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# Neutron Scattering from Polymers: Five Decades of Developing Possibilities

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## Keywords

neutron scattering, polymer molecular dynamics, polymer blends, spinodal decomposition, polymer interfaces

## Abstract

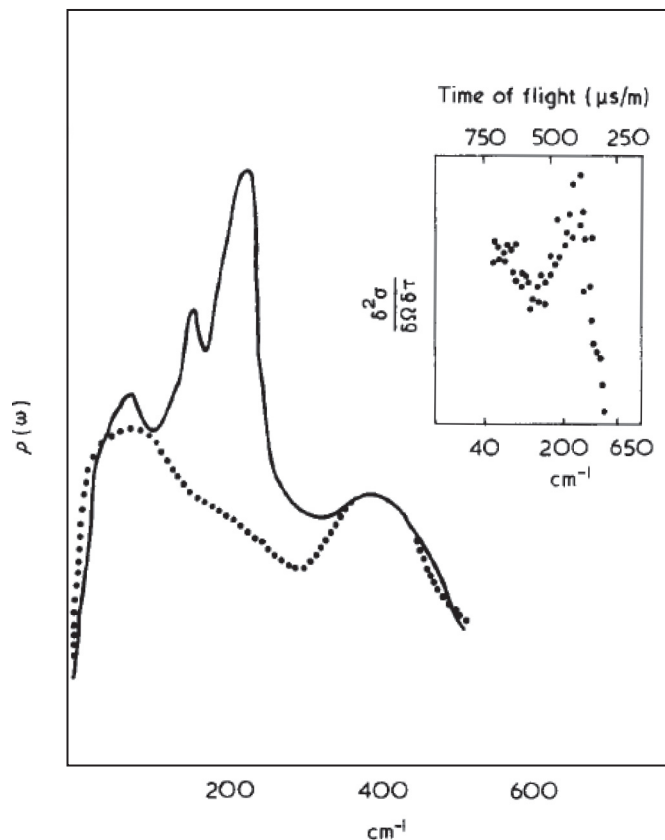
The first three decades of my research career closely map the development of neutron scattering techniques for the study of molecular behavior. At the same time, the theoretical understanding of organization and motion of polymer molecules, especially in the bulk state, was developing rapidly and providing many predictions crying out for experimental verification. Neutron scattering is an ideal technique for providing the necessary evidence. This autobiographical essay describes the applications by my research group and other collaborators of increasingly sophisticated neutron scattering techniques to observe and understand molecular behavior in polymeric materials. It has been a stimulating and rewarding journey.

## INTRODUCTION

One day in autumn 1968, I found myself saying to a colleague during a phone call, “And do you realize they are paying me to do what I love doing?” I had just returned to academic life as a research fellow in the Department of Chemistry at the University of Manchester, having spent the previous two years teaching physics to school children. I have chosen this as my starting point for an academic biography because that appointment in Manchester was the moment when the two key threads of my research career, neutron scattering and polymer molecules, first came together.

The first thread was spun in Oxford where, after an undergraduate physics degree, I had moved to the chemistry department for my PhD. This was something of a bold move, as I had studied only maths and physics for my final school years and at university! My supervisor, John White, had very recently moved to Oxford from Sydney and had been hearing from a scientist working at the Harwell reactor about the potential for studying molecular behavior with neutrons. Peter Egelstaff was something of an evangelist to the academic community, selling the potential of the neutron beams at Harwell for studying materials at a molecular level. John White was particularly interested in the possibilities of neutron scattering from deuterium-labeled molecules or parts of molecules. As I detail further below, the neutron sees hydrogen and deuterium nuclei differently, and John aimed to use this attribute to pick up the low-frequency motion of molecules trapped within a structure formed by a different species. He had the idea that someone trained in physics would take to using neutrons more readily than a chemist. He took me on as his first doctoral student, happily ignoring my severe deficiencies in chemistry! These became very apparent when we discussed my project. The idea was to look at molecules trapped within cages formed by clathrate inclusion compounds. Hydroquinone forms such cages and is a compound containing a great deal of hydrogen. The trapped molecules also contained hydrogen, and my job was to make them visible by replacing the hydrogen in hydroquinone with deuterium, thus reducing its visibility to the neutrons. Bearing in mind my lack of chemistry, this was something of a daunting task. There was a recipe in the literature for replacing H with D by heating the hydroquinone to approximately 200°C under pressure—written in Russian! A fellow student translated for me, and after many adventures, I did succeed in producing 10 g of perdeutero-hydroquinone and then trapping various molecules in the cage structure—and the experiment worked! The vibrations of the trapped molecules were clearly detectable in the scattered neutron beam (1–3).

The second thread arose from my move to the University of Manchester. After I obtained my doctorate, I had moved into school teaching in the North of England but quickly found I missed research. Nevertheless, that experience of teaching science in school has frequently been useful during my career in academic teaching. Having decided to attempt to return to research, I had written to a contact in the University of Manchester and, through the intervention of Sam Edwards (then a Professor in the Physics Department and later to be very influential in and supportive of my career), received a reply from someone completely different. Geoffrey Allen was a professor in the Chemistry Department working on polymeric materials. He also was intrigued by the labeling potential of the neutron scattering techniques. He was working mainly with infrared and nuclear magnetic resonance (NMR) spectroscopy. He recruited me based on my experience with neutron scattering techniques. In this case, he was interested in picking out the torsional motion of methyl groups attached to the (usually) carbon-carbon backbone of polymer molecules. This time, the problem was not detecting the methyl groups but the fact that the methyl torsion was infrared inactive. Luckily, I was not expected to do the chemical synthesis, and one of our chemistry colleagues provided polymers with either CH<sub>3</sub> or CD<sub>3</sub> groups attached. Using incoherent neutron



**Figure 1**

Inelastic incoherent neutron scattering from poly(propylene oxide). Solid line scattering from the polymer with  $\text{CH}_3$  side group and dotted line with  $\text{CD}_3$  (from Reference 5).

inelastic scattering from poly(propylene oxide) and poly(methyl methacrylate), we identified the methyl rotations by their absence in the deuterio versions of the molecules (4–6). **Figure 1** shows the inelastic neutron scattering spectrum from the polymers, with the torsional motion absent in the version with a deuterated methyl group. Although happy to have measured the required frequencies in the inelastic spectrum, I found myself rather more interested by that part of the scattered spectrum where very small energy transfers from the scattering molecules are observed. This is termed quasi-elastic scattering, and at the time it was being applied by other colleagues who were using the beams at Harwell to investigate the diffusive motions of molecules in liquid samples. Having very little experience of polymeric materials, I had thought of my rubbery polymers as more or less solid. I was surprised to find they produced quasi-elastic scattering very like simple liquid samples. It appeared that my polymers were moving nearly as fast as water molecules! As I subsequently realized, this was because I was observing the polymer molecules moving over only very short distances, and in this spatial range, the motion is like a liquid. Effectively, the neutron was picking up the high-frequency wriggling of small segments of the molecule (7). I spent several years following up this observation, as I describe later, but I think it is time to consider the neutron scattering technique in a little more detail.

## NEUTRON SCATTERING

As is already apparent, neutron scattering techniques were key to my early experimental research, and in fact they have remained important throughout my career. The techniques were in the relatively early stage of development in the 1960s when I first started to apply them, and there have been enormous improvements and innovations in subsequent years. I was fortunate to be in at the beginning of several of these new developments, and these have been of considerable influence in my research. I describe these developments in detail as they occur in my biographical narrative, but here is a brief introduction. Rather than reference in detail the science and the development of neutron scattering, I shall make a single reference to the book I eventually wrote with my friend and mentor, Henri Benoit (8). This covers all the basics and specifically the applications of the techniques to polymeric systems.

### THE NEUTRON: SOURCES AND DETECTION

Very soon after uncontrolled fission was unleashed in the atomic bombs developed in the Manhattan project toward the end of World War II, the potential for building reactors based on controlled fission was explored. Physicists realized that because they are uncharged, neutrons can penetrate into samples and through containment vessels. Moreover, neutrons from thermal reactors are endowed with wavelengths equivalent to X-ray beams but with very much smaller energy of the order of  $k_B T$  (where  $k_B$  is the Boltzmann constant and  $T$  is the core temperature). They are ideal for exploring the structure and relatively low frequency dynamics of molecular materials. Add to this the fact that the strength of the interaction of a neutron with a nucleus is only weakly dependent on atomic number and may vary for different isotopes of the same element. In particular, hydrogen and deuterium scatter neutrons as strongly as much heavier nuclei, unlike X rays, which find the light elements difficult to detect. And finally, hydrogen and deuterium are two isotopes with very different interactions with neutrons. In the years immediately following the war, reactors were built at the Atomic Energy Research Establishment at Harwell, just south of Oxford, specifically aimed at producing neutron beams for physics experiments on materials. When I started my PhD, there were two so-called medium flux reactors at Harwell, Pluto and Dido, which differed somewhat in the arrangements and properties of the beams they produced. My work initially used time-of-flight spectrometers focused on a cold source on Dido.

The neutron is a wonderful probe for molecular materials, but scientists are constantly up against two problems. The first is that reactors produce beams that are many orders of magnitude less intense than X-ray sources. The second is that neutrons, being uncharged, are difficult to detect. Early detectors were based on the absorption of the neutron by a suitable nucleus followed by detection of the charged fragments produced in the event. The detectors were usually gas filled and as large as possible to improve experimental statistics, but large collection areas were detrimental to spatial resolution. The sources were thermal reactors—a term that means that the radioactive core was cooled to thermal temperatures. The clouds of neutrons produced in the chain reactions effectively form a gas, and the neutrons have an energy distribution similar to a gas, with an average value around  $k_B T$ . The familiar de Broglie relationship between wavelength and particle momentum (or energy) means these neutrons have wavelengths of approximately 0.1 nm, similar to interatomic spacing. If longer wavelengths are desired, the neutrons can be equilibrated in a cold source, which is a container of cold liquid in the neutron beam path (liquid hydrogen or deuterium is usually used). The spectrometer I used at Harwell was arranged to access beams emerging from such a cold source. Dido was a medium flux reactor, and subsequently high flux reactors and spallation sources have been built, while more efficient detectors covering larger

collection angles have been developed. Nevertheless, anyone using neutron techniques is in a constant struggle to improve experimental statistics and hence resolution. Many of the innovations in neutron scattering have been clever ways of achieving high resolution with limited intensity and detection efficiency.

## SCATTERING EXPERIMENTS

Conceptually, a neutron scattering experiment is very simple. A neutron in a beam is scattered by a nucleus and may change direction and/or energy. The spatial distribution of the scattering contains information about the shape, size, and arrangements of the scattering molecules, whereas the neutron energy distribution is determined by the incident neutrons gaining or losing energy to relatively low-frequency vibration, rotation, or translation of the molecules. The time-of-flight spectrometer I used at Harwell focused on a cold source that provided a beam of neutrons with a band of selected velocities (i.e., energies) incident on my sample and banks of detectors arranged at measured distances around it. The number of neutrons detected at a given angle and a given time of flight was recorded on a magnetic tape and subsequently provided for analysis on punched cards. Much of the data analysis was done with a slide rule. One of the two key experimental parameters arises from the change in direction at a given neutron wavelength (or energy). Formally, it is the change in wave-vector on scattering and given the symbol  $Q$  [ $Q = (4\pi/\lambda)(\sin(\theta/2))$ ], where  $\lambda$  is the neutron wavelength and  $\theta$  is the angle of scatter. The distribution of scattered neutrons as a function of  $Q$  contains information about spatial structure in the sample. Essentially,  $Q$  varies as  $R^{-1}$ , where  $R$  is a spatial dimension. Small values of  $Q$  are related to large-scale structures, which is why most polymer experiments are focused on cold sources with long-wavelength neutrons and detectors at small scattering angles. The second parameter is  $\Delta E$ , the change in energy of the scattered beam. This was determined by measuring the flight time of the neutron from the sample position to the detector.  $\Delta E$  is directly determined by the dynamics of the scattering molecules. There is an interrelationship between  $Q$  and  $\Delta E$ . For small  $Q$  (i.e., small scattering angles), the motion of large sections of molecules is picked up, and conversely, for high  $Q$ , very local motion is dominant. For my polymer molecules at small  $Q$ , I could hardly detect any motion, but for the higher scattering angles, the quasi-elastic spectrum looked very like a liquid such as water.

