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NEUTRON REFLECTIVITY STUDIES OF HOT POLYMER MELT INTERFACES

Helen E. Hermes[1], David G. Bucknall[2], Simon A. Butler[1], Julia S. Higgins[1]*

[1]Department of Chemical Engineering, Imperial College, London SW7 2BY, UK
[2]ISIS Facility, Rutherford Appleton Lab., Chilton, Didcot OX11 0QX, UK

Abstract

Neutron reflectivity data have been obtained using a specially designed cell that allows the investigation of the interfaces between polymers in the melt state. Systems which are semicrystalline at room temperature can be investigated for the first time. Example results from a polystyrene (PS)/ polyethylene (PE) interface (both with and without copolymer) and an isotactic polypropylene (PP)/ high density polyethylene interface are presented.

INTRODUCTION

Over the past decade neutron reflectivity (NR) has been widely used to investigate the interfaces between thin polymer layers and the effects of copolymers on such interfaces (1). However, these investigations have previously been limited to amorphous systems. This is because at room temperature the surfaces of thin films of semicrystalline polymers are molecularly rough. In "traditional" room temperature NR measurements this surface roughness results in a drastic loss of specular reflection, making such measurements at best very difficult, or more likely impossible.

Previous attempts to overcome the problem of surface roughness of semicrystalline films by heating the polymer film supported on a silicon wafer into the melt regime were unsuccessful (2). Although the molecular roughness associated with the polymer crystallinity was lost in

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the melt regime, the surface still suffered from long range waviness which adversely affected the reflectivity profile. To overcome these problems we have developed the cell shown schematically in figure 1. By providing a molecularly smooth and flat template surface for the polymer both the molecular roughness and the long range waviness were successfully removed in the melt regime enabling NR investigations of the interfaces within the specimens.

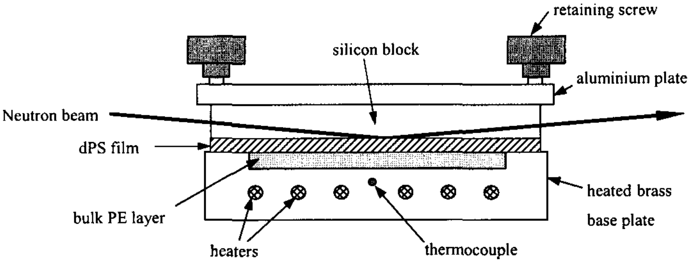

Figure 1: Schematic illustration of the melt cell used in the neutron reflectivity measurements described in the text.

To date the cell has been used to investigate two systems:

(i) amorphous PS/ semicrystalline PE and the effect of diblock copolymer addition on this interface

(ii) semicrystalline isotactic PP/ semicrystalline high density PE

The possibility of combining the high modulus of PS with the ductility of PE has led to much interest in PS/PE blends over the last 20 years (3). However, it has generally been found that merely mixing PS with PE results in a blend which demonstrates the low strength of PE and the brittleness of PS. It is usually thought that these poor mechanical properties are at least in part due to poor interfacial properties. Brown, Creton, Kramer and co-workers have shown that addition of a diblock copolymer to an amorphous interface can lead to a large increase in interfacial strength (4). Shull and Kramer have modelled the behaviour of such copolymers at interfaces (5) and Russell and co-workers have investigated their behaviour experimentally using NR (6).

The melt cell described here has enabled us to measure the width of a PS/PE interface in the melt (in fact at the temperature used to anneal peel test specimens) and to determine the behaviour of polystyrene-(hydrogenated polybutadiene) diblock copolymers (PS-b-hPB) when added to this interface.

PP and PE are two of the largest volume commodity plastics in the developed world and hence make up a large proportion of consumer plastic waste. Due to their similar densities they are difficult to separate from one another which means that any attempt to recycle plastic waste will inevitably lead to blends of PP and PE being produced in large quantities. This has led to much research being carried out on these blends (7). As with the PS/PE blends, an understanding of the interfacial behaviour is believed to be the key to understanding the properties of these blends and the melt cell has enabled us to measure this at several temperatures.

