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Neutron reflectometry investigation of polymer–polymer reactions at the interface between immiscible polymers

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Abstract

Primary amine end functionalised deuteropolystyrene has been mixed with unmodified hydrogenous polystyrene and a thin film placed on top of a film of an acrylic polymer that either has carboxylic acid groups located at one end of each molecule or as substituents on each repeat unit. After holding at 453 K for defined times, the interfacial excess layer at the interface between the two polymers has been quantitatively analysed using neutron reflectometry and the extent of grafting of the deuteropolymer at the interface determined. Whilst maintaining the concentration of carboxylic acid units constant (fixed reacting groups) the extent of grafting increases with concentration of the functionalised deuteropolystyrene in the polystyrene layer. On changing the molecular weight of the functionalised deuteropolystyrene but maintaining the molar concentration of reactive end groups constant, the extent of grafting is larger for the lower molecular weight polymer. Although, the qualitative variation of the extent of grafting with time is in agreement with theories for interfacial grafting, exact correspondence cannot be obtained. The initial rate of grafting corresponds to second order rate constants of $\sim 0.1-0.2\ \mathrm{l\ mol^{-1}\ s^{-1}}$ but saturation of grafting is evident at far lower values (and hence earlier in the reaction process) than predicted by theory. Moreover, this saturation extent of grafting is at a level much lower than anticipated if brush-like layer formation is encouraged by interfacial grafting.

Keywords: Interfacial reactions; Immiscible polymers; Kinetics; Neutron reflectometry

1. Introduction

Interfaces in immiscible polymer blends are the locus of mechanical failure and the improvement in properties anticipated on dispersing one polymer in another often may not result in the dispersion. Improving the mechanical properties by adding a block copolymer of the two polymers has long been known and the increase in mechanical strength at such interfaces has been experimentally demonstrated [1]. However, the block copolymer is another component that needs to be dispersed in the mixture and may itself form micelles [2,3] and thus become effectively inactive with regards to the primary reason for their addition. Although the use of random copolymers [4–9] may overcome this micellisation problem and strengthen the interface such copolymers may not locate at the interface in sufficient quantity due to thermodynamic influences on the diffusion coefficient.

A more attractive method of strengthening the interface between immiscible polymers is by reactive processing [10–12] where each phase contains a percentage of polymer molecules with reactive functionalities that will combine with each other. Consequently, due to the intrinsic immiscibility of the two polymers reaction can only take place at the interface leading to copolymer formation and subsequent strengthening of the interface. Ultimately, if this grafting reaction at the interface goes to a sufficiently high extent, the interfacial tension may be reduced to such a degree that the interface becomes unstable, roughens and ‘droplets’ escape into the surrounding phase [13]. This latter effect may be desirable, a dispersion of small particles

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leading to improved mechanical properties. An assessment of the probability for the success of this approach requires an understanding of the intrinsic kinetics of the grafting reaction. Some questions that arise include; to what extent may the rate of grafting be diffusion controlled and at what stage does diffusion control become evident; what role does the concentration and molecular weight of reactive polymer play in defining the grafting kinetics? Does saturation (i.e. prevention of further interfacial reaction) intervene to control the kinetics at some point? There have been a number of theoretical studies of interfacial grafting of varying degrees of complexity [14–20] and we provide a précis of those that are relevant in the succeeding section.

Experimental investigations that conform to a greater or lesser extent to the conditions used by theoretical approaches are rare. Although, conforming closely to actual conditions used in reactive processing, those experimental investigations [10] where mixing was used are not suitable to observe the fundamental kinetics because the interface is continually renewed. Comparison of the extent or degree of grafting, Σ (chains per unit area), with the predictions of theory requires that the interfacial region be well defined and of unchanging area. A priori we anticipate the grafted layer thickness in either polymer phase to have dimensions of circa the radius of gyration of the block early in the reaction but as saturation is approached this layer thickness may increase markedly approximating to a polymer brush layer. Consequently, the experimental techniques employed need to be able to distinguish an excess polymer layer at the interface over length scales of ~50–500 Å depending on molecular weight and extent of grafting. One technique that covers this range admirably and with a resolution of circa 20 Å is neutron reflectometry [21,22], a disadvantage is that deuterated polymers are required. We report here the application of neutron reflectometry to investigate the reaction between end functionalised polystyrene and polymethyl methacrylate at the interface between thin films of the two polymers. Aspects investigated include concentration of reactive ends and molecular weight of polymer.

2. Theory

Tethering of polymer chains by the reaction of a functional end with a fixed reactive site constitutes a grafting of the functional ended polymer to the surface bearing the reactive site [23–28]. The progress of the reaction can be followed by the increase in grafting density (number of molecules per unit area), Σ, with time and as Σ increases an interfacial excess of the reacting polymer is formed, the relation between interfacial excess, z^*, and grafting density being given by

$$z^* = N\Sigma/\rho_0 \quad (1)$$

where N is the degree of polymerisation of the reacting polymer that has a segment number density of ρ_0. There are currently three major theoretical descriptions of the kinetics of reactions at the interface between immiscible end functionalised polymers leading to grafting of the interface and formation of a block copolymer [15,29,30]. The situation is shown schematically in Fig. 1, with interfacial grafting leading to the formation of a brush-like polymer layer when Σ exceeds a critical value.