There is one further facet of neutron scattering that needs to be introduced. The neutron can be scattered coherently or incoherently by nuclei, and each nucleus possesses both a coherent and an incoherent scattering cross section. Coherent scattering preserves information about spatial arrangements of the scattering nuclei; incoherent scattering does not. The coherent cross section for deuterium is very different from that of hydrogen, facilitating labeling applications, and the incoherent cross section is an order of magnitude larger for hydrogen than for deuterium, also favoring labeling. It is clear why neutron scattering looks so promising for polymeric samples.

## FROM MANCHESTER TO GRENOBLE VIA STRASBOURG

Before this diversion into neutron scattering, my description of my career had reached the point at which I was applying incoherent inelastic and quasi-elastic neutron scattering to study some spectral features in the infrared range and beginning to puzzle over the liquid-like wriggling revealed in the quasi-elastic spectrum. During my three years in Manchester, I concentrated my efforts on interpreting this feature. The quasi-elastic scattering from liquid-like motion is usually characterized by the breadth of the energy distribution as a function of  $Q$ . For a simple liquid, the scattered energy distribution is a Lorentzian curve where the breadth varies as  $\Delta E \sim DQ^2$ ,



where  $D$  is a diffusion coefficient. This looks simple to interpret, but the incident neutrons are not monochromatic and have a Gaussian energy distribution shaped by the velocity selector. Thus, interpretation of the scattered spectrum always involves the deconvolution of a measured incident energy distribution from the scattered distribution, and knowledge of the functional form of the scattering spectrum is needed before the data can be interpreted. I spent many hours struggling with this inconvenience. Work was being published explaining how to analyze scattering from simple liquids, but there was very little on polymers in either the solution or the bulk state. Two models had been developed to describe the dynamics of a polymer chain. Rouse (9) represented the molecule as a series of beads connected by springs of length  $\sigma$  with the effect of surrounding molecules or solvent acting as a frictional drag on the beads. Zimm (10) added the effect of hydrodynamic coupling between the beads. Despite the lack of any structure except the spring length  $\sigma$ , these models were very successful in describing viscoelastic behavior of polymers in solution. The model clearly broke down when distances smaller than a spring length were explored, which was unfortunately the case for the  $Q$  range available in the Harwell spectrometers. Nevertheless, we were interested in publications in the early 1960s by the French Nobel Prize winner Pierre-Gilles de Gennes, who predicted the broadening behavior to be expected from polymers. Using the Rouse model for polymers in the melt he predicted  $\Delta E \sim Q^4$ , while using the Zimm model for solutions the prediction was  $\Delta E \sim Q^3$  (11, 12). However, we had to struggle with the resolution problem again. The function describing the whole quasi-elastic energy spread for these models is not a nice Lorentzian, as for a simple liquid. It was presented in the literature as the scattering law  $S(Q, t)$  from which by Fourier transformation the energy spread  $S(Q, \Delta E)$  had to be calculated, and the Fourier transform did not yield an analytical function. In Manchester, using the Harwell spectrometer, and with limited energy resolution and no small  $Q$  detectors, we did not obtain evidence for the specifically polymeric behavior indicated by the  $Q^3$  and  $Q^4$  power laws (13), and this had to wait until I moved to Grenoble.

At this time (in 1973), the Americans had available to them reactors with much higher fluxes than the Europeans but, interestingly, not much interest in the techniques from chemists and materials scientists. The Germans and French had been building the high flux reactor at the Institut Laue-Langevin in Grenoble (ILL) for several years, and in 1972, just as the United Kingdom joined the European Economic Community, the politicians suddenly switched from a plan to build a UK high flux neutron source to becoming a third partner in the ILL. This was a wonderful development for us neutron scatterers. Not only did the ILL have a 50-MW reactor with much more powerful beams, but through the innovative approach of its first director, Professor H. Meier-Leibnitz, and the young scientists he recruited, it had a truly innovative array of spectrometers coming on line during the 1970s. I return to the way some of these spectrometers helped me solve my problems with quasi-elastic scattering, but first I must turn my attention to the reason I was recruited firstly by Henri Benoit to Strasbourg and then by the ILL in Grenoble in 1973. It was my experience scattering neutrons from polymers that led to these moves. I might interject here that the move to France transformed my life.<sup>1</sup> My French colleagues in Strasbourg and Paris became good friends and progressed my education both in science and in the French lifestyle. I arrived with schoolgirl French and a small number of scientific papers in a limited field and left four years later capable of discussions in (and even lecturing in) French, with a wide range of collaborators, a tool kit of neutron techniques, and the germ of an international reputation.

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<sup>1</sup>In this review I have generally concentrated on the scientific story, and not the more personal details. However, I have recorded some hours of interviews for a British Library series, "Voices of Science" (<http://www.bl.uk/voices-of-science/interviewees/julia-higgins>). These are much more wide ranging and would fill in the background for anyone interested.

Anyone considering the application of neutron scattering to polymers these days would first turn to the small angle neutron scattering (SANS) literature. It is perhaps surprising that until now I have not mentioned this technique. The reason lies in the limitations I mentioned earlier of flux and detection sensitivity. SANS is a coherent elastic technique in which the scattered intensity is focused in a small angular range around the incident beam direction (one or two degrees, perhaps). The angular range can be expanded if long-incident wavelengths are used, and the SANS equipment at ILL was arranged to use a cold source built into the reactor. Even so, to resolve the small angle scattering, detectors covering a small area were needed so that, even with high flux, experiments would be prohibitively long if the scattering was measured point by point. The technique was waiting for the equivalent of a photographic plate to cover many angles simultaneously, and at ILL the first neutron area detector was built into the small angle diffractometer, famously called D11.

## SMALL ANGLE SCATTERING AT THE ILL

I often comment that it is not usually the case that the prototype experimental apparatus remains the field leader for decades, but this was the case for D11. It was and still is an enormously powerful small angle diffractometer, and it remained the most powerful internationally for several decades. To anyone used to laboratory experiments, D11 was also physically enormous. It viewed the cold source through a 40-m stretch of neutron guide (the neutron equivalent to a light guide), and the detector (of which more anon) could be shifted to different distances away from the sample position with a maximum of 20 m (now increased to 40 m) to give the highest angular resolution. The detector consisted of an array of vertical and horizontal wires a centimeter apart, held within a gas-filled space. The charged particles arising from a neutron hitting one of the gas nuclei would be detected in a horizontal and a vertical wire, thus pinpointing the event to within 1-cm resolution. The detector covered an area of 32 cm  $\times$  32 cm, and thus 1,024 detector positions could be observed simultaneously. The design and construction of this detector was a tour de force in itself. I was hugely privileged to be among the first users of D11 as a member of a collaboration of French scientists.

At this time, the French owned a medium flux research reactor at Saclay fortuitously near Paris, where polymer physics was arousing considerable interest through de Gennes and his coworkers in the universities as well as at Saclay. At the same time, in Strasbourg, the Centre National de la Recherche Scientifique had set up the CRM (Center de Recherche sur les Macromolécules). The director of the latter, Henri Benoit, was a most distinguished polymer physicist with considerable expertise in light scattering. The Parisians were focused on the use of neutrons, and the Benoit team had the expertise in interpreting scattering data, as well as colleagues who could synthesize polymer molecules—including deuterated ones. Both groups were intent on a problem with which polymer scientists had been wrestling for a considerable time: What is the shape of a molecule in a melt sample when it is surrounded by identical molecules? As is often the case when a fundamental question is open, there had been discussion and at times fierce argument. An earlier Nobel Prize winner, Paul Flory, had hypothesized that the molecules would adopt a random coil shape. This is the shape they adopt in a so-called theta solution, where interactions with the surrounding molecules are screened out, and the hypothesis reduces to a simple prediction. The coil size,  $R$ , will vary as the square root of the molecular weight  $M$ . I was recruited by Henri Benoit into the Paris-Strasbourg collaboration to be involved in the first experiments on D11 on a melt polymer containing labeled (i.e., deuterated) molecules. From November 1972, I was employed at CRM, though I spent most of my time in Paris or Grenoble, and then in July 1973 I became one of the first UK scientists to join the staff at the ILL. In 1974, the first data supporting the Flory

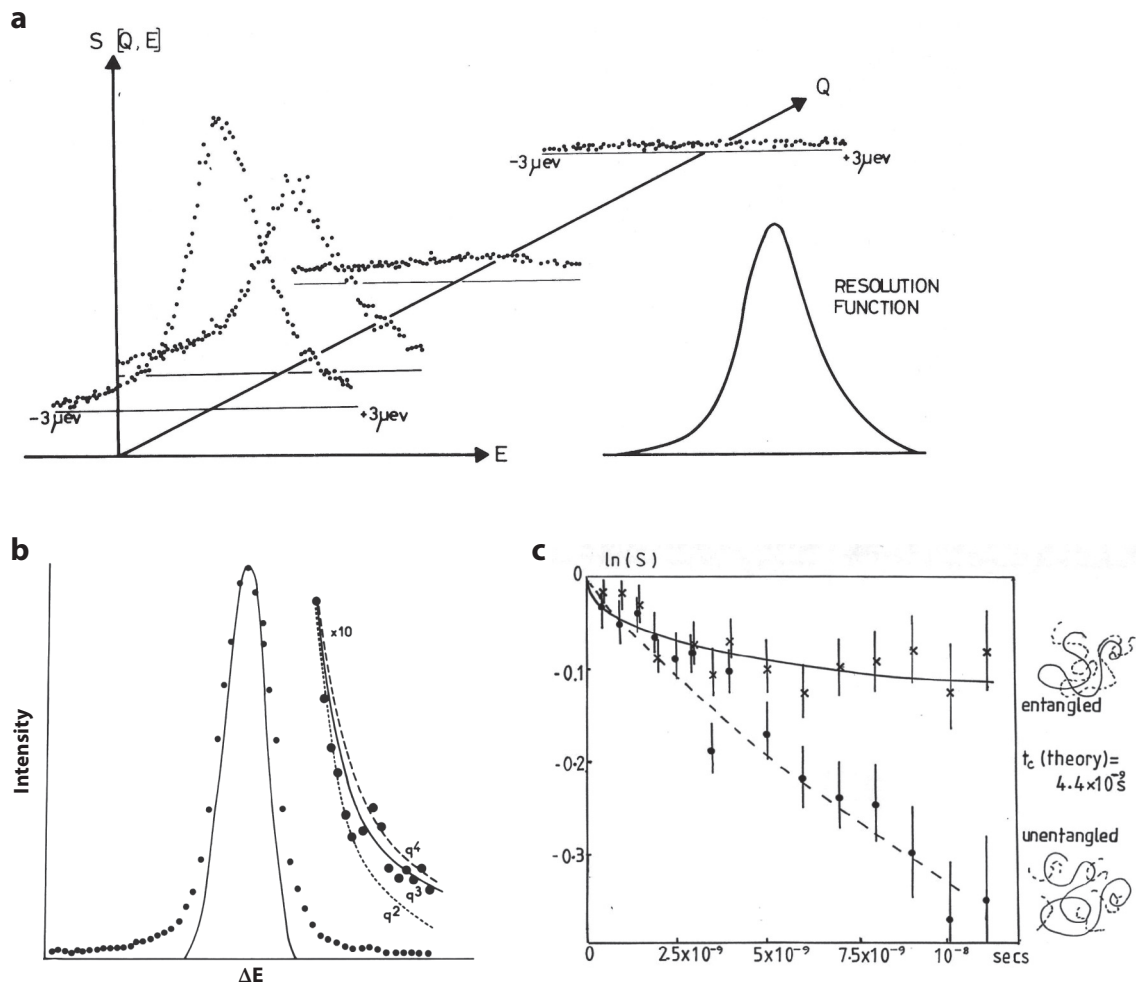


hypothesis obtained on D11 were published, showing that  $R$  did indeed vary as  $M^{1/2}$ . Our chosen polymer was amorphous polystyrene with a small concentration of d-polystyrene dissolved in a matrix of h-polystyrene of the same molecular weight (14). At the same time, and also using D11, two groups from Mainz in Germany were doing similar experiments on different polymers. Lieser et al. (16) were working on polyethylene, and Kirste et al. (15) studied poly(methyl methacrylate). We all made the assumption that d- and h-versions of our polymers were identical. However, the deuterium substitution does make small differences in molecular behavior owing to the slightly different volume occupied. This effect is particularly evident near any phase boundary, so the crystallization temperature of polyethylene is different in the deuterated version, and we knew when we did those first experiments that the theta temperature of polystyrene in cyclohexane differed in the two versions. Polymer scientists learned to be careful when using deuterium labeling close to any phase changes (see, for example, the discussion on p. 116 of Reference 8). Nevertheless the SANS confirmation of the Flory hypothesis still stands in all the textbooks.