EXPERIMENTAL

Polymer Characteristics

The molecular characteristics of the polymers used in these investigations are shown in tables 1 and 2.

Table 1 Homopolymers used

	M_w	polydispersity	supplied by
PS	278300	2.7	DSM Research
dPS	190000	1.1	R.W. Richards, Durham University
PE	≈43700	5.6	DSM Research
dPP	273600	5.5	Cambridge Isotope Laboratories
HDPE1	350000	10.0	BP Chemicals
HDPE2	156000	8.2	BP Chemicals
HDPE3	75000	1.9	BP Chemicals

Table 2 Copolymers used (all supplied by DSM Research)

copolymer	PS block		overall	
code	M_w	polydispersity	M_w	polydispersity
10d8hPB	9,900	1.0	≈26,000	≈1.1
96d8hPB	96,000	1.1	≈250,000	≈1.2

Neutron reflectivity

NR enables the determination of the composition profile of a sample normal to its surface. It can provide detailed information about layer thicknesses, density and interfacial profiles of the sample. Typically, NR has a resolution of 0.2 nm at 100 nm depth (8).

The basis of an NR experiment is to measure the specular reflection as a function of the wave vector transfer, Q, perpendicular to the reflecting surface. The measurements presented were performed on the CRISP and SURF reflectometers at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. These instruments and the technique have been described in detail elsewhere (9).

The reflectivity data obtained from a NR experiment cannot be directly transformed into a scattering length density, $\rho_z(d)$ profile (from which the composition profile can be deduced). Instead NR data are usually analysed by proposing models for $\rho_z(d)$ and using these to calculate a reflectivity profile which can then be compared to the experimental profile. By varying the parameters of the model the differences between the experimental and calculated reflectivity profiles can be minimised. To achieve this we have used a combination of maximum entropy fitting (10) and model fitting using matrix formalism methods (11).

The melt cell

The cell has been described in a previous publication (12). Briefly, it consists of a brass trough that holds one polymer, against which a silicon block, which has been spin coated with a second polymer, is placed and held in position with a metal retaining plate (see figure 1). During the NR experiments the neutron beam passes through the silicon block with a transmissivity of the order 90%. The whole cell is housed within an inert atmosphere box with neutron transparent quartz windows front and back in order to minimise degradation of the polymers at the elevated temperatures used in the experiments.

RESULTS AND DISCUSSION

PS/PE interface and the effect of diblock copolymer addition

The experimental reflectivity profile (symbols) and the calculated reflectivity profile (line) (corresponding to the inset scattering length density profile) for a dPS/PE interface at 150 °C are shown in figure 2. From this an interfacial roughness for the dPS/PE interface of (1.18 ± 0.33) nm was obtained (12).The measured interfacial width consists of a true interfacial width, w_t, convoluted with a width, w_0. The latter has been variously described by a number of authors as a capillary wave interfacial width (13, 14) or an initial width (15, 16). From the true interfacial width the Flory-Huggins-Stavermann interaction parameter, χ, can be calculated (15, 17). Depending on the definition of w_0 used we have shown that values of χ calculated from the measured interfacial width can vary by almost an order of magnitude (12). If the problem of the definition of w_0 can be overcome, this NR method of determining χ would have great advantages over other techniques such as calorimetry (18), solubility parameter determination (19) etc., since it is applicable to all polymer systems and is equally adaptable to crystalline and amorphous systems.

Figures 3 and 4 illustrate the experimental reflectivity profiles and the corresponding fits for dPS-b-hPB diblock copolymer modified hPS/PE interfaces. The copolymer was introduced between the PS and PE homopolymers by spin coating a thin layer of copolymer (approximately 15nm thick) onto the PE prior to the PS coated silicon block being placed on it. This was possible as warm toluene is a solvent for the copolymer but not for the PE. The copolymer layer thickness used is such that the interface is not expected to be saturated with copolymer.

