Neutron scattering by partially labelled chains

R. Duplessix
ILL, BP 156X, Grenoble Cédex, France

J.P. Cotton
CEN Saclay, BP2, Gif-sur-Yvette, France

H. Benoit and C. Picot
CRM 6 rue Boussingault 67083 Strasbourg Cédex, France

(Received 26 June 1979)

By tagging selectively specific sites of a system by deuteration, the neutron scattering technique makes it possible to study the spatial correlations or interactions between labelled parts. This method has been fruitfully used for studying macromolecular chain configuration in the solid state[1,2] and in concentrated solution.[3]. In these latter experiments, measurements have been carried out on completely labelled chains leading to information on intramolecular correlations in the case of infinite dilution of tagged species, while for the semi dilute or concentrated case intermolecular correlations are superimposed.

An interesting experiment was to study systems consisting of chains in which a certain proportion of the structural units were deuterated and the remainder protonated in order to obtain a predominant intermolecular scattering contribution. The preliminary results described in this note concern a 107 000 molecular weight polystyrene (PS) prepared by anionic polymerization, in which the central part of the chain is made of perdeuterated monomeric units, the molecular weight of this central part being 13 000. In fact we are dealing with a triblock copolymer PSH-PSD-PSH (denoted PSHDH), but a copolymer in which there is no chemical difference between the three sequences. There is thus a conformation in solution, or in the bulk state, identical to the conformation of a homopolymer of the same molecular weight.

By tagging the molecules in this way we have labelled the centre of mass of the polystyrene coils. The interaction between chains can then be studied over the whole range of concentrations up to the bulk state. It was in fact particularly interesting to study the behaviour between dilute and semi dilute regime when the coils start to overlap.

The experiments have been performed on the instrument D17 at the Institut Laue-Langevin (ILL) in Grenoble. This apparatus is a two axis spectrometer with a BF_3 multidetector. This multidetector 64 x 64 cm^2 in area, can be positioned at 1.4 or 2.8 m from the sample and rotated around it from 0° to 90°. Two mechanical se?ectprs permit selection of a wavelength λ between 8 and 16 Å with resolution $\Delta\lambda/\lambda$ of 10% and 4%. These parameters determine the range of q vector ($|q| = (4\pi/\lambda) \sin \theta/2$, θ scattering angle) available. At low angle it depends also on the collimation of the incident beam, thus an approximate lowest value is $q = 5.10^{-3}$ Å^{-1}. An on line computer permits data acquisition and treatment.

The samples in solution were studied in quartz cells of various thicknesses between 1 and 10 mm depending on the incoherent scattering contribution of the mixed medium. We have chosen as solvent carbon disulphide (CS_2), which is a good solvent for PS and is particularly convenient for neutron scattering experiments.*. Bulk samples has been moulded above *Tg* (130°C) under vacuum; they are disc shaped with a thickness of 1 mm and a diameter of about 15 mm.

Dilute solutions of completely labelled chains lead to a small angle scattering signal in the Guinier domain decreasing with q, and at the opposite extreme bulk samples result in a flat scattering. The striking result in the case of our system is that the scattering function exhibit a strong maximum over the whole domain of concentration. *Figure 1* shows typical curves obtained in dilute solutions (a), in semi dilute solutions (b) in the bulk state (c). In each case the scattering maximum is uncontestable.

The q vector range available in one experiment in the apparatus configuration used is narrow and it is impossible to reach the lowest q value needed for a complete description of the scattering distribution. It is however noticeable that for dilute solution the intensity does not become zero for $q = 0$ whereas in the other cases it tends to vanish.

The q value for the maximum intensity noted q_{max}, varies with the concentration c, thus without making any assumption about the origin of the scattering peak it was interesting to look at the variation of q_{max} with c. *Figure 2* shows the results obtained for the angular position of the maximum q_{max} versus the concentration expressed in polymer per g solution for CS_2 solutions over the whole domain of concentration.

There is no ambiguity for the peak angular position determination above 1% concentration. Below this value the small angle scattering signal becomes too large in comparison to the peak intensity. It is then hazardous to determine a q_{max} value, however the scattering function is still not of the coil type in this q range. From *Figure 2* one can notice that q_{max} variation exhibits two distinct types of behaviour characterized by different slopes. The slope change corresponds roughly to the overlapping concentration, calculated from the mean dimensions of the chains, generally called c^x. Below this value the slope is 1/3 which is a typical volume exponent. Above c^x up to the solid state the slope is 0.087 and is difficult to interpret at this stage of the investigations.

---

* Because of a very low incoherent scattering.