This interaction with the French scientists was the beginning of a long and happy series of collaborations and friendships, most especially with my mentor, Henri Benoit. This latter culminated in our joint book, *Polymers and Neutron Scattering* (8). We worked on this over approximately four years together, during short visits by me to Strasbourg or by post, telephone, and email, publishing in 1994. It seems strange, but it is true that writing a book in English considerably improved my spoken French!

## NEW TECHNIQUES AT ILL FOR QUASI-ELASTIC SCATTERING

When I arrived at ILL, a bigger and better time-of-flight machine, called IN5, was nearing completion. This certainly helped in the quest to follow polymeric dynamics, but it was the arrival of two real innovations in quasi-elastic scattering that allowed serious progress. The first of these was the back-scattering spectrometer IN10, designed and built by Tony Heidemann. Here the trick was to abandon observation of the whole energy spectrum and concentrate the experiment on very small changes close to elastic scattering. The term back scattering refers to the fact that a beam reflected by a crystal at  $180^\circ$  has an extremely sharp wavelength (or energy) distribution. Small energy shifts were added by driving the reflecting crystal back and forth, thus Doppler shifting the energy. If these energy changes were matched by shifts in the neutron energy on scattering, then the beam was detected by a second analyzer crystal (or crystals at a range of scattering angles). By this means, the quasi-elastic energy resolution could be improved by one or two decades (17, 18). There remained two problems. The first was the deconvolution problem. The form of the scattering,  $S(Q, \Delta E)$ , had to be assumed, convoluted with the incident energy spread, and then fitted to the data. This could be done using  $S(Q, \Delta E)$  obtained as Fourier transform of the theoretical forms for  $S(Q, t)$  where these were available. And therein lies the second problem. The range of  $Q$  available experimentally was not low enough to access the range assumed by the theoreticians for calculating long chain motion (11, 12). Thus, the scattering law was not really appropriate, and this showed up in a mismatch of the broadening obtained from spectrometers with different resolution (18). This deficiency in available  $Q$ -range was interesting to some theoreticians, who turned their attention to the intermediate  $Q$ -range. I had some very pleasurable interactions with the groups of Akcasu (19) in the United States and Allegra (20) in Italy, who modeled how the broadening should vary at  $Q$  values where the local structure of the molecules became important. **Figure 2** shows some examples of the resolution problem in quasi-elastic scattering. **Figure 2a** shows the back-scattering spectrum from poly-(dimethyl siloxane) at several scattering angles ( $Q$ -values) with rapidly increasing broadening as  $Q$  increases. **Figure 2b** shows how difficult it is to distinguish between the various models of the broadening when the resolution is not high enough.



**Figure 2**

Quasi-elastic scattering from (a) poly-(dimethyl siloxane) using the back scattering spectrometer, IN10, as described in Reference 17; (b) expanded section of the wings of the  $Q$ - $E$  scattering showing the difficulty of distinguishing between different models; (c) adapted from Reference 28 with permission from the Royal Society of Chemistry showing the IN11 (spin-echo) data for two mixtures of high-molecular weight polytetrahydrofuran (PTHF) entangled in a matrix of high-molecular weight deuterated PTHF and unentangled in a low-molecular weight matrix.

Both the resolution and the  $Q$ -range difficulties were overcome with the advent of the neutron spin-echo spectrometer IN11. The idea for the spin-echo technique, initiated by Ferry Mezei, was realized as IN11 by John Hayter, Jeff Penfold, and others at ILL. In this technique, the precession of the neutron spin as it travels through a magnetic field is exploited. Very small  $Q$  values could be accessed because of the narrow collimation of the beam in the long magnets, and very high energy resolution is available by the trick of counting the number of precessions before and after scattering. Energy resolution an order of magnitude or two better than IN10 can easily be achieved. But the big win is that in this one technique,  $S(Q, t)$  is measured directly. The combination with the incident energy spread is a simple multiplication, and the incident scattering can be divided

out point by point, thus providing the scattering law for the sample without any assumption about its analytical form. **Figure 2c** shows such data, though the interpretation is discussed later. The equivalent of the broadening  $\Delta E$  is the initial slope at time zero of the scattering law. In the early 1980s, working with colleagues at Imperial College, we were able to use IN11 to observe unambiguously the dynamics of long-chain polymers in solution and particularly in entangled melts (21, 22). I describe the key experiments in more detail later.

It is interesting to note that this property of  $S(Q, t)$  was subsequently exploited for quasi-elastic scattering experiments by using fast Fourier transformation of the observed  $S(Q, \Delta E)$  so that the resolution function could be divided out with no assumption about the analytical form of  $S(Q, \Delta E)$ . One of my students, Valeria Arrighi, in later years went on to solve many problems using this process (23).

## TO CHEMICAL ENGINEERING IN IMPERIAL COLLEGE, LONDON

In 1974–1975, Geoffrey Allen moved from Manchester to the Department of Chemical Engineering and Chemical Technology at Imperial College London. This was part of a move by the College to augment research on polymer science and engineering in this department and others. Geoff immediately set about recruiting two of his previous group in Manchester, and David Walsh and I arrived in consecutive years, David in 1975 and I in 1976. I had been offered a permanent post at ILL, and my colleagues were surprised that I wanted to move away. It was clear in my own mind why I swapped the Alps for South Kensington and dramatically reduced my salary. In ILL I was associated with the development and exploitation of the neutron techniques, mainly working with and supporting scientists from outside ILL who brought their scientific questions and their samples to us. I wanted rather to own the problems myself, and for that I needed an academic position in a research-intensive university. Imperial College amply fulfilled that description, as well as being home territory for me. The department was then and still is staffed by people with a very wide range of academic backgrounds from many countries. Whereas approximately half the staff members have always been chemical engineers by training, the rest have moved across from various scientific disciplines, so that I did not feel completely out of place. Nevertheless, I was on a steep learning curve, especially on the teaching front! However, over the nearly 40 years I have spent in the department, I have never regretted my move to engineering. The mix of scientists and engineers I have met has provided a wonderful group of colleagues, some of whom I have collaborated with directly but many more of whom have provided advice and support.

Now established as an academic, I was in a position to recruit my own research group of students and postdocs—assuming I could find the funding and the students. Neither of these were trivial problems. Overall, students in chemical engineering were more disposed to move into industry than to continue into research, and more importantly, my research needed students with a bent toward chemical physics. Although I did supervise some wonderful chemical engineering graduates from Imperial and elsewhere, over the years the majority of my students have come from undergraduate degrees in physics or chemistry either in Imperial, elsewhere in the United Kingdom, or very frequently overseas. The same has been true of my postdocs. I also hosted several visiting young scientists as research fellows, from places as wide ranging as Norway, Japan, the United States, Greece, and Uzbekistan!

Funding was also a challenge. At that time in the United Kingdom, university start-up funds were unheard of. I had to apply to the Research Councils for grants, and these took time to materialize. However, the funding regime for use of the facilities at ILL had been set up in an enlightened way, so that a proposal once accepted was fully funded in terms of both use of the equipment as well as travel for the experimental team. My expertise and reputation meant that

I usually obtained the beam time I needed. I still had to beg, borrow, or steal samples, which were often not cheap, as deuterated versions of the molecules had to be purchased or synthesized. I became well known to colleagues when discussing a potential experiment for posing the early question—“Can you make a deuterated version?”

## INITIAL RESEARCH PROGRAM QUASI-ELASTIC SCATTERING

During my first years at Imperial, I was focused primarily on furthering the studies on quasi-elastic scattering from the main-chain dynamics of polymer molecules in solution and the melt. For solution work, the deuteration was no problem, as we could cheaply purchase solvents used in NMR experiments. Not so for the all-important experiments on the melt samples. By now de Gennes (24) had proposed his reptation model for single-chain dynamics, and these ideas had been developed by Doi & Edwards (25) into a full molecular model of polymer rheology. The molecules are conceived as wriggling like a snake along a tunnel or tube formed by the surrounding molecules. The width of the tube,  $d$ , is not a nearest neighbor distance, but a dynamic image of the maximum excursion local sections of the molecule can make before being severely constrained by the network formed by the other molecules. The tube width  $d$  is related to the distance between entanglements, and is of the order of nanometers. This key molecular parameter can be obtained from data for the plateau modulus in rheological measurements, but it had not been observed directly in molecular dynamic experiments, such as neutron scattering. However, an analytical form for the scattering law  $S(Q,t)$  of a polymer molecule in the melt in the reptation model had been developed recently (26, 27). In the appropriate  $Q$ -range, exploring distances greater than a monomer length but less than a molecular radius of gyration, this  $S(Q,t)$  function showed a rapid slowing down at a time corresponding to the effect of molecular entanglements.

The spin-echo technique realized in IN11 was potentially able to observe this coherent scattering law directly from a sample with a mix of deuterated and hydrogenous polymer molecules. The choice of polymer was crucial. The resolution of IN11 was still limited to discerning relatively rapid motion, so we wanted a polymer well above its glass transition temperature ( $T_g$ ) and moving fast. Poly-(dimethyl siloxane) (PDMS, a silicon backbone chain with pendant methyl groups) was well known to me as satisfactorily fast (17, 18), but deuterated samples were unavailable and too expensive for custom synthesis. We needed a large amount of material for IN11 experiments—of the order of tens of grams. Polytetrahydrofuran (PTHF, an ethylene-like chain with one oxygen in the backbone every four carbons) is another rapidly moving polymer with a low  $T_g$ , and deuterio-tetrahydrofuran is an NMR solvent—and so is available at low cost. Colleagues at Imperial synthesized the polymer in the h and d forms, and the spin-echo experiments on mixtures of h-PTHF in d-PTHF were planned. We highlighted the effect of entanglements by comparing two mixtures. In one sample, long PTHF molecules were mixed with long deuterated PTHF molecules so that the whole mix was entangled. In the other sample, the long molecules were mixed with deuterated PTHF molecules that were too short to entangle. As shown in **Figure 2c**, we could clearly see the slowing down at a spatial distance corresponding to the entanglements impeding the molecular motion (28). The tube diameter,  $d$ , we obtained by fitting the model for  $S(Q,t)$  to the PTHF data was approximately 3 nm.

