The Development and Application of Stray Field Magnetic Resonance Imaging to Polymer Dynamics

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Background

The proposal was the cornerstone of a plan to maintain and grow a consortium of academic and industrial scientists interested in the further development and exploitation of the stray field magnetic resonance imaging (STRAFI) facilities previously established (1995) with EPSRC funds at the University of Surrey. The scientific programme was strongly focussed on polymer dynamics. It had three main themes: small molecule transport in polymers, polymer chain motion in thin polymer layers and technique development.

The programme has been an unequivocal success. Substantial new understanding has been achieved in the area of liquid transport in polymers in particular. New capability has been firmly established. A substantial collaboration of active researchers has been maintained throughout the period of the grant.

Key advances and supporting methodology

1. Context

To place the work in context, in 1965, Alfrey classified two distinct modes of liquid ingress into glassy polymers: Fickian and Case II. The former is, in some sense, normal diffusion. Liquid concentration profiles in the swollen polymer are smooth and advance with time as $t^{1/2}$. A diffusion coefficient, albeit strongly concentration dependent, is readily defined and measured. The latter is very different. A sharp liquid ingress front, which advances as $t^1$, is observed. This front separates a region of swollen polymer (rubbery phase) from unswollen and uninvaded glass (glassy phase). In 1982, Thomas and Windle proposed a model of Case II diffusion that forms the basis of much current understanding. Case II ingress occurs when the visco-elastic macromolecular-swelling of the polymer at the liquid front is the rate-limiting step to advance of the liquid. The swelling rate at the glass-rubber interface imposes a maximum forward liquid flux. According to the Thomas and Windle model, the front velocity is a function of the intrinsic properties of the polymer and solvent system only. The concentration of liquid in the rubber is large and close to the swollen equilibrium. When swelling is not rate limiting, then Fickian diffusion is observed. Then, the rate-limiting step is diffusion of liquid molecules through the swollen polymer. In order to improve understanding, to test relevant models and to address pertinent questions, the research focussed on different methods of accessing the anomalous regime encompassing the Fickian to Case II crossover, where the diffusion is most sensitive to the details of the polymer-solvent system.

2. MRI studies of liquid transport in polymers.

Experiments carried out as part of the current research programme at the University of Surrey have impacted on our understanding of liquid transport in polymeric systems in three key areas leading to three substantive publications. First, we have identified surface flux limited Case II diffusion as an

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alternate mechanism of linear ingress\textsuperscript{3}. Second, we have used chemically resolved MRI to help resolve long standing questions about three component systems (polymer and two solvents)\textsuperscript{4}. Third, we have developed a new model for water transport into compacted, swelling, polymer powder that critically incorporates vapour transport\textsuperscript{5}. These three are discussed below along with other related work.

2.1 Surface flux-limited Case II ingress: It is now clear that the Thomas and Windle model and its derivatives are insufficient to explain all apparent observations of Case II diffusion. We have unambiguously shown that a sufficiently low flux of liquid molecules impacting the surface of a polymer with a swelling induced glass-rubber transition also leads to the \textit{linear} ingress of a sharp solvent front. However, now the front velocity is controlled by the surface flux and is largely independent of the intrinsic properties of the polymer and solvent. Indeed, we have shown using MRI and simple theory, that the velocity is directly proportional to the flux of liquid at the surface. Moreover, the concentration of liquid in the polymer is small and close to that required to induce the glass-rubber transition. This is quite different to normal Case II diffusion where the liquid concentration in the rubber is close to the swollen equilibrium. We propose that this observation is sufficient to explain a number of apparent discrepancies and inconsistencies in literature data – both our own and those of others – going back several years when trying to explain case II ingress data\textsuperscript{3}. The data and modelling make clear that in the long-time limit all Case II type ingress must revert to Fickian ingress.