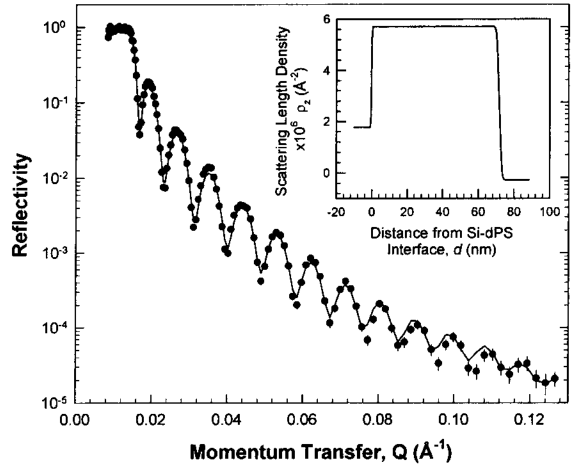

Figure 2: Neutron reflectivity profile obtained from a dPS-PE system in the melt cell at 150 °C. The data are overplotted by the fit to the data using the scattering length density profile shown in the inset.

From the data (symbols) and fits (lines) shown in figures 3 and 4 we can show that the 10d8hPB modified interface has a roughness of approximately 3.2 nm whilst the 96d8hPB modified interface roughness is approximately 7.7 nm. Furthermore, the dPS block of the 10d8hPB does not mix significantly with the PS homopolymer, whilst that of 96d8hPB penetrates the homopolymer and exhibits an average length approximately equal to that expected if it has random conformation. This rather modest increase in interfacial roughness with copolymer addition agrees well with the results of Russell and co-workers for a PS-b-PMMA (polymethylmethacrylate) modified PS/PMMA interface (6). The difference in penetration behaviour with block molecular weight can be related to the effects of homopolymer molecular weight on morphology when a homopolymer is added to a segregated copolymer. It has been reported that there are three ways in which a homopolymer A can be accommodated in the microstructure of microphase separated A-B copolymer (20). It is found that the ratio of the molecular weight of the homopolymer to that of the corresponding block molecular weight (=r) determines which of these occur. If $r>>1$, homopolymer A is found not to mix with the blocks of the copolymer. If $r<<1$, homopolymer A is found to mix uniformly with the A block of the copolymer. If $r\approx1$, homopolymer A enters the A domain of the copolymer but only partially mixes with the A block of the copolymer. For the dPS block of copolymer 10d8hPB r≈28 whilst for copolymer 96d8hPB r≈3. Therefore, as observed the dPS "brush" formed by copolymer 10d8hPB is expected to be "dry", i.e. not to mix significantly with the homopolymer. The dPS block of copolymer 96d8hPB mixes better with the homopolymer than predicted by considering the value of r, and the expected behaviour when homopolymer is added to segregated copolymer. This can be explained by considering that copolymer confined by the immiscibilty of the non-corresponding blocks with the homopolymers to the interface between the homopolymers, will have a different entropy than a copolymer in the bulk which can rearrange to counteract addition of homopolymer.