It turned out that we had been rather lucky in our choice of polymer. Our first choice, PDMS, though in rapid motion, has a much larger value for  $d$  than PTHF owing to its chunkier cross section, and the slowing down is barely within the experimental range. There is a coda to this story: I subsequently presented the results at a conference also attended by colleagues working in polymer rheology. Bill Graessley from Northwestern University in the United States asked me how our neutron value for  $d$  compared with the value from the plateau modulus. I pointed out that

no one had ever bothered to study the rheology of PTHF. (It is a singularly useless material as a pure polymer.) Bill replied, “Then we will measure it.” Some months later, I received a phone call from a colleague of Bill’s, Dale Pearson. *Would I like to know the value of  $d$  they had obtained from the plateau modulus?* I can still vividly remember that call. Their entanglement value was 3.1 nm.

## DIVING INTO POLYMER BLENDS

While continuing my studies of polymer motion, I was developing several national and international collaborations, and also getting involved in a homegrown research program studying polymer blends. A description of my group’s research that attempted to be linear in time would thus become a series of intertwined research threads. For clarity, I disentangle them and deal first with my ongoing studies of blends (up to the present even) and then describe the many collaborative programs that mainly exploited my knowledge of and access to neutron scattering techniques.

Some two years after I arrived in Imperial, Geoff Allen moved away to head the UK Science Research Council (SRC), and David Walsh and I inherited a program of study of polymer blends that Geoff had initiated. (Geoff never returned to Imperial, going from SRC to become research director of Unilever.) The program I inherited was focused on partially miscible binary polymer blends. My experiments on quasi-elastic scattering were basic polymer science and generally a long way from understanding practical problems. The blends program brought me much closer to these practical problems, and consequently to the interests of my engineering colleagues. Applications of many polymeric materials involve mixtures—sometimes with a low-molecular weight plasticizer but often as a mix of two high-molecular weight polymeric species. Thermodynamic descriptions of molecular mixtures are focused on an entropic term—mostly favorable to mixing because it is dominated by configurational entropy—and an enthalpic term often unfavorable to mixing. The configurational entropy to be gained by mixing becomes vanishingly small as molecular weight becomes high, and as a consequence, it was thought that high-molecular weight polymers would not mix. However, it became clear that if the difficulty of mixing highly viscous fluids could be overcome (perhaps using a common solvent and then evaporating it, or maybe by in situ polymerization of one of the components), then several polymer pairs were completely or partially miscible. This unexpected behavior was attributed to specific interactions between the molecules. Understanding and controlling the mixing behavior is essential in the production of materials containing more than one polymeric species. Theoretical descriptions of polymer miscibility from statistical mechanics formulation based on lattice models go back to the 1940s. The early and much-quoted Flory-Huggins (F-H) development suffered from the deficiency that as originally conceived it could only describe phase separation in a binary blend that occurred as temperature lowered—to reach the so-called upper critical solution temperature (UCST)—whereas real high-molecular weight blends were almost exclusively lower critical solution temperature (LCST) phase separating as temperature was raised. Very extensive literature developed over subsequent decades focused largely on modifying the original simple F-H formalism to deal with real systems. The development of a thermodynamic understanding of polymer blends is comprehensively covered in the book by Koningsveld, Stockmayer & Nies (29). The book also includes many illustrations of experimental results from real systems. I knew two of these authors well over many years. Walter J. Stockmayer (from Dartmouth College) was on sabbatical leave in Oxford when I was working for my PhD, and to my surprise, he remembered me when we later started to meet at conferences. We had many helpful discussions. Ron Koningsveld was working for the company DSM but was closely involved in basic research on blends. I was introduced to Ron and his colleague Ludo Kleintjens in the Netherlands through a collaboration with Manfred Gordon at Essex University.

The work at Imperial was focused on experimental observation of miscibility limits in binary polymer blends as a function of molecular weight, using light scattering (30–32), the effects of pressure on miscibility, and attempts to measure the enthalpy of mixing in low-molecular weight systems (33). While making sure we were aware of the different theoretical descriptions being developed, I never felt that these were adding much to my understanding of polymer thermodynamics. This was because the usual approach was to introduce new parameters, at best semiempirical and often arbitrary, which were inevitably temperature and concentration dependent. I was unconvinced and remained unconvinced until some 15 years ago, when I started work with Jane Lipson. She had theory, and I had data. We shall return to this collaboration much later in the story.

Very early in my career at Imperial, I accepted an invitation to speak on blends at a Gordon Research Conference in the United States. The invitation had been made originally to Geoff Allen, and I stood in. With hindsight, I am amazed at my temerity! My background in thermodynamics was thin to say the least, barely covered in my undergraduate years and with some tutorial experience in Manchester. Nonetheless, the Americans were very kind to me, and I certainly learned a lot from the experience!

I very quickly turned to neutrons to see what I could add to the experiments already under way at Imperial. Because of my own experience, I was at first focused on determining whether the molecular conformation changed in blends from the pure component Gaussian distribution. However, I soon realized that in SANS, the forward scattering intensity is also an important parameter. It is the inverse of the second derivative with respect to concentration of the free energy of mixing. It is in effect a measurement of the free energy of mixing. When we first started SANS measurements from binary blends containing deuterated molecules, we were faced with the problem of calibrating and interpreting the data. We eventually developed a protocol correlating the data against the known molecular weight of a well-defined polymer sample. There was as yet no helpful theoretical literature. Mark Warner had come to the United Kingdom to study for a PhD with Sam Edwards and had become a good friend of mine when based in Imperial in the late 1970s. Now an academic in Cambridge, he provided the vital theoretical understanding and developed equations allowing us to extract quantitative values for both molecular dimensions and this free energy derivative (34).

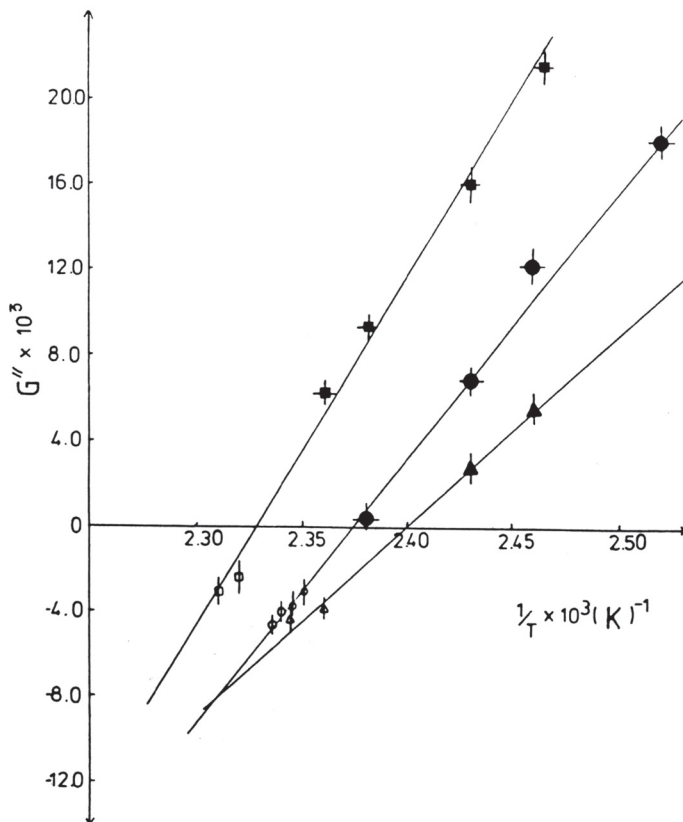
All our SANS studies of polymer blends depended on the availability of deuterated polymers. Because they are rarely available to purchase, this usually meant begging letters to colleagues who might have suitable material or might even be prepared to synthesize it. One such lucky interaction involved colleagues in Dupont Research Labs in Wilmington, Delaware. My interactions with Dupont were facilitated by the move of my colleague David Wash from Imperial in the mid-1980s, and continued over many years. The research scientists in Dupont had been making supports for NMR samples from very high-molecular weight perdeutero-poly(methyl methacrylate) (a component of several interesting blends). I was kindly sent approximately 100 g of the workshop turnings of this treasure. When the small parcel arrived, I was within seconds of discarding what looked like packaging material searching for a small bottle containing a sample. The packaging was the polymer and provided invaluable samples for years of experimental work.

David's departure left the blends program in my hands, and inevitably the center of gravity moved further toward scattering experiments. At first more interested in the molecular dimensions, I soon realized that the free energy term (which we labeled with the symbol  $G''$  in all our papers) could give insight into the blend behavior. This was especially true if we had some enthalpy measurements on the same system because comparing the two gave us information about the entropic contribution to mixing—something impossible to measure directly (35). In recent years, it has been the availability of this  $G''$  from our SANS measurements on blends that has supported my very fruitful collaboration with Jane Lipson.



## PHASE SEPARATION IN BINARY BLENDS

Given my continuing work on dynamics of polymer molecules, it is not surprising that I became keenly interested in the process of phase separation when a binary blend crosses the UCST or LCST. We had been using the light scattered from the cloudiness that ensues as the blend becomes heterogeneous to detect the phase boundaries, but around 1983 I became aware that these heterogeneities could give rise to interesting time-dependent scattering. Partially miscible binary blends separate into coexisting phases via two processes, nucleation and growth or spinodal decomposition. The latter process, which follows when the blend is plunged into an unstable region close to the critical temperature, gives rise to a scattering halo, which increases in intensity and eventually collapses toward smaller scattering angles as the structure formed by the coexisting phases ripens. I was aware of some early light scattering experiments following this halo, in particular a seminal paper by Snyder and coworkers (36) at Dupont in which they followed the phase separation of polystyrene-poly-(vinyl methyl ether) blends using light scattering. I first observed the process experimentally while we were doing measurements with SANS at ILL on a UCST blend, polystyrene mixed with polybutadiene. We had run the experiment at a temperature above the UCST, and for a reason I have now forgotten, we let the sample cool down in the beam, leaving the data-gathering programs running. A beautiful scattering ring slowly appeared on the screen, intensified, and collapsed toward the beam center, exactly as predicted! Fired by this, I instigated a program investigating spinodal decomposition at Imperial. We built our own light scattering apparatus and set about exploring the spinodal decomposition kinetics of a series of blends and comparing the results with the theoretical literature (37, 38). Thermodynamics provides the driving force for growth of the unstable concentration fluctuations, and rheology governs the dynamic response. The driving force increases as the quench depth inside the phase boundary increases, and response rate increases rapidly with temperature. The development by Cahn, Hilliard, and Cook (39, further described in references 37 and 38) related the initial position of the spinodal ring to the derivative term,  $G'$ , that we had been observing in SANS experiments in one-phase samples. There was a lively discussion in the literature about the quantitative relationship between the position of the spinodal ring  $Q_{\max}$  and  $G'$ . [Remember  $Q$  is defined as  $(4\pi/\lambda)\sin\theta/2$ .] Everyone agreed that the size of the initial growing phases ( $Q^{-1}$ ) would be of order of the molecular dimensions. However, given a few factors of  $\pi$ , this left enough leeway to suggest that the initial ring might be observable in light scattering experiments or in SANS, where  $Q$  is several orders of magnitude larger. The theory predicted some characteristic behavior that should be observed during the early stages, but the light scattering data were somewhat ambiguous about whether the very initial stages were being caught. We were very keen to extend measurements on spinodal decomposition to SANS, as we believed it likely that phase separation was occurring on the much smaller spatial scale explored by SANS. We had been lucky in our initial SANS observations, because with our UCST blend we were at a temperature quite close to  $T_g$  when we were inside the phase boundary, so the growth of the spinodal ring was slow. However, we were particularly interested in LCST systems where “inside the phase boundary” meant high temperatures and rapid responses. This required collection of SANS measurements much faster than hitherto possible. Typical SANS experiments were tens of minutes long, and we believed we needed to explore timescales of tens of seconds. To do this, the electronics of the D11 diffractometer had to be modified. As set up in the 1980s, a spectrum was recorded on the hard disc of the computer and then downloaded to a storage disc. This downloading process took several tens of seconds, costing precious measurement time in a kinetic experiment. To accommodate our timescale, the data collection process was altered so that subsequent scattering patterns were written to different areas of the hard disc at a rate of approximately 10 s or less per pattern, and when the hard disc was

