

Ch 10

Polymer gels

Chemical

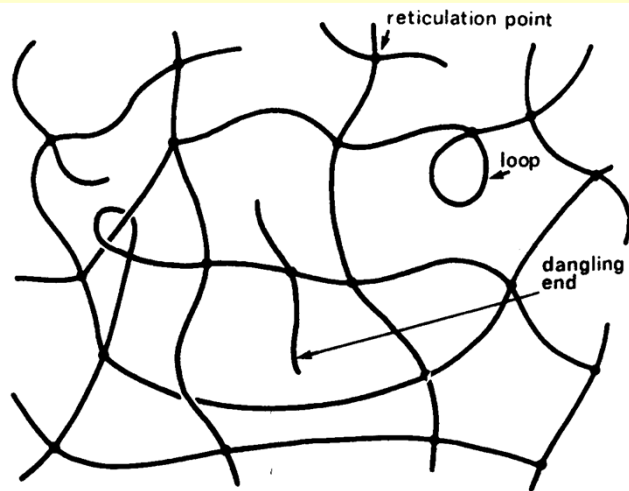


Figure 5.1 A typical polymer gel network. (Reprinted from Pierre-Gilles de Gennes, *Scaling Concepts in Polymer Physics*. Copyright © 1979 by Cornell University. Used by permission of the publisher, Cornell University Press.)

Physical

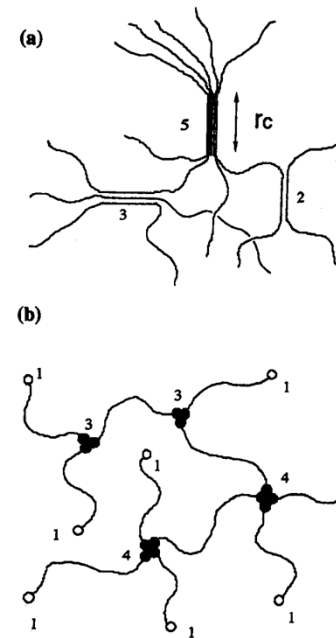


Figure 5.2 Illustrations of physical gels. In (a), the junctions are formed by microcrystallites, while in (b) the junctions are formed by the end groups of telechelic polymers. The functionalities of the various cross-link points are indicated by numbers beside the junctions. (Reprinted with permission from Tanaka and Stockmayer, *Macromolecules* 27:3943. Copyright 1994 American Chemical Society.)

Rheology of chemical gels

p ; the fraction of bonds that are filled

Percolation; the process of network formation by random filling of bonds on a lattice, or by random filling of regions of space

Near equilibrium

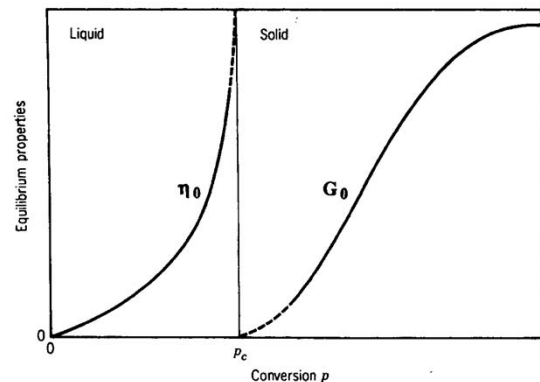


Figure 5.5 Illustration of the dependence of zero-shear viscosity η_0 and equilibrium modulus G_0 on conversion p for a cross-linking system. (From Winter, *Encyclopedia of Polymer Science and Engineering*, Copyright © 1989. Reprinted by permission of John Wiley & Sons, Inc.)

