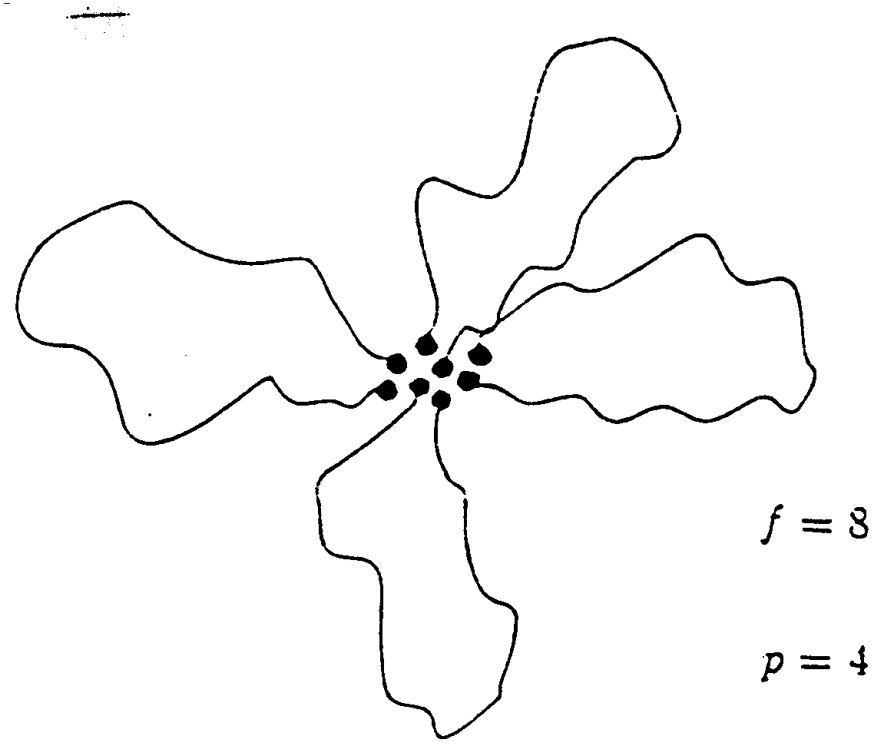



**Figure 1.** A flower consisting of $p = 4$ chains; the core is an aggregate of $f = 8$ insoluble end groups.

Above some critical concentration flowers connect one to another forming larger (impermanent) aggregates, and eventually a network.

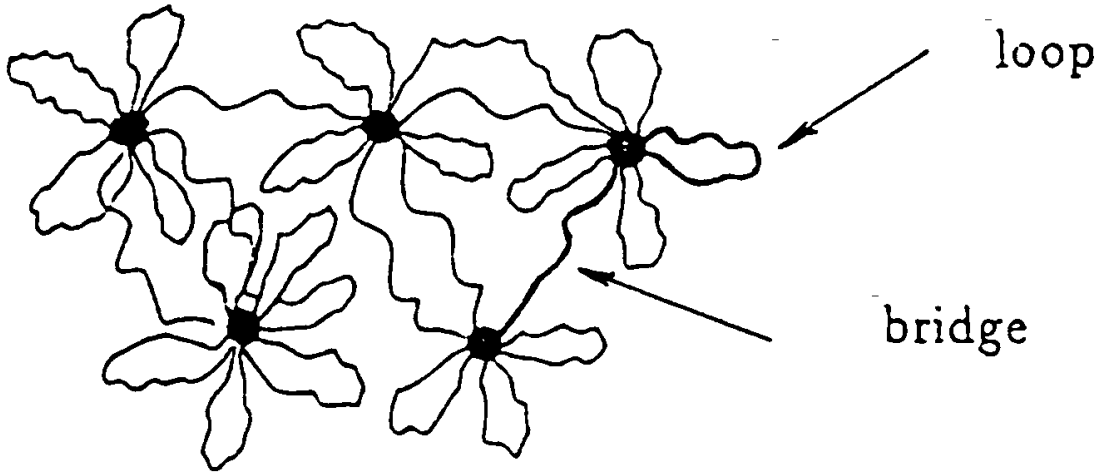



**Figure 2.** A transient (reversible) network of flowers connected by bridges.

Above some critical concentration, viscosity jumps up by orders of magnitude. Actual values depend on length of both hydrocarbon chain ends and PEO chain.

