UK 50 at ILL

Early Science Polymers, membranes……

Julia Higgins

Emeritus Imperial College

Physics of polymer molecules and polymeric materials

1920   Hermann Staudinger first proposed plastics were composed of very long molecules with co-valent bonds

1953   Paul J Flory described the shape and size of individual polymer molecules in solutions and melts. In the melt molecular dimensions increase as $\sqrt{N}$, but they are larger in solution because of excluded volume effects
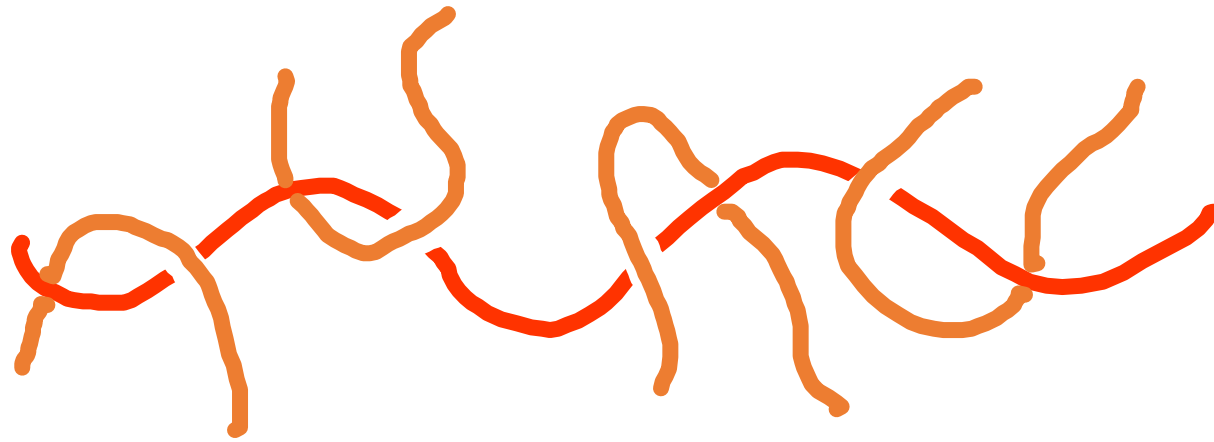
Physics of polymer molecules and polymeric materials

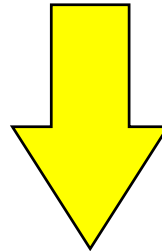**1967**   Sam Edwards – polymer molecules in rubbers and glasses are trapped by their neighbours in a "tube

1971   Pierre Gilles de Gennes – in rubbers the trapped molecules move like snakes in their tube and eventually escape - reptation
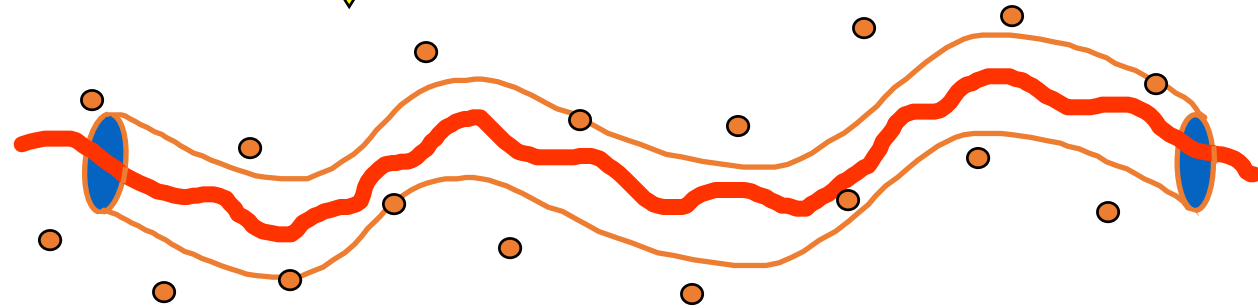
The Tube Model

Polymer chains in the melt

Each chain can be considered to be constrained within a tube

Big questions for polymer scientists still open in 1970

- Is the individual polymer molecule a "random walk" in a melt sample (Flory)?