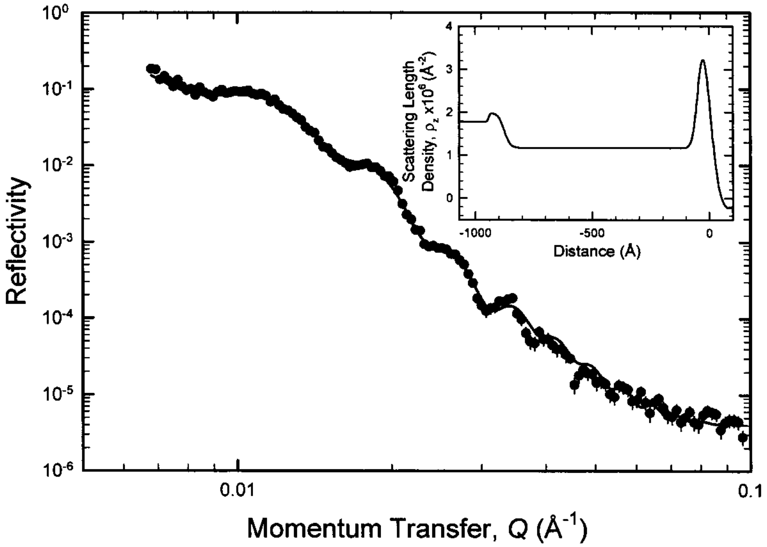

Figure 3: Neutron reflectivity profile obtained at 150 °C from a PS-PE system modified by a low molecular weight partially deuterated copolymer 10d8hPB. The fit to the data (solid line) is obtained using the scattering length density profile shown in the inset.

This work, the effect of changing the copolymer layer thickness and the effect of copolymer addition on interfacial strength, will be described in more detail in another paper (21).

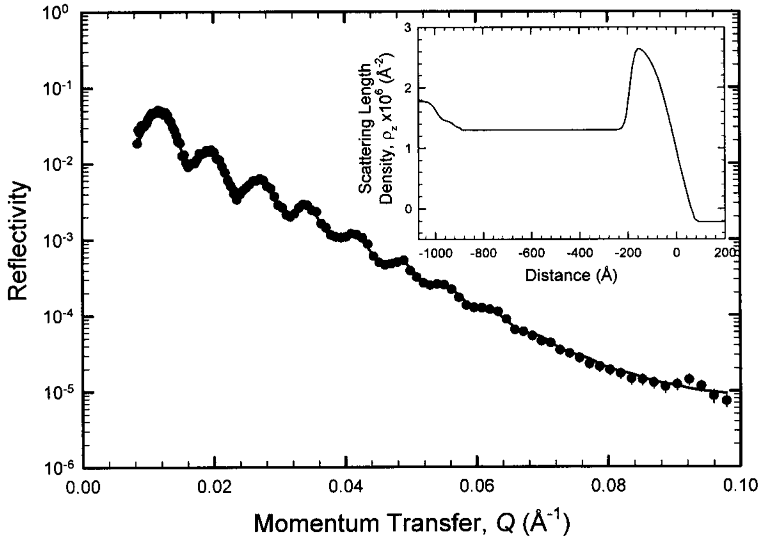

Figure 4: Neutron reflectivity profile obtained at 150 °C from a PS-PE system modified by a high molecular weight partially deuterated copolymer 96d8hPB. The fit to the data (solid line) is obtained using the scattering length density profile shown in the inset.

iPP/HDPE interface

The effect of using three different molar masses of HDPE and four temperatures (150, 175, 200 and 225°C) on the PP/HDPE interface were investigated. Interpretation of the data obtained was made difficult by poor adhesion of the PP to the silicon. It was found that this could be improved by treating the silicon blocks with buffered hydrofluoric acid prior to spin coating.

A typical set of data and a corresponding fit are illustrated in figure 5. At room temperature PP and HDPE are immiscible. However, preliminary fits to the data suggest that the interfacial roughness between the polymers is of the order (12.0 ± 0.5) nm in the melt at 175 °C, with only an estimated 5% increase at 225 °C. At 175 °C the interfacial roughness obtained from fits to the reflectivity data is equivalent to a total interfacial width of (30.0 ± 1.2) nm calculated by applying the formula $w = \sqrt{2\pi}.\sigma$ (where w is the interfacial width and σ is the interfacial roughness).