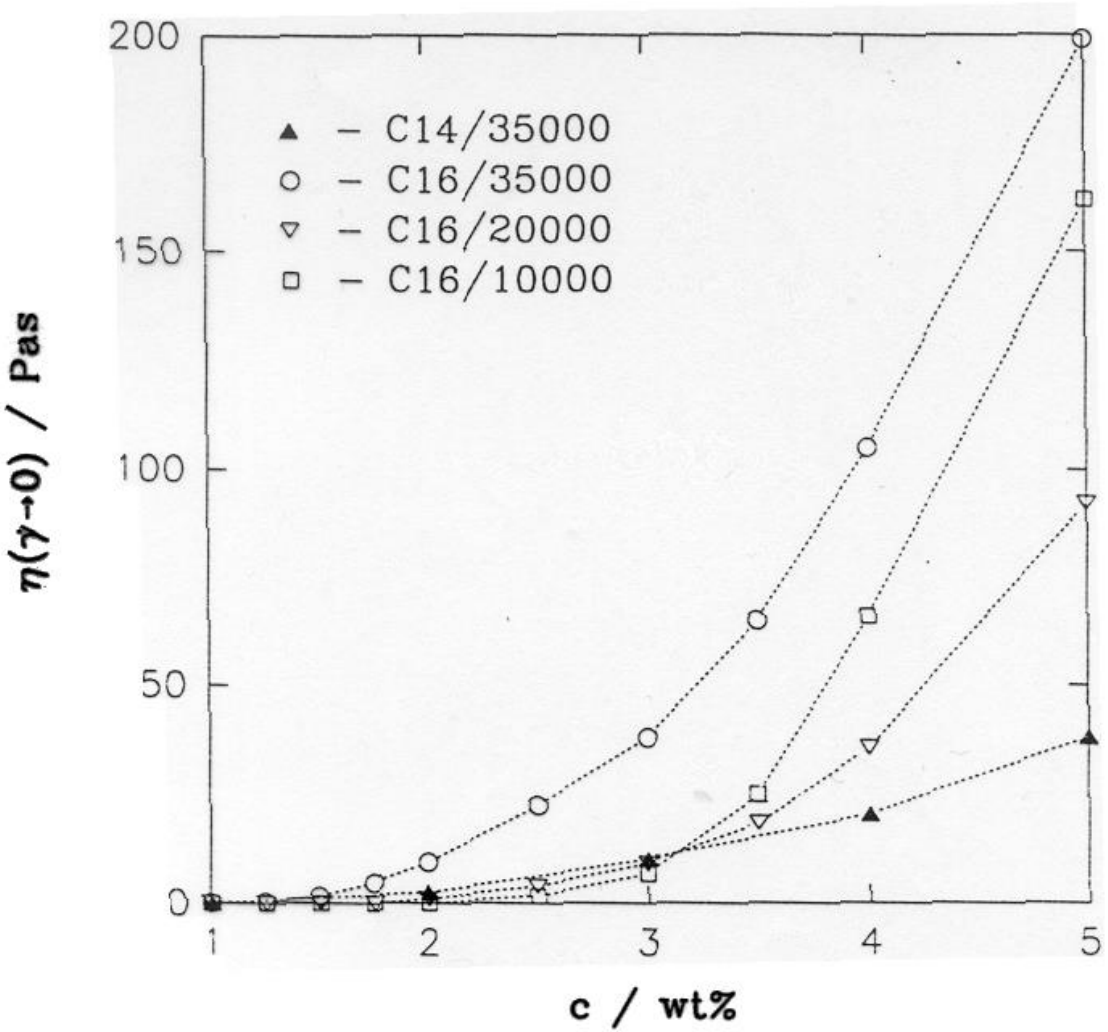



FIG. 1. Effect of polymer concentration (%w/v) on the Newtonian viscosity of four HEUR-AT. $T$ = 298 K.