- Does the individual polymer molecule deform affinely in a stretched sample and how does it relax.

- Testing theoretical models describing the movement of the polymer molecules and relating this to their stickiness (viscosity) and stretchiness(elasticity)

- REQUIRED molecular labelling (deuteration), small angle scattering, high resolution quasi-elastic scattering – D11, IN5, IN10, IN11, D27, ...

# The guide Hall in 1973 with skeleton of IN5 in front

Conformation of Polymer Chain in the Bulk

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ABSTRACT: Neutron coherent scattering techniques have been used for the determination of the conformation of polymer in bulk and experimental details are given about the application of this method to the study of polymeric systems. Measurements have been made for small and intermediate momentum ranges on a series of eight mono-disperse deuterated polystyrenes of molecular weight ranging from 21,000 to 1,100,000. The results lead to the conclusion that in amorphous state the conformation of the polymer molecule is indistinguishable from that in θ solvent and that the Debye scattering function which is valid for unperturbed chains applies for q^{-1} as low as 10 Å.
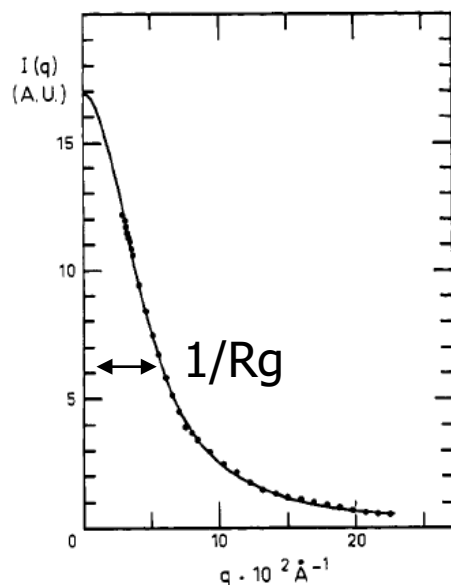
Figure 6. Intensity, in arbitrary units, obtained as a function of q by difference of the curves of Figure 5. The full line is a calculated curve which is explained at the end of this paper.
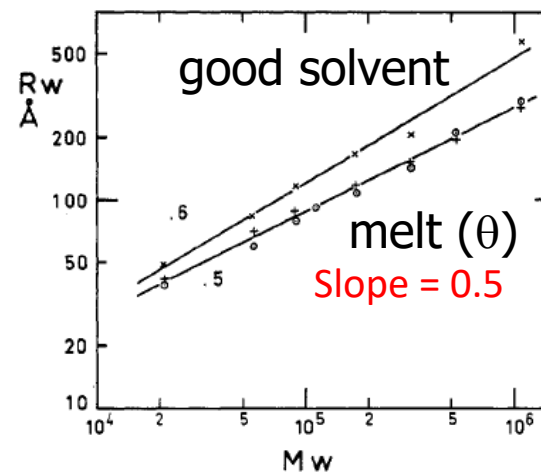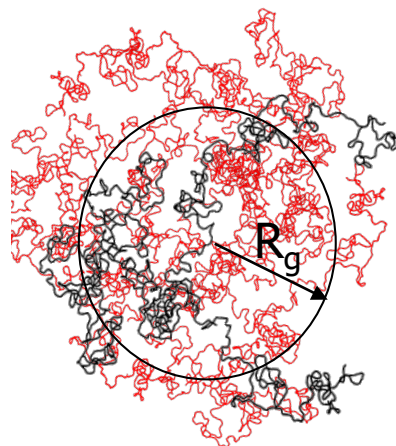
Figure 8. Log R_w is plotted $vs.$ log M_w. The experimental data are obtained in different environments: (X) in a good solvent CS_2, (+) in a θ solvent, (⊙) in the bulk. The slopes of 0.6 (in CS_2) and of 0.5 are obtained by a best fit method.