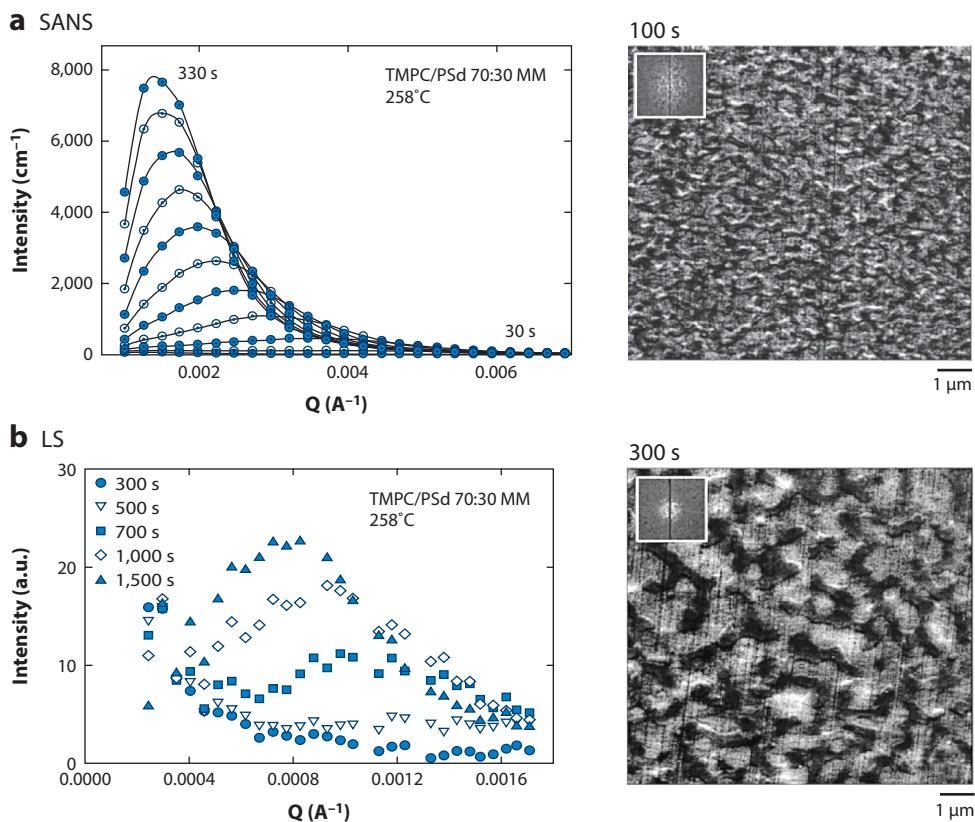


**Figure 3**

The free energy derivative  $G''$  on either side of the phase boundary for three compositions of a polymer blend. Above  $G'' = 0$ : single-phase measurements; below  $G'' = 0$ : from phase-separating samples. From Reference 40, ©1989 Am. Chem. Soc.

full, all these patterns were downloaded to disc. This allowed us some 300 s of measurement time at a repeat rate of 10 s (40). We were now able to correlate measurements of  $G''$  in the one-phase region with the spinodal process inside the phase boundary on the same blend (40). **Figure 3** shows the measurements of  $G''$  inside and outside the phase boundary and the correlation across it for a blend of poly(methyl methacrylate) with poly( $\alpha$ -methyl styrene-co-acrylonitrile).

It has become clear from our observations on several blends that the initial phase size is of order of the molecular dimensions within a factor of two or three, and that the initial stages can be very rapid and may be over in some tens of seconds or less (41–43). During a short sabbatical visit to the University of California, Santa Barbara, I was persuaded to see if atomic force microscopy (AFM) could detect the phase-separated morphology in spinodal decomposition in real rather than reciprocal space. At first skeptical, I was won over by micrographs of microtomed samples that we had allowed to phase separate by spinodal decomposition for a measured time inside the spinodal and then quenched. The spinodal structure was clearly visible, and moreover, when Fourier transformed into reciprocal space, the AFM structures demonstrated the same behavior we observed for the same samples in light and neutron scattering experiments (44, 45). **Figure 4** shows the time development of (a) neutron and (b) light scattering and (c) AFM micrographs for a



**Figure 4**

(a) Neutron scattering and (b) light data and two atomic force microscopy micrographs for a phase-separating blend at elapsed times as marked after a temperature jump into the two-phase region. Inset in the micrographs are the Fourier transforms that correspond to scattering data.

phase-separating blend of deuterated polystyrene with tetra-methyl bis-phenyl A polycarbonate. Inset in the micrographs are the Fourier transforms that correspond to scattering data.

## EFFECT OF PROCESSING

During processing, polymeric materials are often extruded and moulded and thereby subjected to strong shear forces. In the late 1980s, the literature began to report experiments that seemed to show that the phase stability and the phase-separation processes in polymer blends were altered in flowing systems. Together with Bob Weiss, then at the University of Connecticut and during his sabbatical year at Imperial, we set about building the apparatus to observe cloud point curves while polymer blends were subjected to shear (46). We observed small shifts of a few degrees in the apparent cloud point temperature of blends subjected to shear and simultaneously heated. At low shear rates, of order  $2 \text{ s}^{-1}$  or  $3 \text{ s}^{-1}$  (47), the blend was less miscible, with a drop of a few degrees in the LCST, and at higher shear rates the opposite behavior was observed. These experiments not only were difficult to set up but also took me into new territory. To understand the rheology, my chemical engineering colleagues, most especially Stephen Richardson, were invaluable

(48–50). The results were also controversial, with a lively discussion between us and colleagues elsewhere about whether we were really observing shifts in miscibility limits or simply breaking up the coexisting phases until they were too small to observe in our light scattering apparatus. Our team at Imperial convinced ourselves it was a true thermodynamic effect by quenching samples and subjecting them to differential scanning calorimetry. We noted two glass-transition temperatures corresponding to the two coexisting phases. This work led to an interesting collaboration with the DSM company (51). Scientists there had observed unusual behavior when processing at high extrusion rates a blend of poly(methyl methacrylate) with poly(styrene-co-maleic anhydride). Cloudiness in some samples was interpreted as phase separation even though the blend was at temperatures below the measured LCST. In practice, both deformation-induced mixing and deformation-induced demixing were observed, along with some intriguing behavior associated with vortices at the capillary entrance, which produced a faint blue spiral through the extrudate.

As well as working with my engineering colleagues, at this time I was developing a collaboration with Tom McLeish and Nigel Clarke (initially Tom's PhD student) to understand the theoretical physics underlying some of our observations on blends. The initial work with Tom and Nigel (52, 53) arose because of some observations we had made on very high-molecular weight blends that showed a distinct delay time before the spinodal ring was observed. The theoretical development was based on the Cahn-Hilliard-Cook expressions describing spinodal decomposition but was modified to include an elastic energy term arising from the finite lifetime of entanglements in these very long molecules. Naturally, we discussed our results in the shear experiments with Tom and Nigel. Intrigued by our data and other reports in the literature, they set about developing a set of equations for spinodal decomposition under shear. Their model was an extension to blends of one already successfully applied to polymer solutions, where concentration fluctuations are coupled to shear stress. Their predictions about the spinodal process were later compared to our experimental data. I have already mentioned the difficulty of designing experiments on spinodal decomposition under shear flow. Finding a polymer pair with appropriate rheology and an accessible LCST was just the start. It was not possible to design a light scattering apparatus with which we could make a temperature jump under constant shear. We therefore made shear jumps at constant temperature. Although the McLeish-Clarke model successfully described many features of the results, I have always thought about this program as unfinished business, and I hope one day to find in the literature answers to some of the remaining open questions. One frustration in particular was that we never managed to carry out real-time SANS experiments on spinodal kinetics under shear. The blend much used in these shear experiments is polystyrene with poly-(vinyl methyl ether), also extensively studied at zero shear. This blend has an LCST in an accessible range around 110°C, but when the PS component is deuterated (as is required for SANS studies), the LCST shifts up by some 40°C, and the consequent increase in diffusion rates at these higher temperatures means the early stages of spinodal decomposition are over in seconds and inaccessible in SANS. We did carry out some SANS on quenched samples that had been phase separated under shear, with mixed success (54). That paper concludes that "further experimental work is required." Sadly, for several reasons, partly owing to my own increasing involvement in senior academic management at Imperial, as well as my contributions to the Academies and the Research Councils, and partly because my coworkers moved on, this further work has not been done. Maybe one day?

## MIXING POLYMERS ACROSS INTERFACES

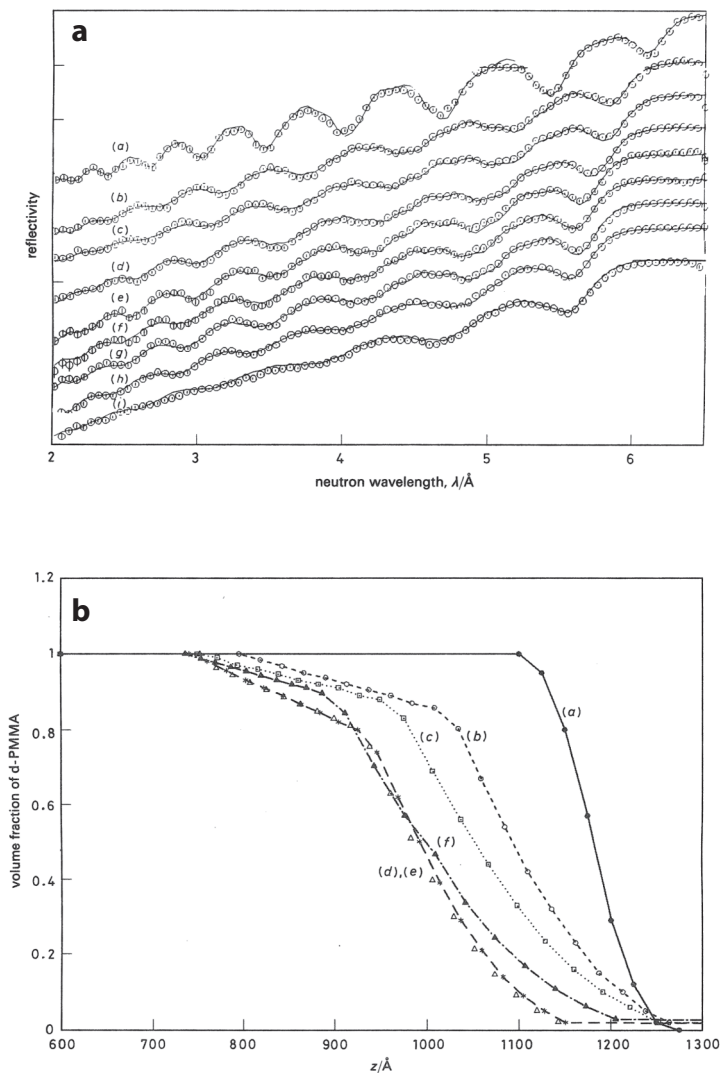
Our interest in demixing of polymers naturally extends to observing mixing across interfaces. In heterogeneous samples of polymer mixtures, the structure of the interface between phases is

crucial in determining material strength. At about the time we were involved in phase-separation experiments, another neutron technique was added to the toolbox. Neutron reflection is in reality a special form of small angle scattering. A neutron beam reflected at grazing incidence carries information about the concentration profile perpendicular to the surface. If the surface is structured in thin layers, interference patterns result, which are analogous to the colored reflections from an oil film on a water surface. The interference frequency is determined by the layer thicknesses, but the detailed shape of the pattern is modified by the interfacial structure. The technique requires a modification of the normal SANS apparatus, and experiments are carried out on thin smooth surfaces—for polymers, layers spin-coated onto silicon wafers. The first dedicated reflectometer, CRISP, was built on the ISIS spallation source at the Rutherford Laboratory near Oxford around 1990.