$$G_0 = \nu kT$$

for fully cured elastic solid

At large deformation

$$\boldsymbol{\sigma} = G_0 \mathbf{B}$$

$$\boldsymbol{\sigma} = 2C_1 \mathbf{B} + 2C_2 \mathbf{C}$$

Mooney-Rivlin equation

Rheology of partially gelled liquids

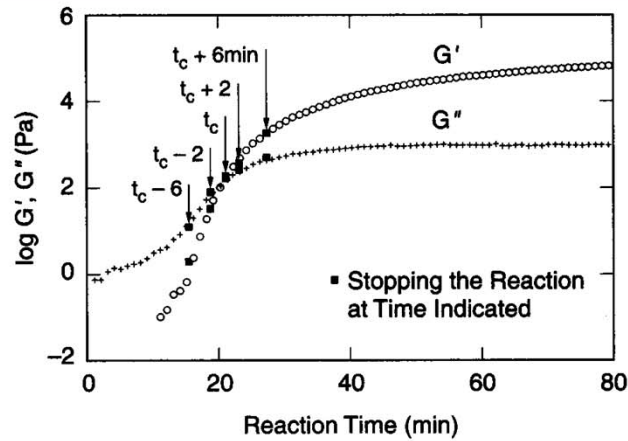


Figure 5.6 Time-dependence of G' (\circ) and G'' ($+$) during cross-linking reaction of subentangled poly(dimethylsiloxane) at balanced stoichiometry with a tetrasilane crosslinker. The gel point is marked as t_c . (From Winter and Chambon 1986, with permission from the Journal of Rheology.)

at the gel point

$$G(t) = S t^{-n}$$

$$G'(\omega) = \frac{G''(\omega)}{\tan(n\pi/2)} = \Gamma(1-n) \cos\left(\frac{n\pi}{2}\right) S \omega^n$$

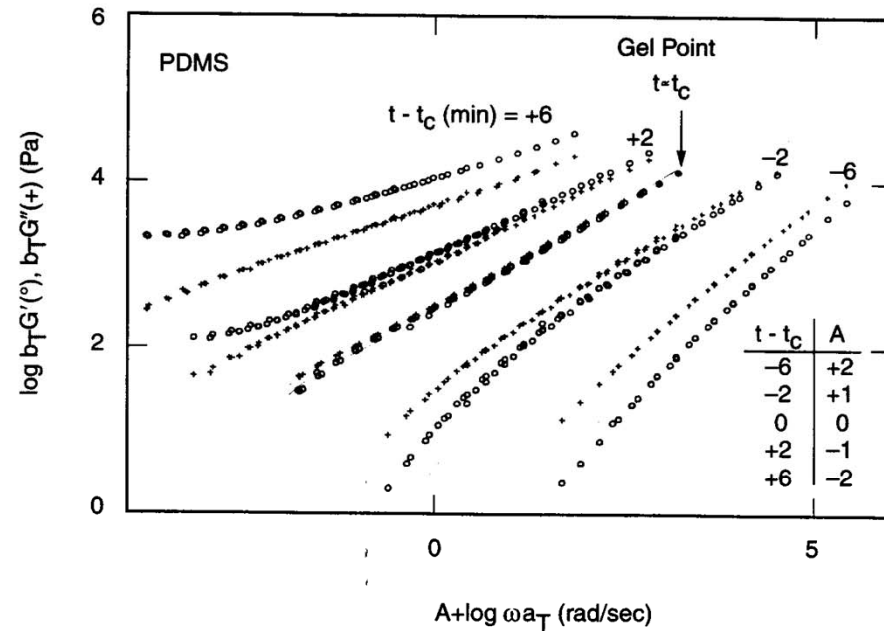


Figure 5.7 Frequency dependences of the storage (\circ) and loss ($+$) moduli for poly(dimethylsiloxane) (PDMS) samples whose reactions were quenched at the times indicated (see Fig. 5-6). The data are time-temperature-shifted to the reference temperature T_{ref} of 34°C, and they are shifted additionally by an amount A on the logarithmic axis to keep the curves from overlapping. The vertical shift factors b_T are given by $\rho(T_{ref})T_{ref}/(\rho(T)T)$, where ρ is the density. (From Winter and Chambon 1986, with permission from the Journal of Rheology.)