0032-3861/79/101181-02$02.00

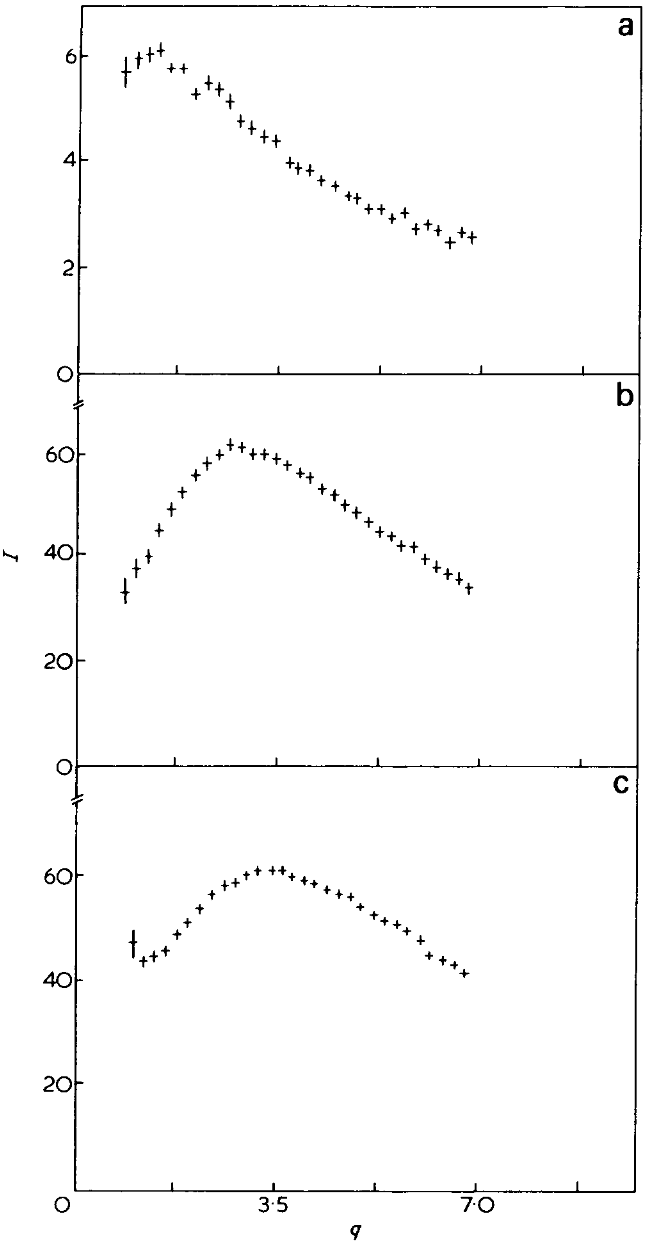

Figure 1 Scattering distribution function obtained with CS_2 solution (a) 1%, (b) 20%, and solid state (c).

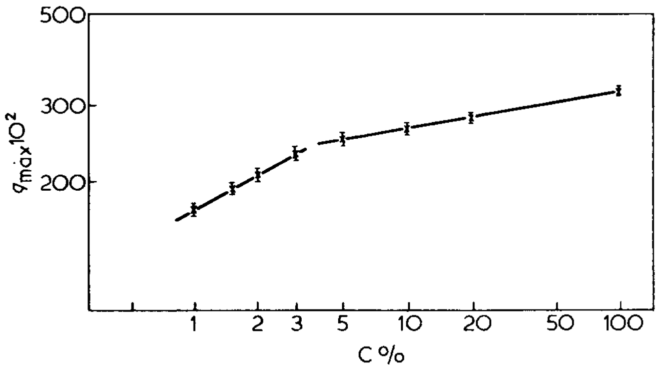

Figure 2 Concentration dependence of q_{max}.

The scattering curve obtained in the bulk could be interpreted in terms of correlation hole [3,4]. Using the theoretical prediction of these references we have shown[5] that there is good agreement between experimental and theoretical values calculated by introducing the ratio between labelled and non labelled sequences.

The hypothesis of the previous theoretical treatment is only applicable in the case of the melted polymer, thus it is now impossible to use it in solution, especially in dilute solutions. However work is being done to extend the field of validity of the theory to the semi dilute regime. This will be the aim of a subsequent paper where more extensive experimental results and their theoretical justification will be given.

References

1 Kirste, R.G., Kruse, W.A. and Schetten, J. *Makromol Chem* 1972, **162**, 299
2 Cotton, J.P. *et al. Macromolecules*, 1974, 7, 863
3 Daoud, M. *et al. Macromolecules*, 1975, 8, 804
4 de Gennes, P.G. *J de Physique*, 1970, 31, 235
5 Cotton, J.P. *et al., I.A.E.A.* Vienna, Vol. 1, 563 (1978).

Ring-opening polymerization of fluorine substituted bicyclo[2,2,1] hept-2-enes and -hepta-2,5-dienes

W.J. Feast and B. Wilson
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE

The production of poly(1-pentenylenes), linear hydrocarbon elastomers, by the ring opening polymerization of cyclopentene is well established.[1] The work reported here stemmed from an attempt to extend this reaction to the polymerization of 1H, 2H-hexafluorocyclopentene prompted by the hope that the resultant polymers would combine the low glass transition temperatures associated with polypentenylenes, with the thermal stability and solvent resistance associated with fluorocarbon polymers. This attempt was unsuccessful but raised the question of the polymerizability of fluorinated monomers by typical metathesis polymerization catalysts. A variety of monomers containing electron-withdrawing substituents have been reported to undergo ring-opening polymerization in the presence of typical metathesis catalysts[2–6] but the only examples of possible metathesis reactions of fluorinated systems known to us are the cyclobutane-diene interconversions described by Gassman and Johnson.[7]

We now report that the monomers I → VI are readily polymerized and copolymerized by ring opening at the unsubstituted double bond under the influence of a variety of metathesis catalysts derived from tungsten

0032-3861/79/101182-02$02.00