Here I need to backtrack a little in my story. Reactors are limited in the flux they can produce by the problems of removing the energy released in the form of heat. Although there have been discussions of building higher flux reactors cooled, for example, by liquid sodium, attention has been focused on pulsed neutron sources. Here the neutrons are produced by spallation (chipping off) from heavy nuclei by pulses of very energetic particles, such as protons produce in particle accelerators. The neutron flux in the pulse can be very high, but to exploit this, the spectrometers have to be designed to use the whole wavelength spread and analyze it by time-of-flight techniques. In the 1970s, the accelerator physics programs at the Rutherford Laboratory were closing down, and it was decided to exploit the site and some of the equipment in building a UK spallation neutron source. Immediately after my return from Grenoble, I became a member of the Science Advisory Group for this project and remained so until the first neutrons were produced in 1984. One of my roles was to argue strongly for the inclusion of long-wavelength techniques suitable for work on soft matter in the instrument clusters being designed. (Given the view then current, that spallation sources would be best for high-energy, short-wavelength experiments, this was important.) CRISP was not one of the first instruments built at ISIS, but it was certainly one of the most successful. Again, I was fortunate to be able to use the techniques from the first experiments. In collaboration with the scientists at the Rutherford Laboratory, we started by analyzing the interfacial profile of bilayers of compatible polymers, superposed on a flat substrate and then annealed and quenched (55–57). **Figure 5** shows the reflectivity from a bilayer of the miscible polymers, solution-chlorinated polyethylene with poly(methyl methacrylate), the latter in its deuterated form (57). The interference fringes formed by the reflections from the top and bottom surfaces of the d-PMMA film initially 118 nm thick are clearly seen in **Figure 5a**. The sample was annealed at 120°C for times a–i [0, 37, 141, 203, 203 (plus 6 months at room temperature), 243, 297, 807, 5,217 min]. The fringes shift as the diffusion of the polymers thins the top layer, and they broaden as the interface broadens. The interface models fitted through the data points are shown in **Figure 5b**. A collaboration with a former postdoc now working at ICI, Sam Rostami, led to funding for a PhD student, David Bucknall, who proceeded to investigate the location of copolymer interfacial agents when added to a bilayer of incompatible polymers (58, 59). In a later collaboration with the DSM company in the Netherlands, we were able to correlate the copolymer ordering with interfacial strength (60). When David moved to Oxford, we turned our minds to the time dependence of interdiffusion across an interface (61, 62). In this way, we obtained data that tested some of the predictions of polymer dynamics in the reptation model.

## INTERLUDE: LIFE AS A NEUTRON SCATTERER

I learned early on not to base my whole experimental program on the availability of neutrons. The sources break down; the proposal for beam time may not be accepted, or not immediately; and



**Figure 5**

Reflectivity data from an annealed bilayer of miscible polymers. (a) The reflection curves with the data (*points*) and the fitted model as continuous lines. (b) The interfacial profiles used in the model fits. The labels *a–f* refer to cumulative annealing times, 0, 37, 141, 203, 203 (plus six months), 243, 287, 807, and 5,217 min (adapted from Reference 57 with permission from the Royal Society of Chemistry).

there are inevitably long gaps between an idea and an experiment. A neutron scattering program has to be based on a solid home-based experimental program, where the neutrons provide the last crucial piece of information, rarely the first. We used largely light scattering in my own laboratory, but as I have described, we also collaborated widely with colleagues who were expert in other methods. These collaborations have, I believe, been of great advantage to my research group in widening the experience of students and postdocs and providing them with a scientific network. Doing experimental work away at a central facility imposes a particular discipline in terms of writing and reporting on proposals, of careful planning for a visit to the neutron source, and of



meticulous timing of the experiments so that the end of the allocated beam time does not find the team with data but no background measurement or perhaps no calibration. The typical beam time allocation for a SANS experiment is approximately two days. This means round-the-clock work, and my teams were, I think, all a little astonished when I insisted on planning a schedule of meals and rest! I was only too aware of the mistakes that can be made by hungry or exhausted scientists. If all went well, we arrived back at Imperial with months of data analysis ahead of us and perhaps a six-month wait for the next chance to add to or verify the measurements. My colleagues were inclined to believe I had spent a relaxed few days in the French Alps! However, it was not all hard work, and I remember some delightful interludes lunching on sunny days before the next sample change was due, with the Alps gleaming around us.

## NATIONAL AND INTERNATIONAL COLLABORATIONS

I have already mentioned some of the many collaborators with whom I became involved. For a decade, they were vital to my research group and to me personally, because during the period 1985 to 1995, there were essentially no academics at Imperial with a strong interest in the molecular behavior of polymers. So far in this account, these collaborative interactions can be seen to have arisen from my own research needs, where the collaborators brought the theoretical expertise that I lacked. These include interpreting quasi-elastic scattering from polymers with Zia Akcasu (19) and Giuseppe Allegra (20, 63), interpreting SANS data from polymer blends with Mark Warner (34), and understanding the physics of entangled polymer blends with and without shear flow with Tom McLeish and Nigel Clarke (52, 53, 64). There were also vital interactions, already mentioned, with my engineering colleagues in the department, supplementing my own deficiencies in rheology, and with scientists in industry.

There have been rewarding continuing collaborations with my own students and postdocs after they began their own academic careers: continuing work with Valeria Arrighi on quasi-elastic scattering from side-chain motion in polymers after she moved into her academic career at Heriot-Watt University (23, 65, 66); extending studies of surfaces and interfaces using neutron reflection with David Bucknall as he moved from Imperial to the Rutherford Lab and Oxford (61, 62, 67); and closer to home, my ongoing collaboration on spinodal decomposition with Joao Cabral, who was one of my last PhD students and is now a successful academic at Imperial (68).

Then there were others who came to me with a problem they thought might be amenable to study with neutrons. Having said I moved from ILL so that I could study my own problems, I was surprised by how many colleagues came to me with such questions. The initial discussions often developed into long-term collaborations—and friendships. Frequently the questions posed and the experimental results shed light on some of our own work on dynamics and on blends. Within the United Kingdom, the first to arrive, almost as soon as I settled in London, were Tony Semlyen from York and John Dawkins from Loughborough. Tony was running a long research program into the synthesis and properties of the ring-shaped polymer cyclic poly-(dimethyl siloxane). SANS experiments initially helped to confirm the ring conformation (69, 70), but we also went on to study the effect on dynamics of the ring structure using quasi-elastic scattering (71). John Dawkins was preparing polymer dispersions stabilized by anchoring di-block copolymers at the surface and asked if we could use SANS to detect the conformation of the copolymers in this complex mix! It took some time, but we did eventually succeed and also extended the studies into investigation of the gel-like structures of the micelles formed by the copolymers themselves in solution (72–75).

Soon after I arrived at Imperial, Bill MacKnight from the University of Massachusetts came to spend a year's sabbatical. His particular interest was in ionomers. These are polymer molecules

with salt groups attached as side chains. At high salt content, they become polyelectrolyte materials, but at low levels—a few mole%—the salt groups form associations. Bill was interested in ionomers in the melt and glassy state, and we used SANS to elucidate how the salt clusters deformed the molecules and also gave rise to heterogeneous structure in the material (76–78). It was through Bill that I met Bob Weiss from the University of Connecticut, who also spent a sabbatical—in fact, two—at Imperial and with whom we collaborated on blends under shear, as mentioned earlier, and later on main-chain liquid crystal polymers. This work was later extended by Valeria Arrighi at Heriot-Watt University (79, 80). Bill also introduced me to the scientists at Exxon Research Laboratories in Clinton, New Jersey, especially Dennis Pfeiffer. Here the interest was the dramatic effect on solution viscosity of the associating salt groups in solutions of a few mole% ionomer. The Exxon connection, which started in 1986, was long-lasting and very successful (81, 82). A student, Anne Pedley (later Anne Young), was supported partly by Exxon, and in a long series of publications continuing well after her PhD was completed, she elucidated the interactions between solution structure and solution rheology (83–87).

A surprising number of collaborators came to Imperial because of our expertise in quasi-elastic scattering. I mention only a couple of such links, which developed into long-term interactions. Barbara Gabrys, who was a postdoc with my group, introduced me to the group in Kyoto led initially by Professor Kitamaru and subsequently by Professors Kaji and Kanaya. With Barbara and the Kyoto group, we had a long series of interactions, mainly on quasi-elastic scattering from polyelectrolyte solutions (Reference 88 is an example). Jan Roots came in the early days from Norway to spend a year with us. His expertise in dynamic light scattering was a key contribution to our work on dynamics using the spin-echo technique (20, 28, 89, 90). In the case of my long-term friendship with Walther Burchard from Freiburg, I was the one who moved, spending a short but fruitful sabbatical in Freiburg in 1987. There I sharpened my knowledge of light scattering, which is such an important complement to neutron scattering (85).

One surprising collaboration on quasi-elastic scattering arose when Andrew Burgess from ICI initiated a project funding research into the rotational motion of side groups attached to polymers. I say surprising because such a fundamental study is not obviously aligned with industrial imperatives. The torsional vibrations from methyl side-groups on a polymer chain were among the first measurements I performed with neutrons (5). As well as vibrating in a threefold symmetric potential well, the methyl group can hop between the three minima, and this rotational motion shows up as another form of quasi-elastic scattering. For a glassy polymer, this is the only contribution to quasi-elastic broadening. We wanted to investigate the structural and packing effects that altered this rotational motion for different polymers. The announcement of the grant coincided with a breakdown of the reactor at ILL, entailing a two-year shutdown. Disaster? Not so, in fact, because I was able to call in all my goodwill with colleagues at neutron sources where there were quasi-elastic spectrometers. The student involved, Valeria Arrighi, traveled the world to do experiments, and by using spectrometers with different resolution, we first highlighted the problem of dealing with resolution clearly, and then solved it (23).

## **DRAWING TOGETHER THE THREADS IN SANS FROM POLYMER BLENDS**

My most recent and ongoing international collaboration was initiated through Walter Stockmayer, who introduced me to his colleague, Jane Lipson, at Dartmouth College in New Hampshire when I visited in about the year 2000. Jane had been developing a theoretical approach that could be applied to polymer mixing and was very interested in comparing her work to experimental data on blends—particularly SANS data. We planned a sabbatical year for her at Imperial and obtained

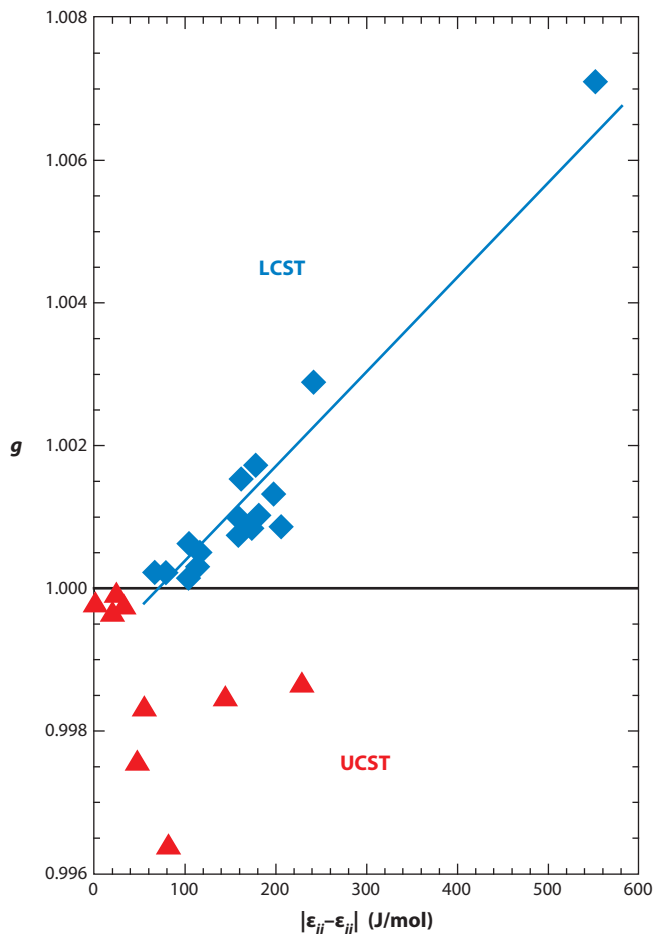
a grant that allowed her to spend five two-week periods throughout that year with us at Imperial and in between keep an eye on two small boys in Dartmouth as well. After this intensive year of interactions, we have pursued our collaboration by email and with annual visits by Jane to London. For me, our work has provided a most satisfactory drawing together of all the results my group has obtained on SANS from polymer blends. I have mentioned already my dissatisfaction with most of the theoretical descriptions of the mixing free energy for partially miscible blends because these always required at least two arbitrary parameters to fit the experimental data. I could never believe these parameters really increased understanding of the mixing behavior. Jane's locally correlated lattice (LCL) model has over the years provided me with increasing confidence in the parameters extracted and answered several outstanding questions.

