Small-angle neutron scattering by polymer networks*

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Small-angle neutron scattering (SANS) has proved to be a very useful method for investigating molecular shape and size in bulk polymers and in concentrated solutions, due to the difference between the coherent scattering lengths of hydrogen and deuterium. With SANS, it is possible to cover scattering vector values q (where $q = 4\pi/\lambda \sin \theta/2$, λ is the wavelength, and θ is the scattering angle) ranging between 10^{-3} and 2×10^{-1} Å^{-1}, matching the characteristic lengths of polymers. For a labelled chain in a specific situation, it is therefore possible to explore its conformation in detail.

Polymer networks are complex topological structures and approximations are necessary in order to interpret their properties. An indirect insight into the molecular behaviour of these materials has been obtained by mechanical and thermodynamic methods. Using SANS, however, a direct observation can be made, showing how the binding of polymer molecules into a permanent network affects their dimensions.

Two principal tagging procedures of a polymer network can be considered:

(a) labelling of the crosslinks, allowing the characterization of their spatial distribution (networks of type A);

(b) labelling of a small proportion of chains leading to the determination of the conformation of individual chains linked to the polymer networks (networks of type B).

The scattering response of these two types of labelled networks can be analysed using different topological models describing the segmental density function. The scattering function is obtained from the Fourier transform of the pair correlation function of the scattering elements.

The first question which arises is how the conformation of the chains is affected by topological constraints introduced during the crosslinking process, and in particular, by the restriction on the motion of the chain ends, and the volume occupied by the monomeric segments of the chain. Different situations can be considered depending on the distances over which the affine deformation occurs when a sample is submitted to an isotropic, or anisotropic, macroscopic deformation (for instance swelling or uniaxial stretching).

(1) The deformation is purely affine, (i.e. each pair of statistical segments of the elastic chains is oriented affinely by the deformation).

(2) Only the junction points deform affinely, the other segments of the chain having a total freedom of rearrangement.

(3) The mean coordinates **R** between chain ends deform affinely; the coordinates of **R** fluctuate about their mean position.

(4) The deformation is never affine on a molecular scale (occurring when chain disentanglement or separation takes place; in this case the chain end deformation may or may not be affine in the network).

It is clear that the non-affine contribution to the scattering will depend on the degree of fluctuation involved in the different situations considered.

The scattering behaviour resulting from departure from pure affine deformation will be discussed in a forthcoming paper, which gives a brief review of some recent theoretical predictions[1–5]. These will then be used to interpret experimental results obtained on 'model networks' whose elastic strands were of a monodisperse chain length, and with crosslinks of calculable functionality.

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