2.2 Mixed solvent ingress: We have observed the ingress of binary solvent mixtures into polymers. We originally proposed watching one solvent enter a polymer already swollen by another – as we had done in preliminary work. In practice, we found studying mixed solvent ingress using chemically resolved MRI techniques much more informative. The studies arise partly from a literature debate as to whether a thermodynamically good but kinetically-bad solvent ingresses ahead of, with or behind, a thermodynamically-bad, but kinetically-good solvent. The debate is driven by the observation that a small fraction of methanol in methyl ethyl ketone actually increases the dissolution rate of poly(methyl methacrylate)\textsuperscript{6}. Questions and divergent ideas are seen in the literature\textsuperscript{7,8} but a paucity of chemically selective, spatially resolved data has hitherto prevented real progress. We studied mixtures of methyl ethyl ketone and ethanol ingressing polystyrene using chemically selective MRI and observed that the two liquid fronts ingress together but that the two liquid concentration profiles are very different\textsuperscript{4}. The methyl ethyl ketone exhibited a sharp concentration front whereas the ethanol had a smooth concentration profile. We were able to explain these results in terms of a simple three component diffusion model which captured the essential physics of the problem. At the same time we have shown that alternate models to be found in the literature\textsuperscript{9} are inadequate to explain the data.

2.3 Water in powdered polysaccharides: In many situations of practical import, the polymer is presented not as a homogeneous material but in compacted powder or tablet form. This is particularly the case in food processing and pharmaceuticals. Here the situation is more complex and for a given polymer matrix a variety of diffusion behaviour can be seen. We have reported experimental evidence, which again reflects the importance of the vapour phase\textsuperscript{5,10}. Our experimental data for water ingressing xanthan shows a pronounced diffusion foot dependent on polymer compaction ahead of the main ingress front. This has been successfully modelled on the basis of coupled vapour diffusion in decreasing vapour space around swelling polymer particles and liquid diffusion in the swelling gel. Locally the vapour and liquid concentration are maintained in equilibrium according to

\textsuperscript{3} P. J. McDonald, J. Godward, R. Sackin, R. Sear \textit{Macromolecules} \textbf{34} 1048 (2001)
\textsuperscript{4} R. Sackin E. Ciampi, J. Godward, J.L. Keddie and P.J. McDonald \textit{Macromolecules} \textbf{34} 890 (2001)
\textsuperscript{8} G.W. Miller et al \textit{Polym. Eng. and Sci.}, \textbf{11} 73 (1971)
\textsuperscript{10} I. Hopkinson, R. A. L. Jones, P. J. McDonald, B. Newling, A. Lecat, S. Livings. \textit{Polymer} \textbf{42} 4947 (2001)
the adsorption isotherm. The diffusion mechanism within the polymer itself, i.e. Fickian or Case II, is of only secondary importance. The model was extended from our own previous work on long-range diffusion in zeolite beds and is therefore likely to be relevant to both swelling and non-swelling polymer matrices used in drug delivery.

In addition to the work on compacted xanthan, measurements of water ingress profiles in a range of chemically modified polysaccharides, some made available to us by Prof. I. W. Sutherland (Institute of Cell and Molecular Biology, University of Edinburgh) have also been made. Significant differences are seen between samples. Adsorption isotherms have been measured in collaboration with Dr J. Cleaver (Chemical Engineering, University of Surrey). These data are still being analysed using the coupled liquid–vapour diffusion model. As proposed, measurements of liquids other than water, which is both polar and swelling, invading powdered xanthan were carried out. These included cinnamaldehyde (polar and non-swelling) and cyclohexane (non-polar, non-swelling). However, these measurements did not greatly increase our understanding.

2.4 Charge-state effects: A range of microbial polymers carrying negative, positive or no charge were examined using NMR relaxometry to determine what effect the charge-state had on the diffusion of manganese ions across the polymer\textsuperscript{11}. The results indicated that the presence of the negative charge on the polymers enhanced cation transport by 2 to 2.5 times compared to a neutral polymer, which, in turn, was twice the value for a positively charged polysaccharide. This supports the theory of cation contact exchange and in part may account for the predominance of anionic polysaccharides surrounding micro-organisms and plant roots. This is a relevant property when considering the results of the STRAFI experiments on water ingress which show that the high water retention and modulated uptake of such polymers can act as a controlling factor in organism-water interactions, adding protection against drought or flood, respectively. Consequently, these polymers can be protective, yet still enhance important cation uptake. The anion exclusion properties were also examined.