Time-cure superposition

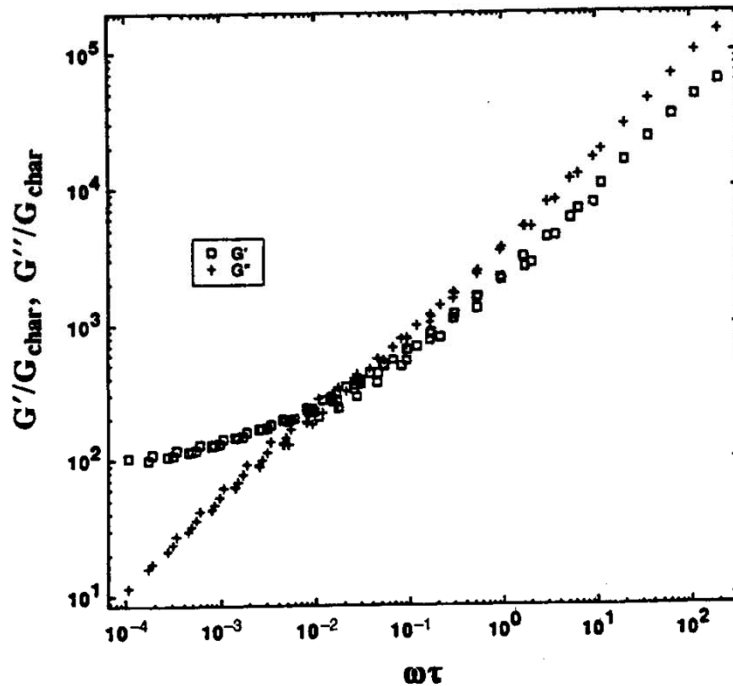


Figure 5.10 Time-cure superposition for a partially cross-linked epoxy obtained by multiplying the frequency ω by $\tau \propto \varepsilon^{-3.9}$ and dividing the moduli G' and G'' by $G_{\text{char}} \propto \varepsilon^{2.8}$, where $\varepsilon \equiv p - p_c$. In the power-law frequency regime, $G' \propto G'' \propto \omega^{0.72}$. (From Martin and Adolf 1991, with permission from the Annual Review of Physical Chemistry, Volume 42, © 1991, by Annual Reviews, Inc.)

Rheology of physical gels

Physical networks; sticker

Associating polymers; water soluble polymers with hydrophobic groups

Hydrophilic groups are associating; dipole-dipole interaction in ionomer, hydrogen bonding

Attractive interactions promote both gelation and phase separation

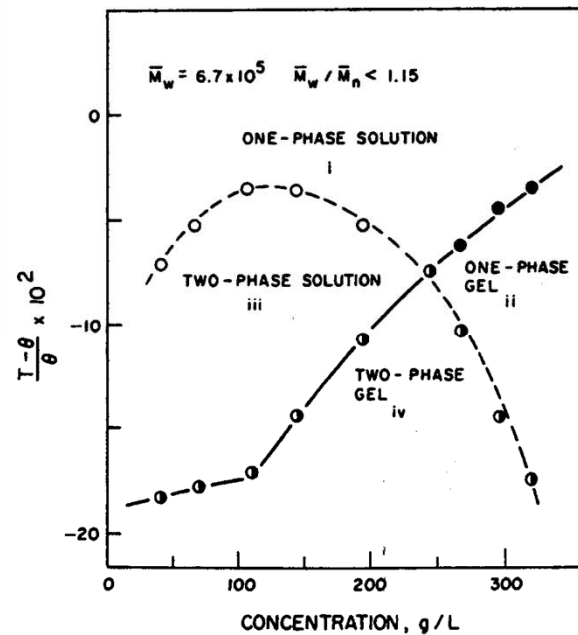


Figure 5.12 Phase diagram of atactic polystyrene in nitropropane. The theta temperature is $\Theta = 200$ K. (Reprinted with permission from Tan et al., *Macromolecules* 16:28. Copyright 1983 American Chemical Society.)

