J. nat. Rubb. Res., 1(1), 51–57

Molecular Mobility in Rubbers

GEOFFREY ALLEN*

Neutron beams can be obtained in pulsed beams of virtually monochromatic character at wavelengths of about 5 Å. The momentum associated with the beam is high and the energy low. Thus neutrons are ideal for studying the diffusional motions of liquids in scattering experiments. In the past ten years, neutron scattering has been used to determine the average dimensions of individual chains in bulk rubbers and plastics, to study the dynamics of polymer chains in raw rubbers and melts and cross-linked networks and to measure the rotation of side groups. Results show that the Rouse model of molecular chain dynamics is more appropriate than the Zimm model for rubber. In networks, the sections of chain between cross-links form essentially the same chain motion as in the raw rubber, but the junction points move more slowly. The energy barrier to internal rotation of the methyl side groups in polypropylene oxide is found to be approximately 15 kJ mol^{-1} in line with the expected value.

The essential properties of rubbers of high extensibility and rapid recovery have their origins in the long-chain structure of the polymer molecules and the fact that each molecule is undergoing rapid changes in shape by virtue of internal rotations about the σ-bonds in the long chain. The chemical process of cross-linking enhances the retention of the strained and unstrained shapes of the rubber without seriously impairing its ability to undergo rapid, large deformations. This is because the chains are chemically linked at infrequent intervals to form a three-dimensional network within which the long segments of chains between cross-links are still able to perform rapid changes in conformation. If as in natural rubber, the rubber molecule has side groups (-CH_3 in this case), these groups undergo internal rotation about the C–C bond relative to the main chain in addition to the main-chain wriggling. When a rubber is cooled to a glass or crystalline material, the main-chain wriggling is frozen out in the glass or crystalline domains, however the internal rotation of the side groups usually continues down to much lower temperatures.

A variety of spectroscopic and scattering techniques have been used to investigate molecular motion in rubbers and to support the rotational isomeric model of the polymer chain which is central to molecular theories of polymeric materials. X-ray scattering has contributed to our understanding of the molecular structure in crystalline rubbers. Light scattering has been used to measure the diffusion of the centre of mass of individual polymer molecules in dilute solutions. In the past ten years, using neutron scattering, it has been possible to determine the average dimensions of individual chains in bulk rubbers and plastics, to study the dynamics of polymer chains in raw rubbers and melts and cross-linked materials and to measure the rotation of side groups. All these measurements are possible because of the unique nature of neutron scattering from molecules.

Neutron Scattering

Intense neutron beams can be obtained from specially designed nuclear reactors. Using crystal filters and mechanical selectors it is possible to isolate pulsed beams of virtually monochromatic character at wavelengths of about 5 Å. The beam is composed of neutrons which have atomic mass 1, zero charge and nuclear spin ½, and velocities of the order of 1000 m per second. Compared with beams of electromagnetic radiation, the momentum

---

*Unilever PLC, London EC4P 4BQ, United Kingdom

associated with the beam is high and the energy low. The energy associated with Avogadro's number of neutrons is only 280 joules.

Thus, neutrons are ideal for studying the diffusional motions of liquids in scattering experiments in which very small amounts of energy are exchanged between these quasi-classical modes of motion and the incident neutron. The scattered neutron may gain or lose energy in the scattering event or may simply be scattered elastically. After scattering its velocity may be increased, reduced or remain unaltered.

Thus, if the energy profile of the neutron beam is measured before and after scattering it will be broader after scattering. The broadening gives a spectrum of the energies of diffusional motion in the sample. This broadening is termed 'quasi-elastic' or Doppler broadening. It is a function of the momentum Q transferred in the scattering event. When the energy exchanged is very small, Q is defined by the angle of scatter:

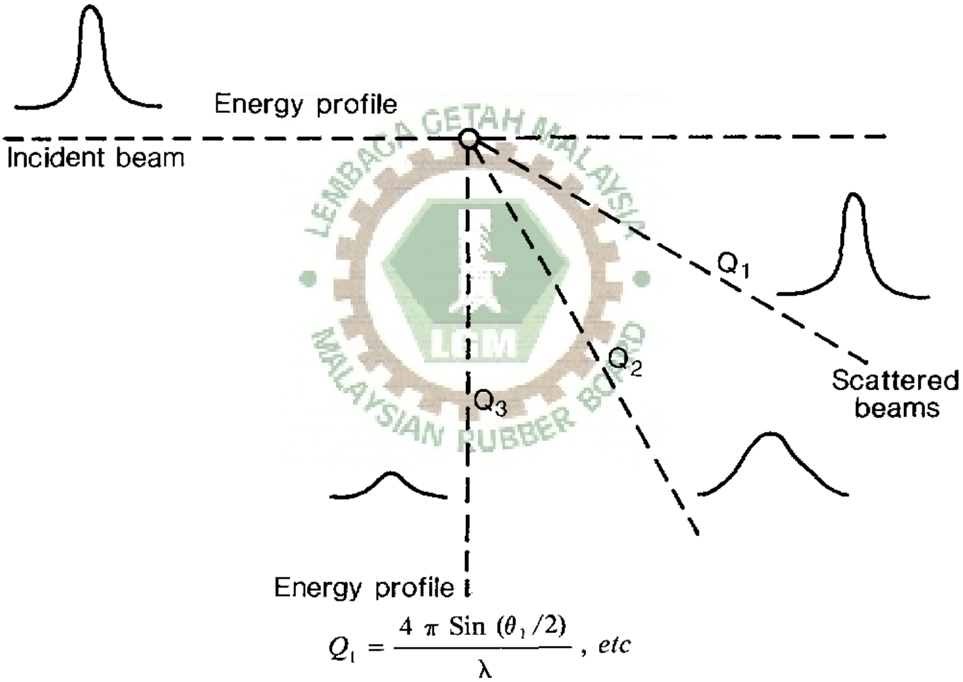
$$Q = \frac{4\pi \operatorname{Sin}(\theta/2)}{\lambda}$$

where λ is the wavelength.

The experiment is shown schematically in *Figure 1.* The incident and scattered velocities of the neutrons are obtained from the times of flight of the neutrons over fixed distances measured at fixed angles before and after the scattering event. A typical plot of the variation in the breadth of the profile of scattered neutrons is shown in *Figure 2* as a function of the momentum transfer (≅ angle of scatter) Q. The fact that broadening is observed shows that molecular motions are occurring in this polypropylene oxide rubber.

Molecular Motion in Liquids and Rubbers

The Langevin equation can be used to predict the shape of the quasi-elastic broadening. For simple liquids such as water and benzene where the molecules diffuse as single units, the shape



$$Q_1 = \frac{4\pi \operatorname{Sin}(\theta_1/2)}{\lambda}, \; etc$$

Figure 1. Quasi-elastic neutron scattering experiment showing Doppler broadening of the energy profile.

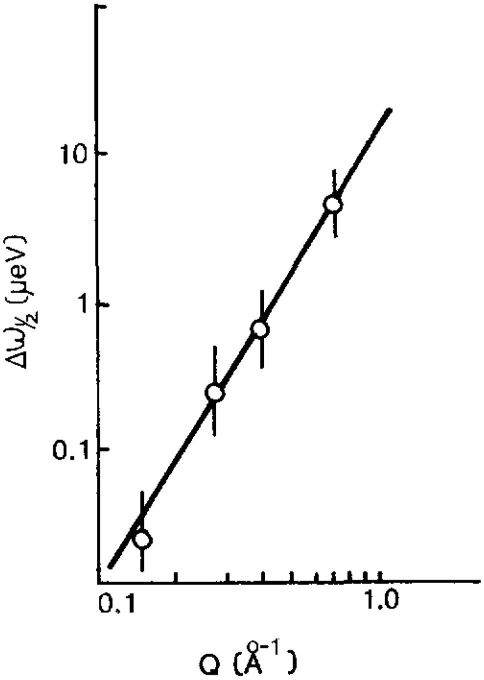


Figure 2. Quasi-elastic (Doppler) broadening plotted as a function of Q for polypropylene oxide $-CH_2-CH(CH_3)-O-$.

of the quasi-elastic (Doppler) broadening is predicted to be Lorenzian with:

width of broadening αQ^2.

The broadening is measured as the increase in width at half the height of the peak, in units of micro-electron volts μeV.

For a polymer chain with no hydrodynamic interactions (*i.e.* the Rouse model), for example in a polymer melt of rubber where the chains are undergoing self-diffusion, (the wriggling motion is coupled with the centre of mass motion) the broadening is similar but now:

width of broadening αQ^4.