The problems with the simple F-H lattice model have already been mentioned. They arise because in a fixed lattice there is no possibility to account for volume changes on mixing (common in real blends), or for specific interactions between component segments that can lead to locally nonrandom mixing. The F-H model has only one blend parameter, the F-H  $\chi$  parameter, but in consequence of these deficiencies,  $\chi$  has to be made concentration and temperature dependent to fit most experimental data. Although it is indeed possible to extract and tabulate the values of  $\chi(\phi, T)$  by fitting data, the results are not intuitively informative about the blend and its behavior. In the LCL model, the volume problem is dealt with by incorporating holes into the lattice and the nonrandom mixing by introducing a Boltzmann factor. All the parameters for describing the blend components are determined by fitting the model to pressure-volume-temperature data for the components. The key pure component parameters are the nearest-neighbor interaction energies,  $\varepsilon$ . The difference between  $\varepsilon$  values of the components ( $\varepsilon_{11} - \varepsilon_{22}$ ) is crucial in controlling miscibility (as is true for any model). There is, however, only one fitting parameter for the blend obtained by fitting the model to the LCST, or other blend data, such as our own  $G'$  values from the SANS data. This provides the blend interaction term  $\varepsilon_{12}$ , as the variation away from a geometric mean of the pure component values via a parameter  $g$ , such that  $\varepsilon_{12} = g(\varepsilon_{11} \varepsilon_{22})^{1/2}$ . Crucially,  $g$  is a single value for a given blend and is neither temperature nor concentration dependent (91, 92).

As we have explored the applications of the model to years of SANS data in the literature and in the theses of my students, we have noted its many advantages. It provides parameters that are translatable across molecular weight differences and across varying temperature ranges (91, 93). Patterns emerge as different blends are compared.  $g$  is always less than unity for UCST systems and always greater than unity for LCST systems. Correlations appear between the  $g$  and  $\varepsilon$  parameters, and our growing confidence has allowed us to interpret the data in terms of specific contributions to the entropy and enthalpy of mixing (94). **Figure 6** shows the correlations that appear in the  $g$  and ( $\varepsilon_{11} - \varepsilon_{22}$ ) parameters for different blends. All the UCST systems have  $g < 1$  and the LCST systems have  $g > 1$ . For the LCST systems, there is also a clear correlation between  $g$  and ( $\varepsilon_{11} - \varepsilon_{22}$ ). We believe we are even close to being able to predict blend behavior if pressure-volume-temperature data for the pure components can be obtained (95). For me, this has provided a very satisfactory sense of closure to all the years of study of polymer blends, as well as a stimulating collaboration across the Atlantic.

## CONCLUDING REMARKS

Quite early in my interactions with Henri Benoit, he made a very perceptive remark. When we were experimenting on D11 in Grenoble to demonstrate the correctness of the Flory hypothesis that polymer molecules in the melt follow random walk statistics, he claimed that no book would be published in future about polymer behavior that did not mention neutron scattering. One has only



**Figure 6**

Correlations between the parameters  $g$  and  $(\epsilon_{11} - \epsilon_{22})$  for several blends reported in the literature (reprinted with permission from Reference 94, ©2012 Am. Chem. Soc.). Abbreviation: LCST, lower critical solution temperature; UCST, upper critical solution temperature.

to look through the content pages of recent editions of journals such as *Polymer* or *Macromolecules* to see his prediction amply fulfilled. There is barely an issue of such journals that does not contain at least one article involving neutron scattering. It has been a privilege to be actively involved in the development of the techniques, and in each case an early user of them to investigate polymers. I have described how my own expertise and the necessity of using other techniques in parallel with the neutrons have led to a wide range of national and international collaborations. These have been one of the great pleasures of my half-century exploiting neutron scattering from polymers.

## DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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## LITERATURE CITED

1. Downes JS, White JW, Egelstaff PA, Ramsey V. 1966. Localised vibrations of trapped molecules. *Phys. Rev. Lett.* 17:533
2. Egelstaff PA, Stretton Downes JS, White JW. 1967. Molecular motion in molecular sieves by neutron scattering spectroscopy. *Mol. Sieves (Chem. Ind.)* 306:308–18
3. Downes JS. 1968. *Inelastic scattering of neutrons from clathrate inclusion compounds and molecules in molecular sieves*. DPhil Thesis, Oxford Univ., Oxford, UK
4. Allen G, Higgins JS. 1971. Spectroscopic studies of molecular motion in polymers. In *Molecular Spectroscopy*, ed. P Heppel, p. 261. London: Inst. Pet.
5. Higgins JS, Allen G, Brier PN. 1972. Methyl group motion in polypropylene oxide, polypropylene and polymethyl methacrylate. *Polymer* 13:157–63
6. Allen G, Wright CJ, Higgins JS. 1974. Effect of polymer microstructure on methyl group torsional vibrations. *Polymer* 15:319–22
7. Allen G, Brier PN, Goodyear G, Higgins JS. 1972. Motional broadening of the quasi-elastic peak in neutrons scattered from polymeric materials. *Faraday Symp. Chem. Soc.* 6:169–75
8. Higgins JS, Benoit HC. 1994. *Polymers and Neutron Scattering*. Oxford: Oxford Univ. Press
9. Rouse PE. 1953. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* 21:1272
10. Zimm B. 1956. Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. *J. Chem. Phys.* 24:269–78
11. de Gennes PG. 1967. Quasi-elastic scattering of neutrons by dilute polymer solutions: I. Free draining limit. *Physics* 3:37–45
12. Dubois-Violette E, de Gennes PG. 1967. Quasi-elastic scattering of dilute, ideal, polymer solutions: II. Effects of hydrodynamic interactions. *Physics* 3:181–98
13. Allen G, Higgins JS, Wright CJ. 1974. Segmental diffusion in rubbers studied by neutron quasi-elastic incoherent scattering. *J. Chem. Soc. Faraday II* 70:348–55
14. Benoit H, Decker D, Higgins JS, Picot C, Cotton JP, et al. 1973. Dimensions of a flexible polymer chain in the bulk and in solution. *Nature* 245:13–15
15. Kirste R, Kruse WA, Ibel K. 1975. Determination of conformation of polymers in amorphous solid state and in concentrated solution by neutron diffraction. *Polymer* 16:120–24
16. Lieser G, Fischer EW, Ibel K. 1975. Conformation of polyethylene molecules in the melt as revealed by small angle neutron scattering. *J. Polym. Sci. Polym. Lett. Ed.* 13:39–43
17. Allen G, Ghosh RE, Heidemann A, Higgins JS, Howells WS. 1974. On the structure of the quasielastic incoherent neutron scattering from polydimethyl siloxane. *Chem. Phys. Lett.* 27:308–11
18. Higgins JS, Ghosh R, Howells WS. 1977.  $Q^4$ -dependent broadening in quasielastic incoherent neutron scattering from a polymer melt. *J. Chem. Soc. Faraday Trans. II* 73:40–47
19. Akcasu AZ, Higgins JS. 1977. Quasielastic scattering of neutrons from freely jointed polymer chains in dilute solution. *J. Polym. Sci. Polym. Phys.* 15:1745–56
20. Ganazzoli F, Allegra G, Higgins JS, Roots JE, Bruckner S, Lucchelli E. 1985. Chain dynamics of polydimethyl siloxane in the intermediate range. *Macromolecules* 18:435–42
21. Higgins JS, Nicholson LK, Hayter JB. 1981. Observation of single chain motion in a polymer melt. *Polymer* 22:163–67
22. Higgins JS, Nicholson LK, Hayter JB. 1981. Dynamics of dilute polymer solutions. *Macromolecules* 14:836–43

23. Arrighi V, Higgins JS, Burgess AN, Howells WS. 1995. Rotation of methyl side groups in polymers: a Fourier transform approach to quasielastic neutron scattering. 1. Homopolymers. *Macromolecules* 28:2745–53
24. de Gennes PG. 1971. Reptation of a polymer chain in the presence of fixed obstacles. *J. Chem. Phys.* 55:572
25. Doi M, Edwards SF. 1978. Dynamics of concentrated polymer systems. Part 1.—Brownian motion in equilibrium. *J. Chem. Soc. Faraday Trans. II* 74:1789–801; Doi M, Edwards SF. 1978. Dynamics of concentrated polymer systems. Part 2.—molecular motion under flow *J. Chem. Soc. Faraday Trans. II* 74:1802–17
26. de Gennes PG. 1980. Coherent scattering by one reptating chain. *J. Phys.* 42:735–40
27. Ronca G. 1983. Frequency spectrum and dynamic correlations of concentrated polymer liquids. *J. Chem. Phys.* 79:1031–43
28. Higgins JS, Roots JE. 1985. Effects of entanglements on the single chain motion of polymer molecules in melt samples observed by neutron scattering. *J. Chem. Soc. Faraday II* 81:757–67
29. Koningsveld R, Stockmayer WJ, Nies E. 2001. *Polymer Phase Diagrams: A Textbook*. Oxford: Oxford Univ. Press
30. Walsh DJ, Higgins JS, Zhikuan C. 1982. The compatibility of poly(methyl methacrylate) and chlorinated polyethylene. *Polymer* 23:336–39
31. Zhikuan C, Ruona S, Walsh DJ, Higgins JS. 1982. A thermodynamic interpretation of the compatibility of chlorinated polyethylene with poly(methyl methacrylate). *Polymer* 24:263–70
32. Walsh DJ, Higgins JS, Rostami S. 1983. The compatibility of ethylene vinyl acetate copolymers with chlorinated polyethylene. 1. Compatibility and its variation with temperature. *Macromolecules* 16:388; Walsh DJ, Higgins JS, Rostami S, Weeraperuma K. 1983. 2. Investigation of thermodynamic parameters. *Macromolecules* 16:391
33. Allen G, Chai Z, Chong CL, Higgins JS, Tripathi J. 1984. Thermodynamics of oligomeric binary mixtures of polyethylene glycol and polypropylene glycol methyl ethers. *Polymer* 25:239–44
34. Warner M, Higgins JS, Carter AJ. 1983. Chain dimension and interaction parameters in neutron scattering from polymer blends with a labelled component. *Macromolecules* 16:1931–35
35. Higgins JS, Carter AJ. 1984. Molecular conformation and interactions in oligomeric mixtures of polyethylene glycol and polypropylene glycol methyl ethers: a neutron scattering study. *Macromolecules* 17:2197–202
36. Snyder HL, Meakin P, Reich S. 1983. Dynamical aspects of phase separation in polymer blends. *Macromolecules* 16:757–62
37. Hill RG, Tomlins PE, Higgins JS. 1985. A preliminary study of phase separation in oligomeric polystyrene/polybutadiene blends. *Polymer* 26:1708–12
38. Hill RG, Tomlins PE, Higgins JS. 1985. A preliminary study of the kinetics of phase separation in high molecular weight polymethyl methacrylate/solution chlorinated polyethylene blends. *Macromolecules* 18:2555–60
39. Cahn JW. 1968. Spinodal decomposition. *Trans. Metal. Soc. AIME* 242:168–80; Huston EL, Cahn JW, Hilliard JE. 1966. Spinodal decomposition during continuous cooling. *Acta Metall.* 14:1053–62; Cook HE. 1970. Brownian motion in spinodal decomposition. *Acta Metall.* 18:297–306
40. Fruitwala H, Higgins JS, Tomlins PE. 1989. Correlation of phase separation behaviour in polymer blends with thermodynamic measurements in the one phase region. *Macromolecules* 22:3674–81
41. Higgins JS, Fruitwala H, Tomlins PE. 1988. Prediction of phase separation behaviour from thermodynamic measurements in the one-phase region. *Makromol. Chem. Makromol. Symp.* 16:313–27
42. Clark J, Fernandez ML, Tomlins PE, Higgins JS. 1993. Small angle neutron scattering studies of phase equilibria in blend of deuterated polymethyl methacrylate with solution chlorinated polyethylene. *Macromolecules* 26:5897–907
43. Cabral JT, Gerard H, Clarke N, Higgins JS. 2000. Phase separation of polymer blend TMPC/PS: dependence on blending method. *Phys. B Condens. Matt.* 276–278:408–9
44. Cabral JT, Higgins JS, McLeish TCB, Strausser S, Magonov S. 2001. Bulk spinodal decomposition studied by atomic force microscopy and light scattering. *Macromolecules* 34:3748–56
45. Cabral JT, Higgins JS, Yeruna NA, Magonov SN. 2002. Topography of phase separated critical and off-critical polymer mixtures. *Macromolecules* 35:1941–50