# Effect of chain end length is dramatic

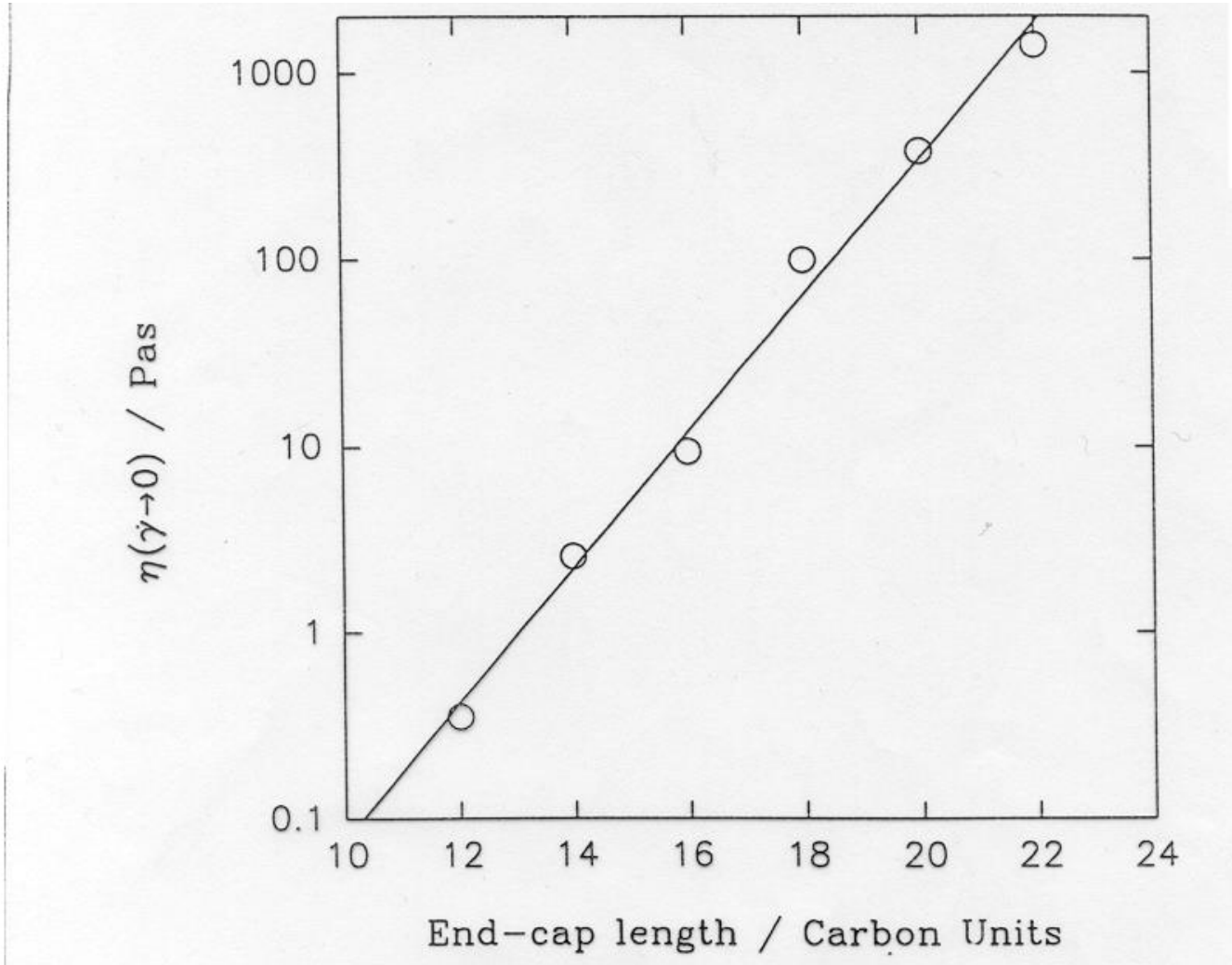