For a polymer chain subjected to hydrodynamic interaction as in a polymer solution, where the polymer chain motion is subject to interaction in the solvent molecules:

width of broadening αQ^3.

Experimental comparison of the three laws is given in *Figure 3* for three different samples — a liquid, a rubber and a polymer solution. In each experiment the scattering intensity is normalised to the same number of scattering units. The results largely confirm theoretical prediction of the variation of broadening with Q for the three different systems. Of course, in a polymer the diffusion process is observed only in the melt or rubber phase or in solution. In the glass the motion is frozen out, so no broadening is observed.

Having established that the broadening is approximately proportional to Q^4 for polymer melts, we can now compare the scattering from different rubbers or polymer melts at the same temperature.

At a given temperature, the higher the frequency of diffusional motion the larger the energy exchange, and hence the larger is the broadening of the quasi-elastic peak. Thus flexible chains, because they will have higher frequencies of motion, will be expected to give larger broadening at a given temperature and angle of scatter than will stiff chains. High molecular weight polymers are used in these experiments and the chain motions are being observed over distances of less than 30 Å at these wavelengths and Q values. *Figure 4* shows logarithmic plots of broadening against momentum transfer Q for a group of four polymers in the melt.

From measurements of the kind summarised in *Figures 2* and *3* we learn two facts. Firstly, the polymers are all closer to the Rouse model in the melt than to the Zimm model. Secondly, the order of chain flexibility as judged from a comparison of the Doppler broadening at the same temperature and Q value is:

Polydimethylsiloxane > polytetrahydrofuran ≃ polypropylene oxide > polyisobutene

i.e. $-O-Si(CH_3)_2 > -CH_2-CH_2-CH_2-CH_2-O-$
$\simeq -CH_2-CH_2-O- > -CH_2(CH_3)_2$

Thus, we have shown that the Rouse model of molecular chain dynamics (*i.e.* chain flexibility) is more appropriate than the Zimm model for

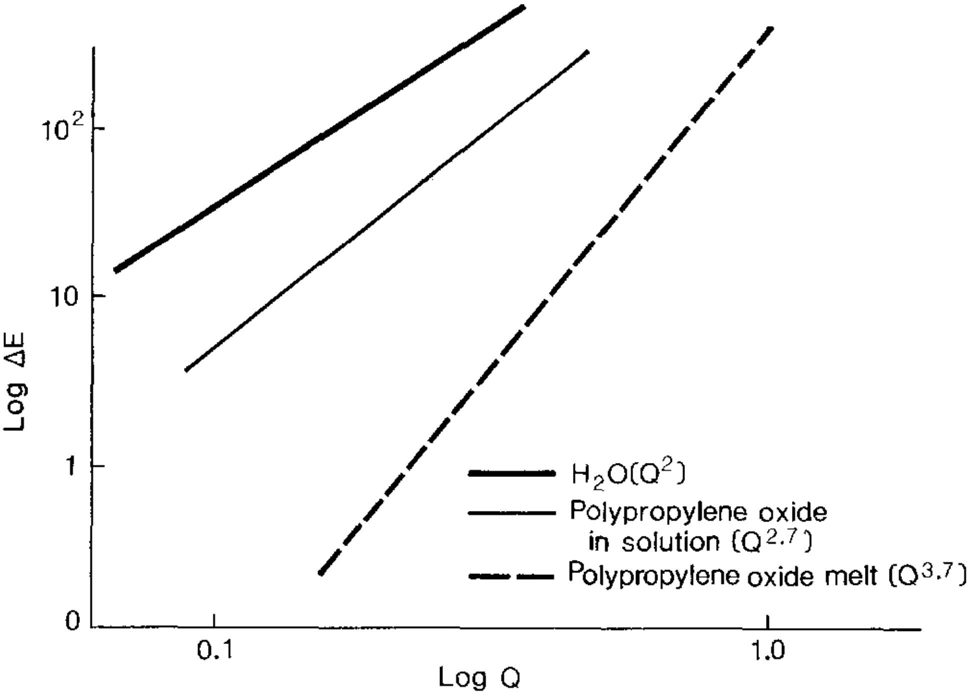


Figure 3. Comparison of the scattering laws for $H_2O(Q^2)$*, polypropylene oxide in solution* $(Q^{2.7})$ *and polypropylene oxide melt* $(Q^{3.7})$.

