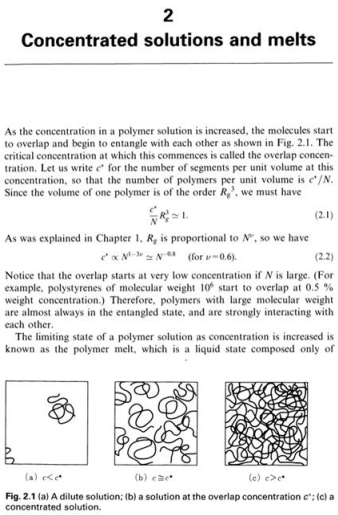

2

Concentrated solutions and melts

As the concentration in a polymer solution is increased, the molecules start to overlap and begin to entangle with each other as shown in Fig. 2.1. The critical concentration at which this commences is called the overlap concentration. Let us write c^* for the number of segments per unit volume at this concentration, so that the number of polymers per unit volume is c^*/N. Since the volume of one polymer is of the order R_g^3, we must have

$$\frac{c^*}{N} R_g^3 \simeq 1. \qquad (2.1)$$

As was explained in Chapter 1, R_g is proportional to N^ν, so we have

$$c^* \propto N^{1-3\nu} \simeq N^{-0.8} \quad (\text{for } \nu = 0.6). \qquad (2.2)$$

Notice that the overlap starts at very low concentration if N is large. (For example, polystyrenes of molecular weight 10^6 start to overlap at 0.5 % weight concentration.) Therefore, polymers with large molecular weight are almost always in the entangled state, and are strongly interacting with each other.

The limiting state of a polymer solution as concentration is increased is known as the polymer melt, which is a liquid state composed only of

(a) $c < c^*$ (b) $c \cong c^*$ (c) $c > c^*$

Fig. 2.1 (a) A dilute solution; (b) a solution at the overlap concentration c^*; (c) a concentrated solution.