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ON THE STRUCTURE
OF THE QUASIELASTIC INCOHERENT NEUTRON SCATTERING
FROM POLY(DIMETHYL-SILOXANE)

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The structure of the quasielastic incoherent neutron scattering from polydimethyl siloxane has been determined at low momentum transfer under conditions of high resolution. Within the limits of experimental error the quasielastic peak is a single component; a two component peak was not found. The findings are consistent with a previous tentative interpretation of the quasielastic peak being due to a Doppler broadening phenomenon attributed to the long range conformational changes of the polymer backbone.

1. Introduction

The rubbery state is essentially the liquid state of polymerised materials and the origin of rubber elasticity lies in the long range wriggling motions of the segments of the polymer chains. Investigation of the dynamics of polymer chains is thus of interest in the development of the theory of the rubbery state. Poly(dimethyl-siloxane) (PDMS ($Si(CH_3)_2-O-)_n$) has been much used for such studies because it has a wide rubbery interval (from $\approx 100°K$) and because even high molecular weight samples in the uncrosslinked form flow surprisingly readily at room temperature and consequently crosslinked samples show viscoelastic phenomena on a relatively short time scale.

The centre of mass motion involved in the self-diffusion of PDMS low molecular weight oligomers and selected high polymers has been investigated by spin echo NMR methods [1, 2]. More recently a similar series of compounds have been studied by neutron inelastic incoherent scattering [4, 5]. Briefly the results the two kinds of experiments are:

(i) For low molecular weight samples of PDMS ($n = 4-20$) the spin-echo technique [1] gives values of the translational diffusion constant in the range 4×10^{-5} to 10^{-6} cm^2 sec^{-1}. Since the measurement involves the net displacement of protons in a macroscopic field gradient on a time scale of the order of milliseconds there is little doubt that the technique gives a translational self-diffusion constant. The diffusion constant, D obeyed a relationship of the form $D \propto (mol. wt)^{constant}$.

(ii) In the case of the high polymers some correction was made for the presence of a low molecular weight component [2] (giving a binodal molecular weight distribution) and the self-diffusion constant for a molecular weight of 32 000 was estimated to of the order of 5×10^{-9} cm^2 sec^{-1}.

(iii) In neutron inelastic incoherent scattering diffusive motions of the nuclei (and principally the protons) produces a broadening of the energy profile of the incident neutron beam [3]. The variation this Doppler broadening with momentum transfer experienced by the neutrons can be used to investigate
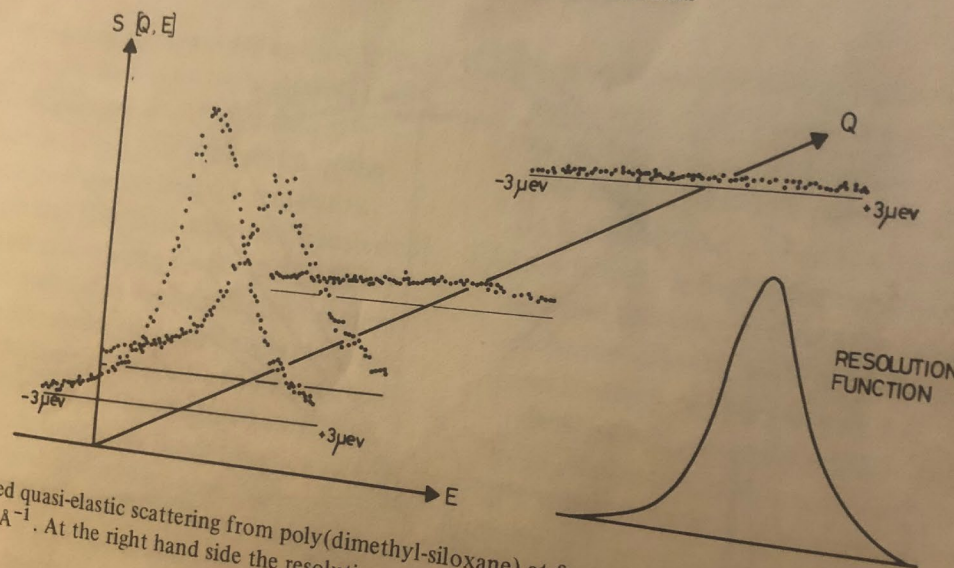
normalised quasi-elastic scattering from poly(dimethyl-siloxane) at four values of Q, the momentum transfer 7, 0.97 Å^{-1}. At the right hand side the resolution function of the machine is shown on the same scale