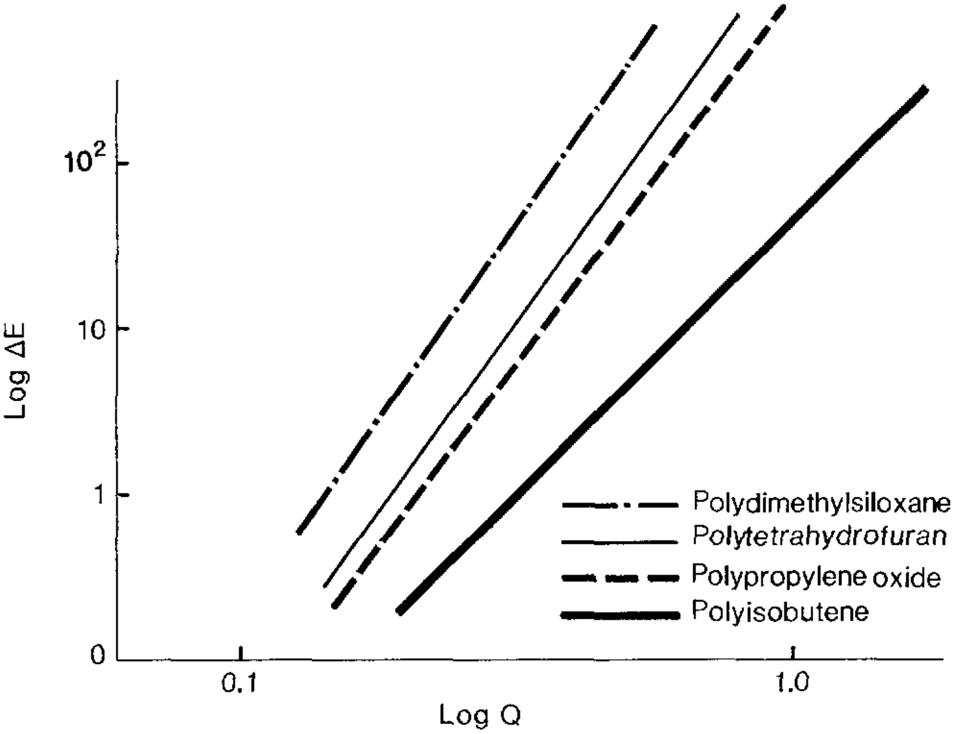


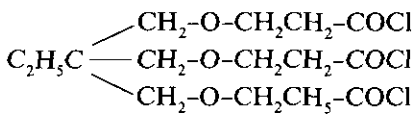
Figure 4. Quasi-elastic (Doppler) broadening plots for four polymer melts: polydimethylsiloxane, polytetrahydrofuran, polypropylene oxide and polyisobutene.

rubber and the four polymers whose chain flexibilities have been compared by quasi-elastic neutron scattering are placed in order of decreasing chain flexibility.

Molecular Motion in Networks

Recently one of my colleagues[2] studied quasi-elastic broadening of neutron scattering from polypropylene oxide networks and compared the results with scattering measurements from partially deuterated networks in which hydrogen was located only around the network function points as in *Figure 5.*

The networks were made by reacting polypropylene oxide diol of molecular weight 2000 with:



$$C_2H_5C\begin{array}{l} \diagup CH_2\text{-}O\text{-}CH_2CH_2\text{-}COCl \\ \text{—} CH_2\text{-}O\text{-}CH_2CH_2\text{-}COCl \\ \diagdown CH_2\text{-}O\text{-}CH_2CH_5\text{-}COCl \end{array}$$

For the partially deuterated network perdeuteropolypropylene oxide diol was used.

In these samples, the observed neutron scattering is dominated by scattering from the hydrogenated parts of the network. In the partly deuterated sample scattering from the deuterated chains is virtually invisible and the broadening is determined by the motion of the cross-links of the networks since they are hydrogenated. The results are shown in *Figure 6.* The lower line represents the broadening observed in the partially deuterated sample. Thus, it can be deduced that the cross-links are moving more slowly than the chains between cross-links because the partly hydrogenated sample shows greater broadening under the same conditions of Q and temperature. If the two sets of scattering data are subtracted from each other, the residues give the broadening as a function of Q arising from the chain segments *between* cross-links.