2.5 Cellulose: P. Laity (School of Metallurgy and Materials, University of Birmingham) became an active member of the STRAFI consortium instigating, primarily with Dr P. M. Glover, MRI studies of water mobility in cellophane layers\textsuperscript{12}. Spatially resolved measurements of water self-diffusion coefficients and nuclear spin-spin relaxation times have provided supporting evidence for a more dense cellulose surface skin and more porous interior.

2.6 Molecular weight and tacticity effects: Measurements of ethanol and methyl ethyl ketone ingress into polystyrene samples of varying molecular weight were made\textsuperscript{13}. MRI revealed little molecular weight dependence in the range 10,000 g/mol through to 1,460,000 g/mol except that ingress was marginally faster in the very lowest molecular weight sample. To explore the effects of surfaces and interfaces on solvent transport, complementary measurements were performed on the same polymers in thin films using ellipsometry.

Other work explored the effects of polymer crystallinity on solvent transport, with the aim of keeping molecular weight constant when comparing amorphous and crystalline systems. Substantial difficulty in preparing high quality, semicrystalline isotactic bulk samples prevented MRI experiments, but comparative measurements of ingress into isotactic and atactic polystyrene were made in thin films using ellipsometry. The ellipsometry data suggested that in isotactic polystyrene, rapid initial ingress of solvent into amorphous regions is followed by slower ingress into crystalline regions\textsuperscript{13}.

3. Chain dynamics in polymer films.

A second theme of the proposal (section 5.3) concerned polymer chain dynamics in thin polymer layers where the sample thickness is comparable to the chain contour length or even the radius of gyration. This arose from literature reports that chain diffusivity is reduced as a result of confinement

\textsuperscript{12} P. R. Laity, P. M. Glover, J. Godward, P. J. McDonald, J. N. Hay, Cellulose \textbf{7} 227 (2000)
\textsuperscript{13} R. Sackin PhD Thesis, University of Surrey, 2000
in thin films\textsuperscript{14}. Moreover, interactions at interfaces could also affect polymer diffusivity. The experiments required substantial efforts of sample preparation, as diffusometry cannot be performed on single films. In order to have a sufficient amount of material, multilayers of polymer films were studied. Methods of making multi-layer sandwiches of poly(ethylene oxide) (PEO) and deuterated polystyrene with up to 300 layers and layer thickness of the order of 150 nm (1/3 of the PEO chain contour length) were developed. (At the temperature of the experiment, PEO is a melt and PS is a glass. No NMR signal is obtained from the deuterated PS.) Stray (fringe) field diffusometry was used to measure the \textsuperscript{1}H diffusion coefficient in PEO in the long time limit – that is the slowest component of the diffusion. Experiments were performed at elevated temperature and under \textsuperscript{N}2 gas (to prevent oxidation). The results suggested a small reduction in the polymer chain self diffusion coefficient of the order of 5\% compared to the bulk\textsuperscript{15}. This was in broad agreement with theoretical expectations\textsuperscript{14}. However, the signal-to-noise ratio of the data was low, and the results were not wholly convincing. Subsequently, we have been trying (and continue to try) to develop automated spin coating procedures to make sandwiches with many more, much thinner layers using spin coating of various combinations of silicones or PEO alternating with sol-gel SiO\textsubscript{2} or glassy polymers.

In a separate initiative, we investigated the self diffusion of different segments of chains in star polymers prepared by Dr Lian Hutchings at the University of Durham in conjunction with Dr C Adams and others within IRC in Polymer Science and Technology. The polybutadiene star polymers were selectively deuterated enabling different segments to be followed with fringe field diffusometry. Unfortunately, the mobility proved too low even for stray field diffusometry and we were only able to place an upper limit on the diffusivity.

4. Technical developments

We have improved our technical capability as a result of this project, as foreseen in section 5.2 of the original proposal.

4.1 Double resonance: At the start of the programme, PJM was on sabbatical at the University of Ulm, where he learnt at first hand the methodology of cyclic cross polarisation (CYCLCROP) weighted imaging as developed there by R. Kimmich. We incorporated CYCLCROP MRI onto the Surrey MR microscope and have used it extensively for chemical selectivity in our studies of, for instance, mixed solvent ingress into polymers. The method allowed us to visualise one solvent and suppress the other with high selectivity and signal-to-noise ratio.

