which is to consider it equivalent of the correlation length in polymer solutions, ξ. In length scales smaller than ξ, monomers are mainly surrounded with solvent molecules. To reach another monomer (either as part of the same chain or an adjacent chain) the distance needs to be travelled is greater than ξ. A similar concept can be adapted for polymer networks, where ξ becomes the mesh size of that network. Based on this definition, the average mesh size of a network at any given swollen state depends on the extent of swelling, q:

$$\xi \sim q^{\beta_1} \qquad 32$$

In Equation 32, β_1 is a positive value and depends on the quality of the solvent. For polymer chains solvated in good solvents β_1 is 0.76 (Rubinstein and Colby 2003). The mesh size can also be defined as the average distance between two adjacent crosslinking points, R_c:

$$R_c \sim M_c^{1/2} q^{\beta_2} \qquad 33$$

In this case, β_2 is 0.12 and M_c is the average molecular weight between two adjacent crosslink points which is controlled by the network synthesis. Both Equations 32 and 33 establish a correlation between swelling ratio, network parameters and mesh size of a network at any given swelling state. When the swelling ratio reaches its equilibrium value, $q \rightarrow Q_{eq,o}$ for equilibrium free swelling and $q \rightarrow Q_{eq}$ for equilibrium swelling under external stresses, Equations 25 and 31 must be used to replace q in Equations 32 and 33 with, respectively, $Q_{eq,o}$ and Q_{eq}.

The magnitude of the mesh size of a network can be considered as one of the main limiting parameters by which the maximum size of molecules that can pass through the swollen network is determined. For instance, for a free swollen network in equilibrium with its surroundings, a smaller crosslink density results in larger M_c values and therefore larger swelling ratios (Equation 25), which in turn results in an increase in mesh size (either Equation 32 or Equation 33). Another indirect conclusion from the effect of external stresses on the swelling ratio is that theoretically it is possible to impact the mesh size of a swollen network through external constraints, although this effect is practically negligible.

The diffusion coefficient of small molecules passing through the swollen network can be expressed from various perspectives. In *the obstruction effect* models, the polymer network is treated as a solid intertwined network which increases the diffusion

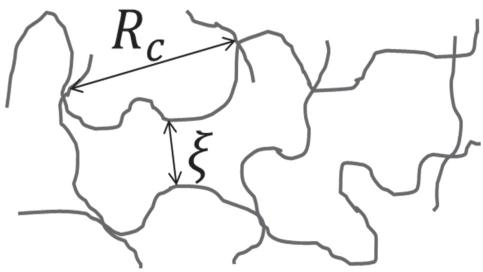

Fig. 6. Schematic representation of ξ and R_c. Depending on the definition, the mesh size can be defined by ξ or R_c. In a swollen polymer network, both parameters are directly related to the degree of swelling.