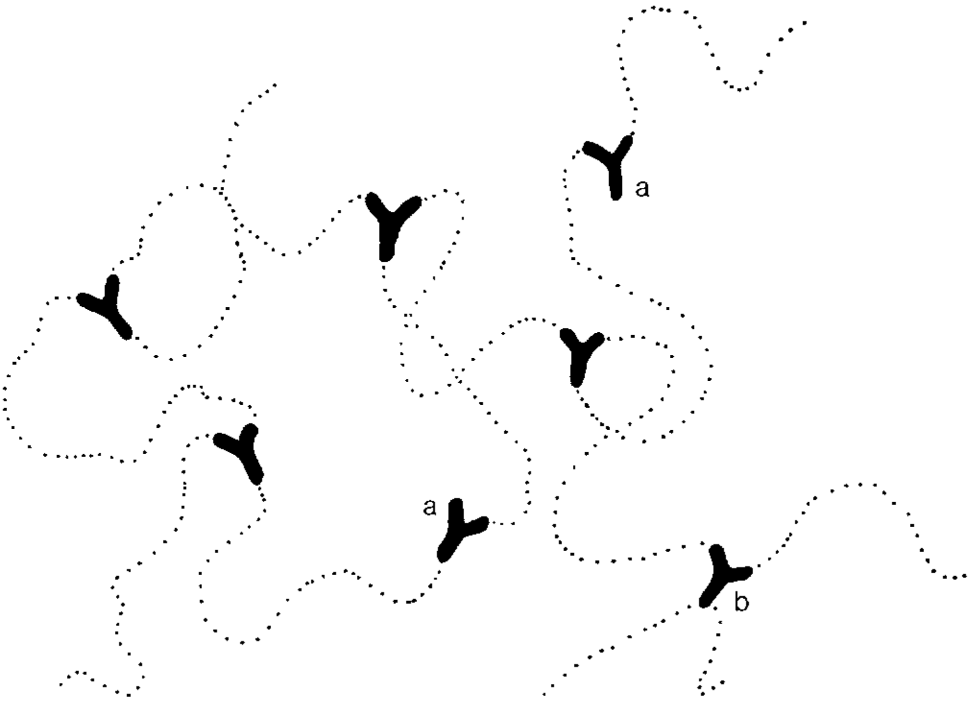


Figure 5. Diagrammatic representation of network showing some incomplete junctions.

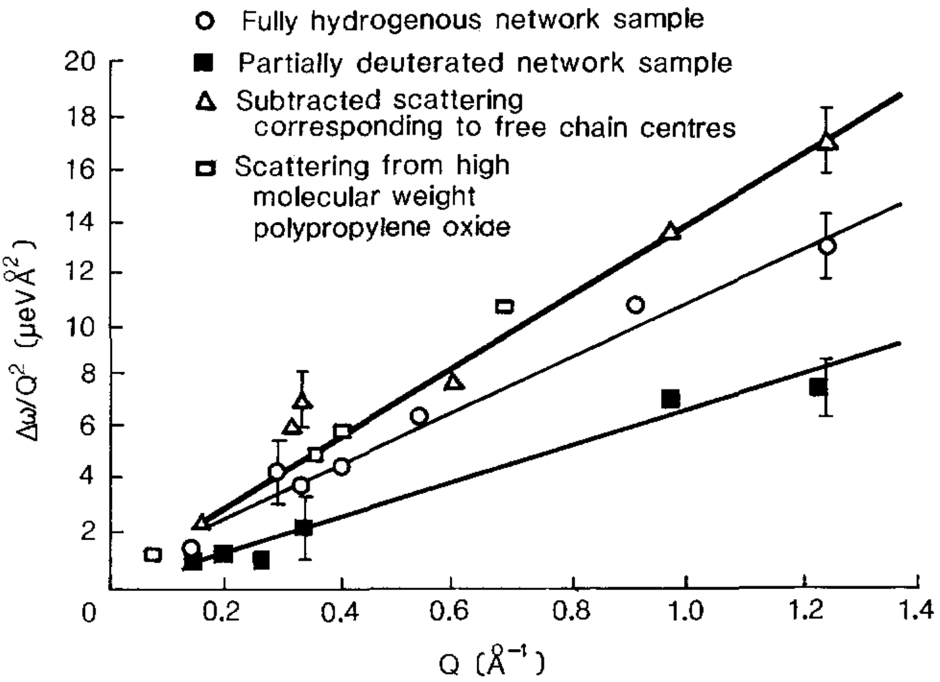


Figure 6. Δω/Q² against Q for scattering from a fully hydrogenous network sample, a partially deuterated network sample, subtracted scattering corresponding to free chain centres and scattering from high molecular-weight polypropylene oxide. The lines are guides to the eye.