4.2 Double quantum filtered imaging: The technique of double quantum filtered imaging is known but not altogether straightforward for routine use. It enables molecules in anisotropic environments to be selectively visualised. We established double quantum filtered imaging on the microscope and used this for studies of soap dissolution in collaboration with Unilever\textsuperscript{16}. The liquid crystalline phases of the dissolution interface are not readily quantified using conventional \textsuperscript{1}H magnetic resonance imaging as they cannot be easily resolved on the basis of their spin relaxation times. In D\textsubscript{2}O, the quadrupolar splitting of the liquid crystalline phases can be used to infer liquid crystal concentrations. The splitting can be unambiguously measured using double quantum spectroscopy. Combining this with imaging enabled us to obtain, for the first time, quantitative maps of the dissolution interface.

It had been hoped that the DQF methodology might elicit information about stress fronts in swelling polymers. However, in spite of varied and repeated experiments, this did not prove to be the case.

4.3 Stray field developments: We continued to develop sequences for diffusion coefficient mapping in the stray field. These are now available as a matter of routine and are widely used as a contrast mechanism in many of our investigations.

\textsuperscript{14} A.N. Semenov, Phys. Rev. Letts. \textbf{80} 1908 (1908).
\textsuperscript{16} Ciampi, E., Goerke, U., McDonald P.J., Chambers, J.G., and Newling B., submitted to \textit{Langmuir}
We attempted to develop both CYCLCROP and double quantum filtered methods for application in the stray field. To date, this has not been successful because of the very high bandwidth of the experiment caused by the field gradient and because of the low sensitivity of experiments in the stray field.

Most recently, and going beyond our original proposal, we have been able to demonstrate the feasibility of orthogonal gradients in the stray field for multi-dimensional imaging without sample rotation. This is an important breakthrough, particularly relevant to our studies of coatings systems in which we should now be able to eliminate the detrimental effects of field curvature and radial variation of the sample from depth profiles.

4.4 Other developments: Dr Gillies, working closely with Prof. E. W. Randall at Queen Mary College, University of London, developed stray field techniques for $^{31}\text{P}$ and applied these to the study of a variety of compounds including bone, bone meal and calcium hydroxyapatite$^{17}$. The paramagnetic $\text{Co}_3(\text{PO})_4$ had a short $T_1$ value of 5 ms whereas the $T_2$ value of 165 ms was only slightly shorter than those found for diamagnetic compounds. The $T_1$ value for chicken bone was 14.7 s. The generation of long Hahn echo-trains produced by the application of many pulses was demonstrated and the so called Long Echo-Train Summation (LETS) technique was used to improve the signal-to-noise ratio of the data. The echo decays are not single exponential and we still do not fully understand the various contributions from spin locking and $T_1$ weighting via different coherence pathways. The improvement in summing more echoes was demonstrated for $\text{NH}_4\text{PF}_6$ as the number of echoes was increased from 1024 to 8192 and the 4096 echoes from the bone sample showed relatively more persistence. Echo experiments on $\text{NH}_4\text{PF}_6$ were also performed in the centre field of a 4.7 T magnet at the same frequency (200 MHz). These also showed similar behaviour. The analysis of the effect of the stray field is not complete and will be the subject of a future paper when it is also hoped that simulations including relaxation might be available for the STRAFI echo trains. Phosphorus STRAFI-techniques are potentially useful in a number of areas, additional to the study of bone and bone-marrow, such as implants, dental materials and for environmental studies involving phosphorus in soils and rocks. They may, however, be restricted to studies in one dimension because of the time factor.

The $^{59}\text{Co}$ STRAFI echoes of a number of diamagnetic and paramagnetic cobalt compounds have been studied. A phantom was constructed which consisted of annular rings of different samples to be placed on top of each other with spaces in between. The purpose was to test for image displacement of paramagnetic samples. However, no displacements outside experimental error were observed.

Project plan review

The project proceeded largely to plan. The work on small molecule transport in polymers went particularly well and dominated the programme. The additional capabilities for iso-centre work, while not technically ground breaking, were incorporated as expected and enabled us to significantly extend the range of experiments we could attempt. Fringe field diffusometry of thin polymer layers was not as successful as might have been hoped largely due to the enormity of the problem of making adequate samples.