46. Hindawi I, Higgins JS, Galambos AF, Weiss RA. 1990. Flow-induced mixing of blends of poly(ethylene-vinylacetate) and solution chlorinated polyethylene. *Macromolecules* 23:670–74
47. Hindawi I, Higgins JS, Weiss RA. 1992. Flow-induced mixing and demixing in polymer blends. *Polymer* 33:2522–29
48. Fernandez ML, Higgins JS, Richardson SM. 1993. When rheology interacts with thermodynamics in polymer blends. *Trans. IChemE* 71:239–44
49. Fernandez ML, Higgins JS, Richardson SM. 1995. Flow instabilities in polymer blends under shear. *Polymer* 36:931–39
50. Soontaranan W, Higgins JS, Papathanasiou T. 1996. Shear flow and the behaviour of polymer blends. *Fluid Phase Equilib.* 121:273–92
51. Aelmans NJJ, Reid MC, Higgins JS. 1999. Change of phase behaviour of SMA/PMMA blends during processing at high deformation rates. *Polymer* 40:5051–62
52. Clarke N, McLeish TCB, Pavawongsak S, Higgins JS. 1997. Viscoelastic effects on the early stages of phase separation in polymer blends. *Macromolecules* 30:4459–63
53. Pavawongsak S, Higgins JS, Clarke N, McLeish TCB, Peiffer D. 2000. Phase separation in entangled polystyrene/poly(vinyl methyl ether) blends. *Polymer* 41:757–63
54. Gerard H, Cabral JT, Higgins JS. 2003. Flow-induced enhancement of concentration fluctuations on polymer mixtures. *Philos. Trans. R. Soc. Lond. A* 361:767–79
55. Fernandez ML, Higgins JS, Penfold J, Shackleton CS. 1990. Structure of thin deuterated poly(methyl methacrylate) films as studied by the specular reflection of neutrons. *Polym. Commun.* 31:134
56. Walsh DJ, Sauer BB, Higgins JS, Fernandez ML. 1990. Reflection methods for the study of polymer interfaces. *Polym. Eng. Sci.* 30:1085–89
57. Fernandez ML, Higgins JS, Penfold J, Shackleton C. 1991. Interfacial structure for a compatible polymer blend for short and intermediate annealing times. *J. Chem. Soc. Faraday Trans.* 87:2055–61
58. Bucknall DG, Higgins JS, Penfold J. 1992. The effect of a diblock copolymer compatibilizer on the interface between immiscible polymers. *Phys. B Condens. Matt.* 180:468–70
59. Bucknall DG, Higgins JS, Penfold J, Rostami S. 1993. Segregation behaviour of deuterated P(s-b-MMA) diblock copolymer in the presence of PMMA homopolymer. *Polymer* 34:451
60. Hermes HE, Bucknall DG, Higgins JS, Scherrenberg RL. 1998. The ordering of semi-crystalline PS-b-hPB copolymers at a PS/PB interface and their effects on interfacial strength. *Polymer* 39:3099
61. Butler SA, Bucknall DG, Higgins JS. 1999. Real-time measurement of polymer diffusion coefficients using neutron reflection. *Macromolecules* 32:5453–56
62. Bucknall DG, Higgins JS, Butler SA. 2004. Real-time neutron reflectivity study of the early stages of diffusion into and dissolution of glassy polymers. *J. Polym. Sci. B Polym. Phys.* 42:3267–81
63. Allegra G, Higgins JS, Ganazzoli F, Luccheli E, Bruckner S. 1984. Dynamics of atactic polystyrene in solution. *Macromolecules* 17:1253–63
64. Gerard H, Higgins JS, Clarke N. 1999. Shear-induced demixing in polystyrene/poly(vinyl methyl ether) blends. 1. Early stages of shear-induced demixing. *Macromolecules* 32:5411–22
65. Arrighi V, Higgins JS, Burgess AN, Howells WS. 1995. Rotation of methyl side groups in polymers: a Fourier transform approach to quasielastic neutron scattering. 2. Polymer blends. *Macromolecules* 28:4622–30
66. Arrighi V, Gagliardi S, Zhang C, Ganazzoli F, Higgins JS, et al. 2003. A unified picture of the local dynamics of poly(dimethylsiloxane) across the melting point. *Macromolecules* 36:8738–48
67. Hermes HE, Higgins JS, Bucknall DG. 1997. Investigation of the melt interface between polyethylene and polystyrene using neutron reflectivity. *Polymer* 38:985–89
68. Cabral JT, Higgins JS. 2009. Small angle neutron scattering from the highly interacting polymer mixture TMPC/PSd: no evidence of spatially dependent  $\chi$  parameter. *Macromolecules* 42:9528–36
69. Higgins JS, Dodgson K, Semlyen JA. 1979. Studies of cyclic and linear polydimethyl siloxanes: 3. Neutron scattering measurements of the dimensions of ring and chain polymers. *Polymer* 20:553–58
70. Arrighi V, Gagliardi S, Dagger AC, Semlyen JA, Higgins JS, Shenton MJ. 2004. Conformation of cyclic and linear chain polymers in bulk by SANS. *Macromolecules* 37:8057–65

71. Higgins JS, Ma K, Nicholson LK, Hayter JB, Dodgson K, Semlyen JA. 1983. Studies of cyclic and linear poly(dimethyl siloxane): 12. Observation of diffusion behaviour by quasi-elastic neutron scattering. *Polymer* 24:793–99
72. Higgins JS, Dawkins JV, Taylor G. 1980. Non-aqueous polymer dispersions: dimensions of adsorbed AB block copolymers of polystyrene and polydimethyl siloxane by small angle neutron scattering. *Polymer* 21:627–31
73. Higgins JS, Tomlins PE, Dawkins JV, Maghami GG, Shakir SA. 1988. Non-aqueous polymer dispersions - investigation of anchor blocks in the adsorbed diblock copolymer poly(styrene-*b*-ethylene-co-propylene) by SANS. *Polymer* 29:121–25
74. Higgins JS, Dawkins JV, Maghami GG, Shakir SA. 1986. Study of micelle formation by the diblock copolymer polystyrene-*b*-ethylene-co-propylene in dodecane by SANS. *Polymer* 27:931–36
75. Higgins JS, Blake S, Tomlins PE, Ross-Murphy SB, Staples E, et al. 1988. Comparison of the structural and rheological consequences of micelle formation in solutions of a model di-block copolymer. *Polymer* 29:1968–78
76. Earnest TR, Higgins JS, MacKnight WJ. 1981. Small angle neutron scattering from sulfonate ionomers. *Macromolecules* 14:192–96
77. Earnest TR, Higgins JS, MacKnight WJ. 1982. Small angle neutron scattering from polypentenamer sulfonates. *Macromolecules* 15:1390–95
78. Forsman WC, MacKnight WJ, Higgins JS. 1984. Aggregation of ion pairs in polystyrene sulfonate ionomers: theory and experiment. *Macromolecules* 17:490–94
79. Arrighi V, Higgins JS, Abis L, Weiss RA. 1996. Characterization of a main-chain semi-flexible liquid crystal polymer: degree of orientational order. *Polymer* 37:141–48
80. Arrighi V, Higgins JS. 1997. Molecular dynamics of a main-chain liquid crystal polymer below the crystalline to nematic phase transition. *J. Chem. Soc. Faraday Trans.* 93:1605–12
81. Peiffer DG, Kaladao J, Duvdevani I. 1987. Time- and shear-rate-dependent rheology of ionomer solution. *Macromolecules* 20:1397–400
82. Lantmann CW, MacKnight WJ, Higgins JS, Peiffer DG, Sinha SK, Lundberg RD. 1988. Small angle neutron scattering from sulfonate ionomer solutions. I. Associating polymer behaviour. *Macromolecules* 21:1339–43
83. Gabrys B, Higgins JS, Lantmann CW, MacKnight WJ, Pedley AM, et al. 1989. Single-chain dimensions in semi-dilute ionomer solutions: a small-angle neutron scattering study. *Macromolecules* 22:3746–51
84. Pedley AM, Higgins JS, Peiffer DG, Rennie AR. 1990. Thermodynamics of the aggregation phenomenon in associating polymer solutions. *Macromolecules* 23:2494–500
85. Pedley AM, Higgins JS, Peiffer DG, Burchard W. 1990. Light scattering from sulphonate ionomers in xylene. *Macromolecules* 23:1434–37
86. Young M, Higgins JS, Peiffer DG, Rennie AR. 1996. Effect of sulfonation level on the single chain dimensions and aggregation of sulfonated polystyrene ionomers in xylene. *Polymer* 36:691–97
87. Young AM, Brigault C, Hanan R, Higgins JS, Peiffer DG. 1998. Small angle neutron scattering from ionomer gels. *Polymer* 39:6685–96
88. Kanaya T, Kaji K, Kitamaru R, Gabrys B, Higgins JS. 1988. Local motions of counter-ions in polyelectrolyte solutions without added salts studied by neutron quasi-elastic scattering. *J. Chem. Soc. Faraday I* 84:3487–500
89. Roots JE, Nyström B, Higgins JS. 1985. Effect of temperature on dynamics of isotactic polystyrene in solution observed by quasi-elastic scattering. *Polymer* 26:229–31
90. Nyström B, Roots JE, Gabrys B, Higgins JS, Peiffer D, et al. 1986. Dynamics of polystyrene sulfonate ionomers in solution: a neutron spin-echo study. *J. Polym. Sci. C Polym. Lett.* 24:273–81
91. Higgins JS, Tambasco M, Lipson JEG. 2005. Polymer blends: stretching what we can learn through the combination of experiment and theory. *Prog. Polym. Sci.* 30:832–43
92. Tambasco M, Lipson JEG, Higgins JS. 2006. Blend miscibility and the Flory-Huggins interaction parameter: a critical examination. *Macromolecules* 39:4860–68

93. Higgins JS, Lipson JEG, White RP. 2010. A simple approach to polymer mixture miscibility. *Philos. Trans. R. Soc. Lond. A* 368:1009
94. White RP, Lipson JEG, Higgins JS. 2012. New correlations in polymer blend miscibility. *Macromolecules* 45:1076–84
95. White RP, Lipson JEG, Higgins JS. 2012. How pure components control polymer blend miscibility. *Macromolecules* 45:8861–71



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## Errata

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