These are the points on the upper line in *Figure 6.* Furthermore, these points lie on the same line representing the broadening from the uncross-linked rubber. Thus, we arrive at the conclusion that in a network the sections of chain between cross-links form essentially the *same* chain motion as in the raw rubber, but the junction points move more slowly. The timescales differ by about a factor of 2. However, we can begin to build up a physical picture of the dynamics of this network.

Side Chain Motions

The same method of quasi-elastic neutron scattering can be used[3] to study the motion of side groups. This has also been done for polypropylene oxide rubber. However, because the side groups rotate so rapidly and because their broadening contribution is convoluted into the main chain broadening, the rubber has to be cooled below *Tg*. This freezes out the main chain broadening because the main chain motion is frozen out. Ultimately, a very small broadening component can be seen *(Figure 7)* in the wings of the elastic peak. It is just within the experimental limits of the present instruments. The fact that this broadening originates from -CH_3 motion can be seen from the comparison with -CD_3 shown in *Figure 7.*

Whereas the main chain broadening is a function of *Q* ($\sim Q^4$) the side chain quasi-elastic broadening is *independent* of *Q*. This is because it arises from rotational diffusion of the CH_3 group as it rotates around a -C-C- bond fixed in space. The main chain motion is self-diffusional and the scattering centres more randomly through a relatively large volume of space. The temperature dependence of the rotational broadening gives an order of magnitude of the energy barrier linking rotation. For this CH_3 group in polypropylene

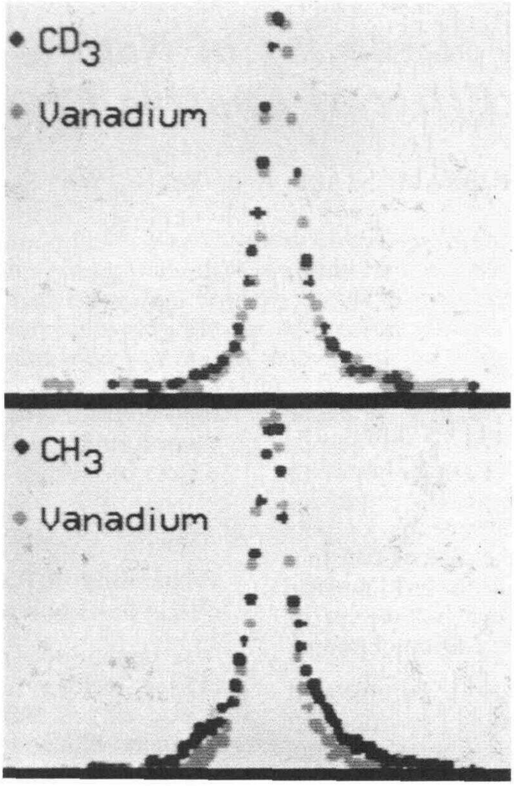


Figure 7. Comparison of the quasi-elastic scattering from polypropylene oxide (CD_2-$C(CH_3)$ D-O-) and $(CH_2\text{-}C(CD_3)H\text{-}O)_n$ at 173 K and Q = 1.62. Also shown is the instrumental resolution represented as the scattering from vanadium.

oxide it is approximately 15 kJ mol^{-1} in line with what would be expected from the spectroscopic value of the barrier to internal rotation.

SUMMARY

Using neutron scattering we can support the current models for molecular motion in raw and cross-linked rubbers. As the technique improves more quantitative values will be ascribed to the various forms of motion.

REFERENCES

1. ALLEN, G. AND MACONNACHIE, A. (1977) *Br. Polym. J.*, 184.
2. HIGGINS, J.S., MA, K. AND HALL, R.H. (1981) *J. phys. Chem, Solid State Phys.*, **14**, 4995.
3. ALLEN, G. AND HIGGINS, J.G. (1977) *Macromolecules*, **10**, 1006.