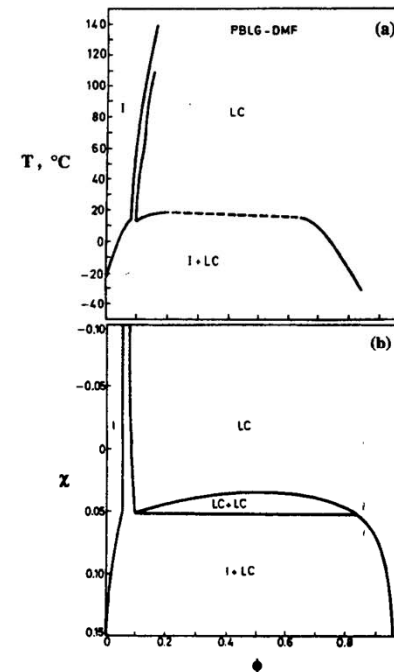


Figure 5.14 (a) Temperature–volume fraction phase diagram for PBLG ($M_w = 310,000$) in DMF, where I denotes an isotropic phase, LC denotes a chiral nematic liquid-crystalline phase, and I + LC is a “gel” that is presumed to be two coexisting phases that are unable to separate macroscopically. (b) The χ -volume fraction phase diagram predicted by the Flory lattice theory for rigid rods of axial ratio (length/diameter) = 150. (From Miller et al. 1974, with permission.)

Telechelic polymers

Linear polymers containing associating sticker groups only on the chain ends
HEUR; hydrophobically modified ethoxylated urethanes

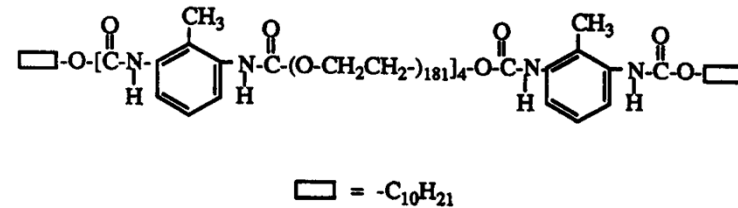
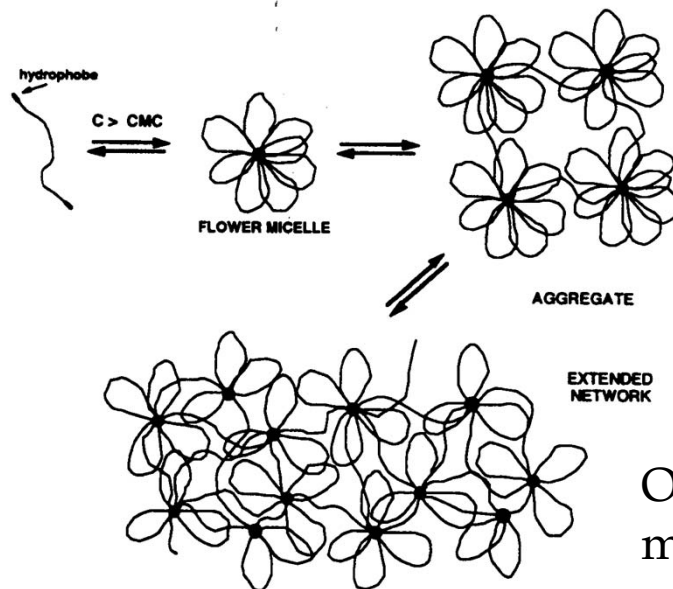


Figure 5.15 Structure of a HEUR polymer. (From Lundberg et al. 1991, with permission from the Journal of Rheology.)