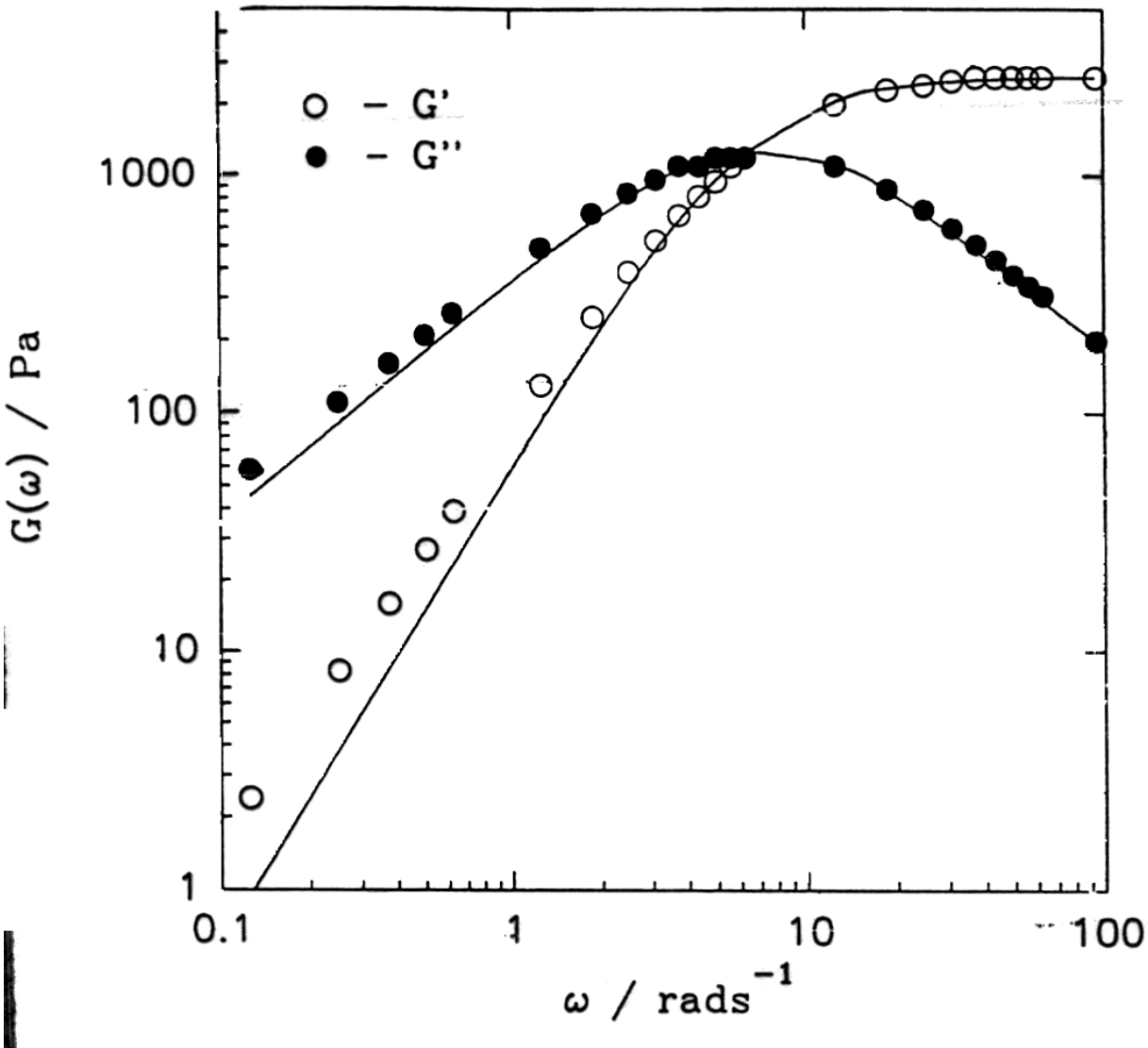



