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Concepts for Understanding Their Structures and Behavior

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Low Frequency Properties of Polymer Melts

Also of interest in Fig. 6.16 is the finding that the shapes of curves in the terminal region remain similar to each other for all molar masses. More specifically, within the limit of low frequencies, a constant slope emerges, indicating a power law $G'(\omega) \propto \omega^2$. It is possible to explain this asymptotic behavior and to relate it to the properties of flowing polymer melts.

For a Newtonian low molar mass liquid, knowledge of the viscosity is fully sufficient for the calculation of flow patterns. Is this also true for polymeric liquids? The answer is no under all possible circumstances. Simple situations are encountered, for example, in dynamical tests within the limit of low frequencies or for slow steady state shears and even in these cases, one has to include one more material parameter in the description. This is the **recoverable shear compliance**, usually denoted by J_{e}^0 and it specifies the amount of recoil observed in a creep recovery experiment when the load is removed. J_{e}^0 relates to the elastic and anelastic parts in the deformation and has to be accounted for in all calculations. Experiments show that, at first, for $M < M_{\mathrm{c}}$, J_{e}^0 increases linearly with the molar mass and then reaches a constant value that essentially agrees with the plateau value of the shear compliance.

At higher strain rates more complications arise. There the viscosity is no longer constant and shows a decrease with increasing rate, which is commonly addressed as **shear-thinning**. We will discuss this effect and related phenomena in Chap. 9 when dealing with non-linear behavior. In this section, the focus is on the limiting properties at low shear rates, as expressed by the **zero shear rate viscosity**, η_0, and the recoverable shear compliance at zero shear rate, J_{e}^0.

Our concern is to find out how the characteristic material parameters η_0 and J_{e}^0 are included in the various response functions. To begin with, consider a perfectly viscous system in a dynamic-mechanical experiment. Here the dynamic shear compliance is given by

$$J = \mathrm{i}\frac{1}{\eta_0 \omega} \ . \tag{6.99}$$

This is seen when introducing the time dependencies

$$\begin{aligned} \sigma_{zx} &= \sigma_{zx}^0 \exp(-\mathrm{i}\omega t) \,, \\ e_{zx} &= J\sigma_{zx}^0 \exp(-\mathrm{i}\omega t) \end{aligned}$$

into the basic equation for Newtonian liquids

$$\sigma_{zx} = \eta_0 \frac{\mathrm{d}e_{zx}}{\mathrm{d}t} \ , \tag{6.100}$$

which results in

$$\sigma_{zx}^0 \exp(-\mathrm{i}\omega t) = -\eta_0 \mathrm{i}\omega J \sigma_{zx}^0 \exp(-\mathrm{i}\omega t) \ . \tag{6.101}$$

In a polymer melt, the viscous properties of Newtonian liquids combine with elastic forces. The latter contribute a real part to the dynamic shear compliance, to be identified with J_{e}^0:

$$J'(\omega \to 0) = J_{\mathrm{e}}^0 \; . \tag{6.102}$$

Combining Eqs. (6.99) and (6.102) gives the dynamic shear compliance of polymeric fluids in the limit of low frequencies

$$J(\omega \to 0) = J_{\mathrm{e}}^0 + \mathrm{i}\frac{1}{\eta_0 \omega} \; . \tag{6.103}$$

As we can see, η_0 and J_{e}^0 show up directly and separately, in the limiting behavior of J' and J''.

The dynamic shear modulus follows as

$$\begin{aligned} G(\omega \to 0) &= \frac{1}{J(\omega \to 0)} = \frac{\eta_0 \omega}{\eta_0 \omega J_{\mathrm{e}}^0 + \mathrm{i}} \\ &= \frac{\eta_0^2 \omega^2 J_{\mathrm{e}}^0 - \mathrm{i}\eta_0 \omega}{(\eta_0 \omega J_{\mathrm{e}}^0)^2 + 1} \; , \end{aligned} \tag{6.104}$$

giving

$$G'(\omega \to 0) = J_{\mathrm{e}}^0 \eta_0^2 \omega^2 \tag{6.105}$$

in agreement with Fig. 6.16, and

$$G''(\omega \to 0) = \eta_0 \omega \; . \tag{6.106}$$

We thus find characteristic power laws also for the storage and the loss modulus that again include J_{e}^0 and η_0 in a well-defined way.

One may wonder if η_0 and J_{e}^0 can also be deduced from the time-dependent response functions, as for example, from $G(t)$. Indeed, direct relationships exist, expressed by the two equations

$$\eta_0 = \int\limits_0^\infty G(t)\,\mathrm{d}t \tag{6.107}$$

and

$$J_{\mathrm{e}}^0 \eta_0^2 = \int\limits_0^\infty G(t) t\,\mathrm{d}t \; . \tag{6.108}$$

The first relation follows immediately from Boltzmann's superposition principle in the form of Eq. (6.38) when applied to the case of a deformation with constant shear rate $\dot{e}_{zx}$. We have

$$(\mathrm{d}x \widehat{=})\, \mathrm{d}e_{zx} = \dot{e}_{zx}\,\mathrm{d}t \tag{6.109}$$