diminishing D_{eff} values recorded in other experiments ... rried out over a wide range of Q [4, 8]. Two now arise: (1) what is the exact physical ... the Q dependence of the scattering law $S(Q,\omega)$ ... hat is its theoretical implication? Any theoretical explanation of the broadening must of course ... r the difference in magnitude of D ... f D obtained from spi...
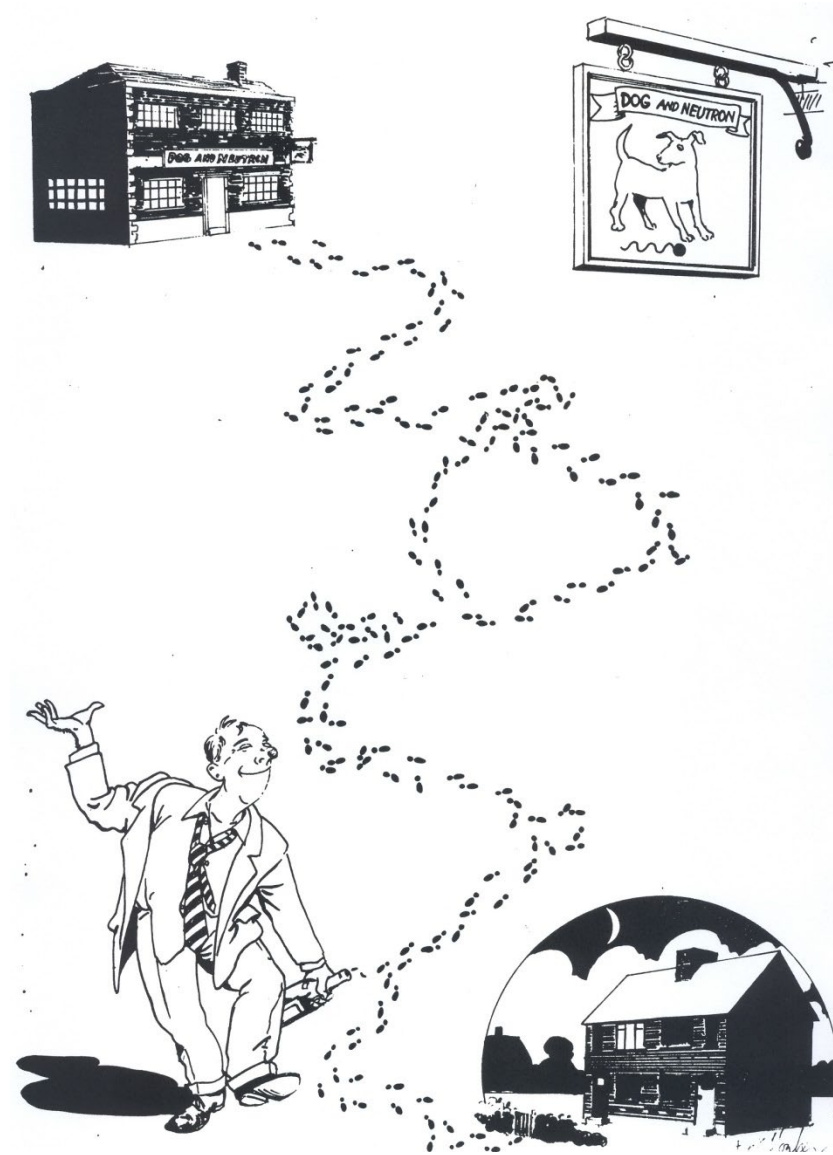
[2] D.W. McCall and C.M. Huggins, Appl. 7 (1965) 153.

[3] T. Springer, Springer Tracts in Modern (Springer-Verlag, Berlin, 1972) p. 64

[4] G. Allen, P.N. Brier, A.G. Faraday S...

The drunkard's walk

L is proportional to square root N

$L \approx N^{0.5}$

Polymers in a melt

Self avoiding walk $L \approx N^{0.6}$

Polymers in solution