Research impact and benefits to society

The work on small molecule transport in polymers is making an impact on industry. As evidence for this, several organisations are now approaching us with a view to further work, collaboration etc. This is particularly the case in the fields of coatings and adhesives, bio-polymers and drug release matrices.

The EPSRC funding has been able to leverage further funding from industrials more than equal to the EPSRC monies spent.

**Explanation of expenditure**

The primary expenditure on this grant was salary. Dr John Godward was employed from June 1998 to April 2001 as the principal post doctoral research assistant responsible for the management of the STRAFI facility. He conducted many of the experiments discussed above (notably on small molecule ingress into glassy polymers), he developed an extensive volume of IDL data analysis and visualisation code, and he collaborated with many visitors to the laboratory, helping them carry out experiments. He also organised the regular meetings of the STRAFI consortium. Mr Conway (Technician, 10%) who had previously attended a manufacturer’s training course, maintained the STRAFI facility.

A Sun computer, extra disk drive, and IDL software were purchased as proposed together with an additional PC and have all been heavily used by University of Surrey and external users.

The travel budget was used to attend conferences as planned, except that three delegates attended the Berlin and Heidelberg meetings, each part funded by the grant, and only one attended the “Cambridge meeting” on Porous Media which was, in fact, moved to Bologna.

**Further research**

As originally planned, numerous industrial and academic scientists have had access to the STRAFI facility over the grant duration. Unilever have funded a post-doctoral researcher for blue skies projects for a total of five years. Most of the work carried out with Unilever is already, or is being, published. Dr Saito (Nippon Steel, Japan) visited each of the project years to explore opportunities with STRAFI for materials science problems of relevance to Nippon Steel. Elizabeth Dodgson (Cereal Partners Worldwide) visited on 3 occasions to make measurements of water in cereals. Other measurements were made on behalf of Nestlé, BNFL, RBB (now part of the Lafarge group) and UCB Films PLC. In every case, substantive work was fully funded by the company but was only possible by virtue of the existence of the EPSRC facility. Varian (Chemagnetics) provided hardware to upgrade the facility in various ways.

E. Crilly (Daphne Jackson Trust Research Fellow) carried out a small examination of a rather unusual soil polymer called glomalin associated with the hydrophobic character of some soils. This was in collaboration with Prof. Sara Wright at the U.S Dept of Agriculture, Beltsville, Maryland. A recent approach to collaborate on related systems has also been received from Prof R.F.H.Dekker, Universidade Estadual de Londrina, Brazil.

A substantial parallel programme of STRAFI work directed towards coatings and adhesives has been built on the back of the EPSRC programme. This now utilises the GARField magnet available at Surrey as well as the main STRAFI facility. This programme is now primarily funded by ICI (post doctoral researcher) and by EC Framework V in collaboration with Traetek, Sweden and WSAB-Lignomat, Germany.

**Dissemination**

Some 9 papers arising principally from the work reported above have been published in peer reviewed journals. More than a further 24 conference presentations have been made. In addition, the results of the project work (including details of most of the industrially led projects) have been made available to users of the facility at regular semi-annual consortium meetings.
CONFERENCE PRESENTATIONS


3. Film Formation from Alkyd Polymers, E. Ciampi, British Radiofrequency Spectroscopy Group meeting, 23 September 1998.


5. Magnetic Resonance Imaging of Film Formation in Alkyd Emulsions, J. L. Keddie, Institut de Chimie des Surfaces et Interfaces, Universite de Haute Alsace, Mulhouse, France, 6 December 1998. INVITED SEMINAR


12. Magnetic Resonance Imaging of the Drying of Waterborne polymer Colloids, J. L. Keddie, University of Leeds, Department of Physics, 29 March 2000. INVITED SEMINAR


15. **The MRI of watching paint dry** P.J McDonald Meeting of the Dutch academic coatings forum, Utrecht, 19-20 December 2000. INVITED LECTURE


22. **Advances in stray field imaging and its application to liquid transport in polymer systems**, P. J. McDonald Symposium on spatially resolved magnetic resonance and 7th NMRS Symposium, NMRS India, Chennai, India, 7-8 February 2001. INVITED LECTURE