Ordered cubic array of bridged micelles

Figure 5.16 Model for associations of telechelic polymers as a function of increasing concentration. For strong associations, isolated “flower” micelles form just above the critical micelle concentration (CMC), which is often around 2 to 10 ppm (Winnick and Yekta 1997). At higher concentrations, the flowers are expected to be connected by “bridges.” (From Winnick and Yekta 1997, with permission from Current Chemistry Ltd.) © 1997 Current Opinion in Colloid + Interface Science.

Telechelic polymers

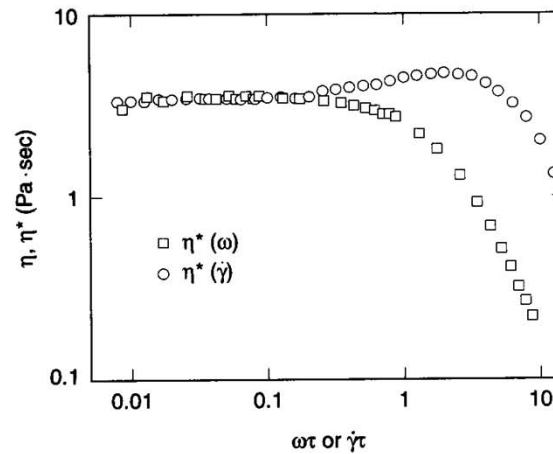
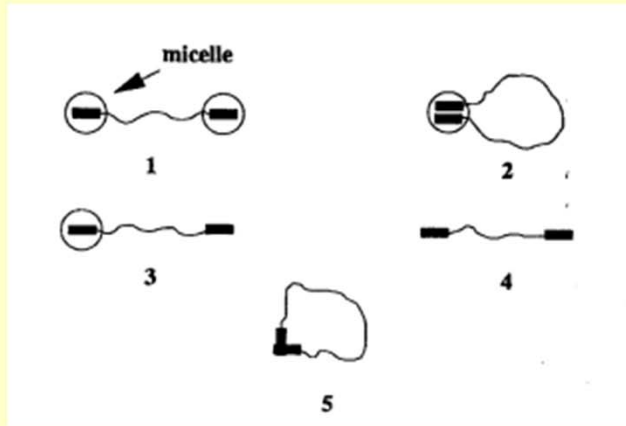


Figure 5.20 Steady-state viscosity $\eta(\dot{\gamma})$ and dynamic complex viscosity $\eta^*(\omega)$ as functions of reduced shear rate ($\dot{\gamma}\tau$) or frequency ($\omega\tau$), for a 1.5% w/v solution of the associative thickener described in the caption to Fig. 5-18. (From Annable et al. 1993, with permission from the Journal of Rheology.)

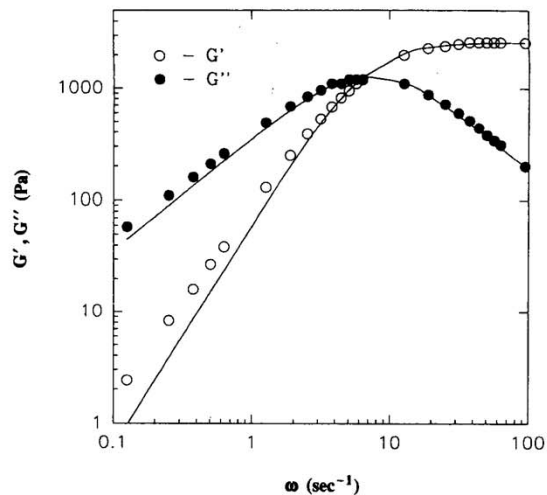


Figure 5.18 Storage and loss moduli for a 7% w/v HEUR associative thickener ($M_w = 33,100$; $M_w/M_n = 1.47$) end-capped with hexadecanol at 25°C. The lines are a fit to a one-mode Maxwell model. (From Annable et al. 1993, with permission from the Journal of Rheology.)