**FIG. 2.** Effect of end-cap chain length on the Newtonian viscosity for MW = 35 000 at a concentration of 2%w/v. $T = 298$ K.

Viscosity $\eta$ is (essentially) the product of the elastic modulus G of the network to the relaxation time $\tau$, i.e., $\eta \approx G\,\tau$.
Values of G and $\tau$ are obtained from the frequency response.



Relaxation time strongly depends on hydrocarbon chain end length.

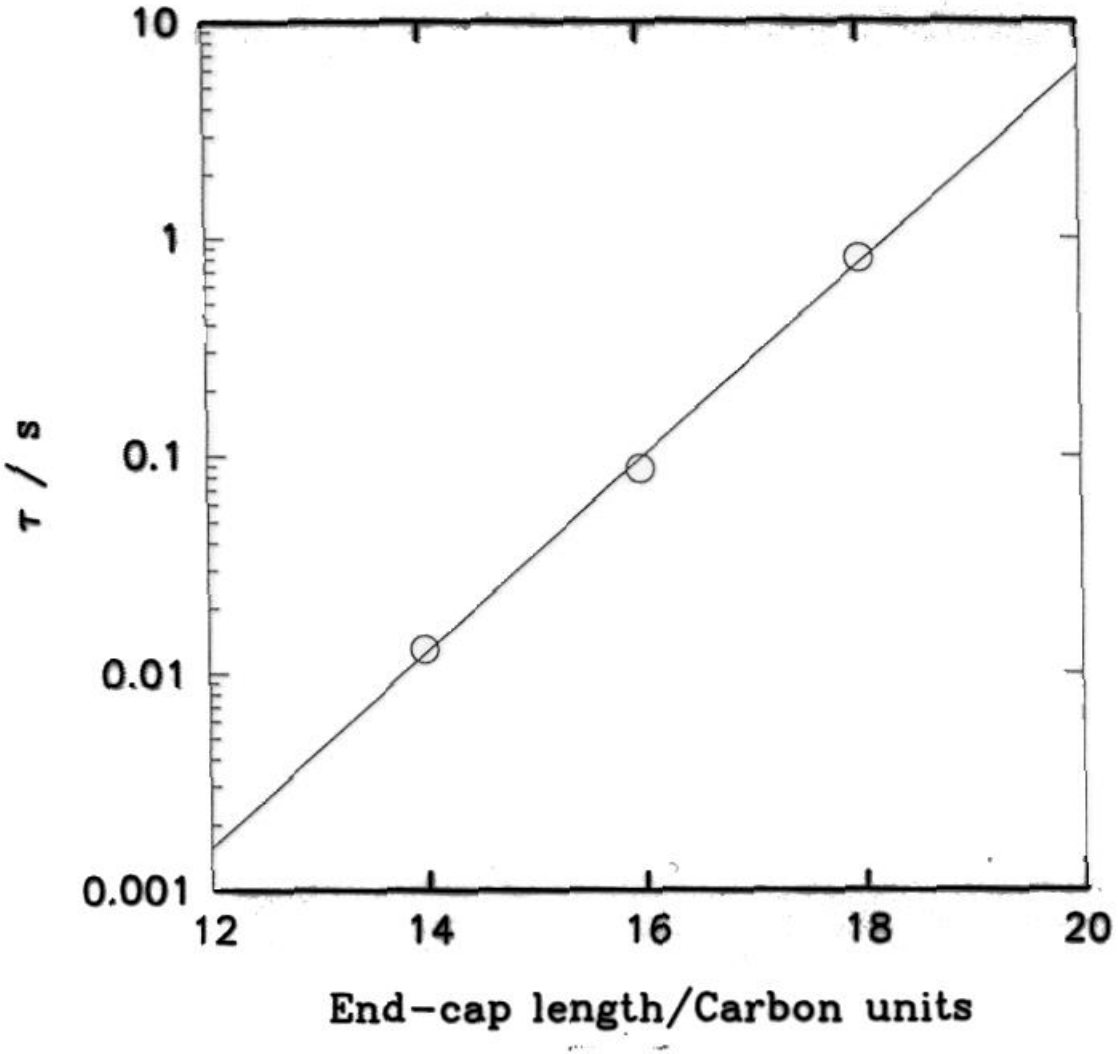
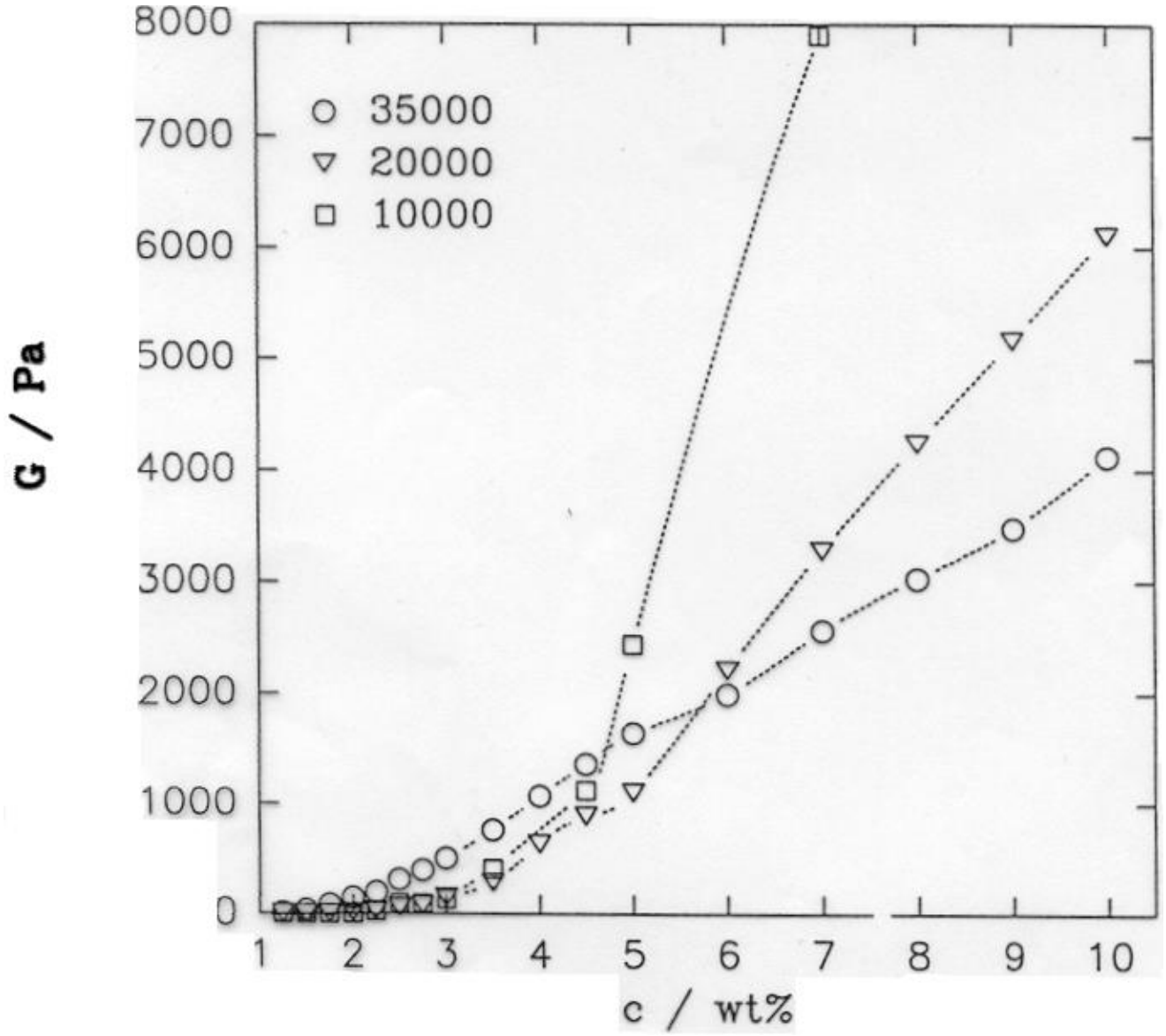



FIG. 6. Effect of end-cap chain length on the relaxation time for MW = 35 K and a concentration of 4%w/v ($T$ = 298 K).

Modulus (connectivity) increases with concentration, and depends on PEO chain length in a complex way.



# Conclusions on this example

- Properties (in this case the viscosity) can be tuned by suitably changing structural and operative parameters.
- Complexity can be resolved by sorting out the factors that determine the property, and hence breaking down the problem to the analysis of those, more elementary factors.
- We encourage you to apply similar tools to deal with the double dynamics networks of the DoDyNet project.