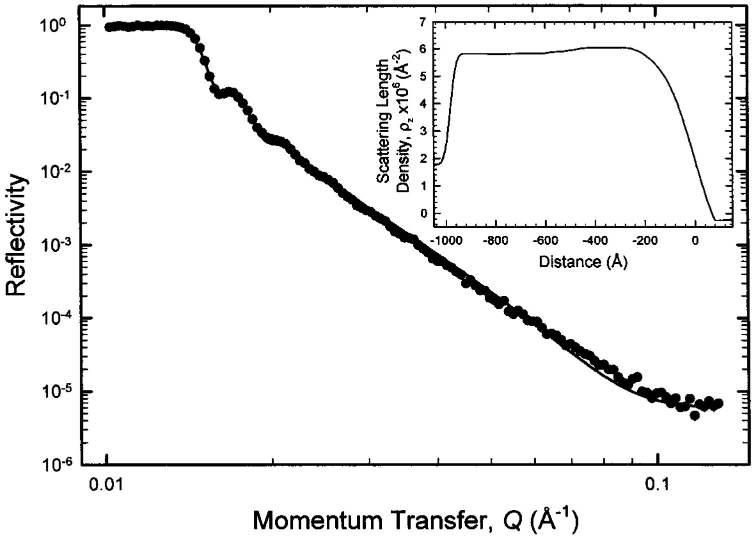

Figure 5: Reflectivity profile obtained from the dPP-PE system at 175 °C with the fit to the data (solid line) obtained using the scattering length density profile shown in the inset.

An interfacial width of this magnitude was maintained for a number of hours as data was collected at a variety of temperatures. This suggests that the two polymers are in equilibrium and hence partially miscible. Allowing for effects of interfacial broadening on the interface from capillary waves, it is possible to extract the Flory-Huggins interaction parameter, χ, from the interfacial width. There is still some discrepancy in the literature about the method of extracting χ (12) but Semenov (22) and more recently Sferrazza *et al* (23) have published convincing theories. The latter is more applicable to the current system due to the similarity of the sample geometries. The interfacial broadening due to capillary waves is dependent on the interfacial tension and logarithmically on the dispersion energy length, which derives from the presence of finite thickness of one of the polymer films. For an interfacial width of (30.0 ± 1.2) nm the χ value obtained by solving the equations numerically is $(3.5 \pm 0.3) \times 10^{-3}$. Balsara and Jeon (24) have performed SANS measurements on PP-PE blends and obtained a χ value at 167 °C of 6.4×10^{-3}. Considering the assumptions made in obtaining both values of χ these values are reassuringly close. Using Sferrazza's theory a $\chi = 6.4 \times 10^{-3}$ corresponds to an interfacial width of 9.0 nm. Both these interfacial widths are in contrast to the theoretical interfacial width obtained by Dudowicz and Freed (25,26) who used lattice cluster theory to calculate phase behaviour of a variety of polyolefin blends. They calculate that the interfacial width for low molecular mass PP and PE at RT is 2 nm. However, they predict that at elevated temperatures at which the NR experiments were conducted these polyolefins would be miscible as indicated by the current measurements. It should also be noted that the tacticity of the PP and the amount of side-chain branching of PE alter significantly the interfacial width (27) and this is being investigated further. In addition, these investigations will be extended to incorporate the study of the interaction of a diblock copolymer of atactic PP and PE with both PP and PE and the effect of this copolymer on the interface between these homopolymers.

SUMMARY AND CONCLUSIONS

The data presented have illustrated that the melt cell described can be used to obtain information on the interfacial structure of polymers in the melt. This has made the investigation of semicrystalline polymers using NR possible for the first time. Since a wide range of technologically important polymers are semicrystalline this technique may be expected to provide valuable information about the polymers in the melt that is not obtainable by any other techniques.