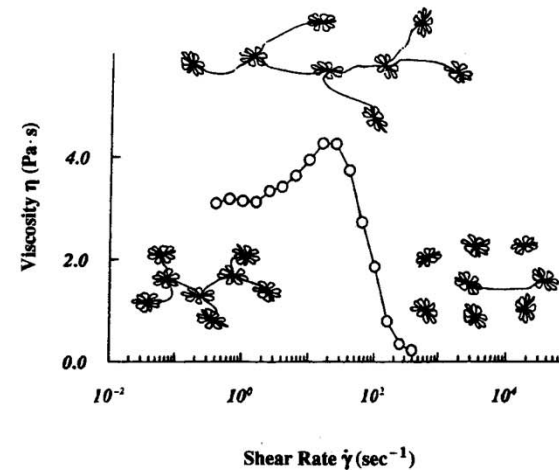
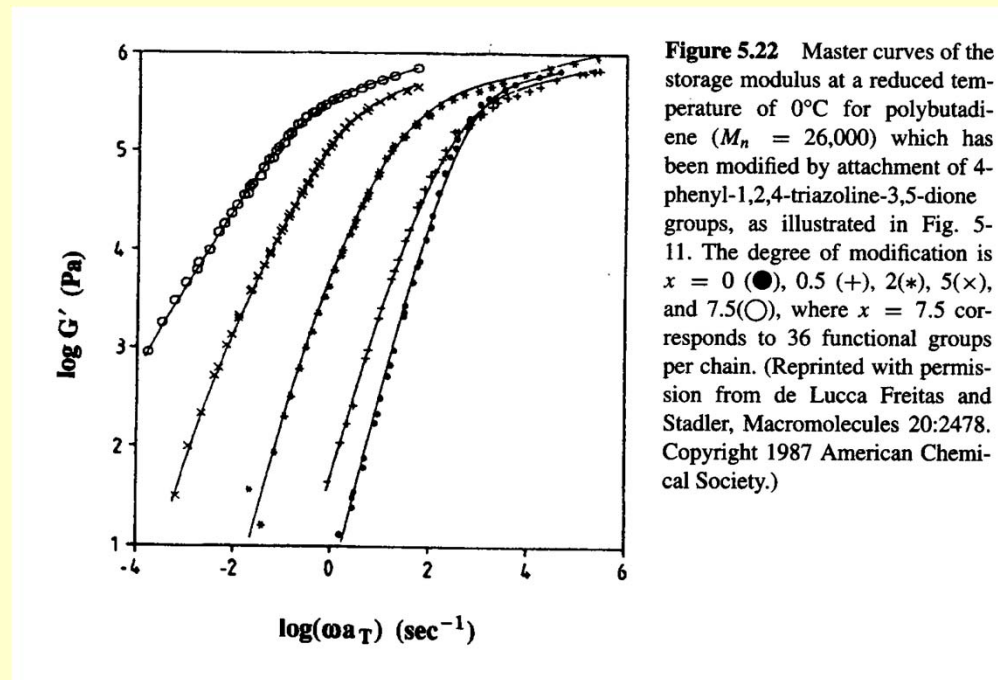


Figure 5.21 Viscosity versus shear rate for 1.0 wt% HEUR ($M_n = 51,000$ $M_w/M_n = 1.7$) telechelic polymers with hexadecanol end caps at 22°C. The illustrations show the structural transitions that are thought to occur as the shear rate is increased. First, the bridging chains are stretched, producing shear thickening. Then, many bridging chains are pulled out at one end from the micelles to which they were attached, and shear thinning occurs. (Reprinted with permission from Yekta et al., *Macromolecules* 28:956. Copyright 1995 American Chemical Society.)

Entangled 'sticky' chains

Many stickers along the chain

HASE; hydrophobic alkali-swellaable emulsion polymers



Shear thickening; caused by a shear-induced change in the balance between intramolecular and intermolecular associations

Shear induced gel formation at high shear rates