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REFERENCES

1 See for example, D.G. Bucknall & J.S.Higgins in *Recent Research Developments in Polymer Science*, Ed. H Hommel, 1997

2 J.S. Higgins, L. Oiarzabal, *ISIS Annual Report*, RB4116, A156 (1993)

3 See for example, W.Barentsen, D. Heikens, *Polymer*, **14**, 579 (1973), S.D. Sjoerdsma, M.E.J. Dekkers, D. Heikens, *J. Mat. Sci.*, **17**, 2605 (1982), R. Fayt, R. Jerome, Ph. Teyssie, *J. Poly. Sci.: Part B: Poly. Phys.*, **27**, 775 (1989), T. Li, V.A. Topolkaraev, A. Hiltner, E. Baer, X.Z. Ji, R.P. Quirk, *J. Poly. Sci.: Part B: Poly. Phys.*, **33**, 667 (1995)

4 See for example, C.Creton, E.J. Kramer, C.-Y. Hui, H.R. Brown, *Macromolecules*, **25**, 3075 (1992), C.Creton, H.R. Brown, V.R. Deline, *Macromolecules*, **27**, 1774 (1994), C.Creton, H.R. Brown, K.R. Shull, *Macromolecules*, **27**, 3174 (1994), J. Washiyama, E.J. Kramer, C.F. Creton, C.-Y. Hui, *Macromolecules*, **27**, 2019 (1994)

5 K.R. Shull, E.J. Kramer, *Macromolecules*, **23**, 4769 (1990)

6 See for example, T.P. Russell, A. Menelle, W.A. Hamilton, G.S. Smith, S.K. Satija, C.F. Majkrzak, *Macromolecules*, **24**, 5721 (1991)

7 J.W. Teh, A. Rudin, J.C. Keung, *Advances in Poly. Tech.*, **13**(1), 1 (1994)

8 M. Stamm, *Adv. in Poly. Sci.*, **100**, 357 (1992)

9 J. Penfold, *Physica* B, 173, 1 (1991) and T.P. Russell, *Mater. Sci. Reports*, **5**, 171 (1990)

10 M. Geoghegan, R.A.L. Jones, D.S. Sivia, J.Penfold & A.S. Clough, *Phys. Rev. E*, **53**, 825, (1996)

11 O.S. Heavens, *Optical Properties of Thin Films*, Butterworth, London 1955

12 H.E. Hermes, J.S. Higgins & D.G. Bucknall, *Polymer*, **38 (4)**, 985 (1997)

13 K.R. Shull, A.M. Mayes, T.P. Russell, *Macromolecules*, **26**, 3929 (1993)

14 M. Muller, K. Binder, W. Oed, *J. Chem. Soc. Faraday Trans*, **91**, 2369 (1995)

15 D. W. Schubert, V. Abetz, M. Stamm, T. Hack, W. Siol, *Macromolecules*, **28**, 2519 (1995)

16 K. Kunz, M. Stamm, *Macromolecules*, **29**, 2548 (1996)

17 M. Stamm, D.W. Schubert, *Ann. Rev. Mat. Sci.*, **25**, 325 (1995)

18 N.E. Clough, I. Hopkinson, R.W. Richards, T. Ibrahim, S.M. King, *Polymer*, **36**,

4245 (1995)

19 *Introduction to Physical Polymer Science*, L.H. Sperling, John Wiley & SOns, New York, 2nd Edition (1992), pg 74 and *Properties of Polymers*, D.W. van Krevelen, Elsevier Science Publications, Amsterdam, 3rd Edition (1990), pg 201

20 H. Tanaka, H. Hasegawa, T. Hashimoto, *Macromolecules*, **24**, 240 (1991)

21 H.E. Hermes, D.G. Bucknall, J.S. Higgins & RL Scherrenberg, *submitted to Polymer*, 1997

22 Semenov, *Macromolecules*, **26** (1993) 6617

23 M Sferrazza, C Xiao, RAL Jones, DG Bucknall, JRP Webster & J Penfold, *Phys Rev Lett*, accepted (1997)

24 See note 24 in H.S. Jeon, J.H.Lee, N.P. Balsara, B. Majumdar, L.J. Fetters and A. Faldi, *Macromolcules*, **30**, 973 (1997)

25 K.F. Freed, J. Dudowicz, *Macromolecules*, **29**, 625 (1996)

26 J. Dudowicz, K.F. Freed, *Macromolecules*, **29**, 8960 (1996)

27 DG Bucknall, SA Butler & JS Higgins, *unpublished results* (1997)