Kramer [16] presents a model for the case where there are an infinite number of reactive sites fixed at the interface with a second polymer that has a finite concentration of end-functionalised polymer. Some of this polymer is presumed

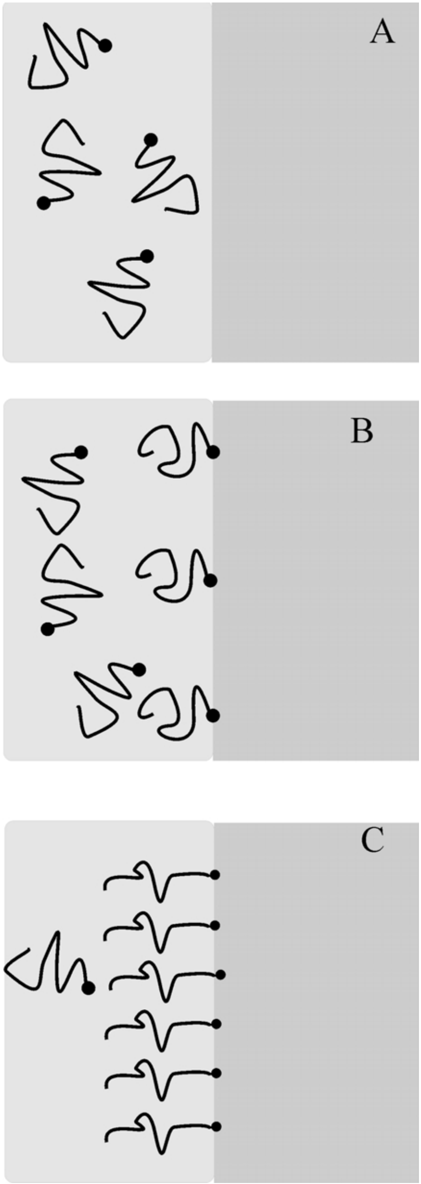

Fig. 1. Schematic illustration of the formation of excess layer due to interfacial reaction between immiscible polymers containing a low concentration of end functionalised molecules at an interface with fixed reactive groups. (A) As formed bilayer, (B) early stages of reaction with isolated grafted chains in mushroom conformation, (C) later stages where grafting density has increased to the extent that a brush like layer is formed.

to have reacted and a brush like layer is already in existence. Unreacted chains have to penetrate this brush-like layer to allow the functional end to approach within a critical distance of the interface (~statistical step length a), so that reaction can take place. The penetrating chain suffers the same entropy penalties as the already reacted chains, i.e. configurational restrictions due to stretching and the necessity to overcome the free energy barrier of the brush layer. Two possibilities are identified; firstly the increase in grafting density is subject to diffusion control over the free energy barrier, secondly control is exercised by the intrinsic second order reaction kinetics of the reaction between the functional end and the reactive sites. Regardless of whether diffusion or reaction control prevails, both use the same integral equation relating Σ to reaction time, i.e.

$$\int_0^{\xi} \mathrm{d}\xi \exp\left(\frac{\mu^*(\xi)}{k_\mathrm{B}T}\right) = t/\tau_\mathrm{c} \tag{2}$$

where ξ is a normalised surface excess given by $\xi = z^*/R_\mathrm{g} = N\Sigma/\rho_0 R_\mathrm{g}$. The free energy of the brush like layer at this surface excess is given by, $\mu^*(\xi)/k_\mathrm{B}T$ and τ_c is a characteristic time the form of which depends on whether diffusion or reaction control prevails;

- diffusion control $\tau_\mathrm{c} = R_\mathrm{g}a/D$ with R_g the radius of gyration of the polymer that has a diffusion coefficient, D.
- reaction control $\tau_\mathrm{c} = R_\mathrm{g}/(ak[\mathrm{R}])$ with k the second order rate constant and [R] the concentration of reactive groups fixed at the interface.

Eq. (2) can be used to obtain Σ as a function of t in the following manner. Firstly, the integral in Eq. (2) is solved numerically for selected values of ξ using values of $\mu^*(\xi)/k_\mathrm{B}T$ tabulated by Shull [31], or in the case of high values of Σ an approximation also given by Shull. Having obtained values of the integral as a function of ξ, these are converted to values of t via Eq. (2) (knowing τ_c). The values of ξ are converted to Σ and thus the dependence on t obtained. This model was later extended to account for a finite concentration of reactive sites that are consumed during reaction [29]. Only reaction control was considered in this latter model and for this case the kinetics of grafting has two behaviour regimes governed by a critical value of the normalised surface excess, ξ_c, defined as the surface excess of tethered chains in the unperturbed state (i.e. having the 'mushroom' configuration at the interface) normalised by their bulk radius of gyration. In the absence of any reverse reactions (explicitly included in the original thesis [29]), and for $\xi < \xi_\mathrm{c}$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = k\phi_0[\mathrm{B}]\left(1 - \frac{R_\mathrm{g}\xi}{d_0 h}\right) \times\left(\frac{\delta}{R_\mathrm{g}}\right)^{2.1}\left(1 - \frac{\xi}{\xi_\mathrm{c}} + \frac{\xi}{\xi_\mathrm{c}}\exp\left(\frac{-u^*(\xi_\mathrm{c})}{k_\mathrm{B}T}\right)\right) \tag{3}$$

for $\xi > \xi_\mathrm{c}$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = k\phi_0[\mathrm{B}]\left(1 - \frac{R_\mathrm{g}\xi}{\phi_0 h}\right)\left(\frac{\delta}{R_\mathrm{g}}\right)^{2.1} \exp\left(\frac{-u^*(\xi)}{k_\mathrm{B}T}\right) \tag{4}$$

where ϕ_0 is the volume fraction of end functionalised chains in the polymer mixture, [B] the concentration of reactive sites at the interface, h is the thickness of the polymer film containing the end-functionalised polymer and δ the thickness of the diffuse interface between the two polymers that is given by the Helfand and Tagami equation [32].

An exhaustive treatment of the kinetics of interfacial grafting has been provided by O'Shaugnessy and collaborators [17–20] in a series of papers. The expression for the kinetics of interfacial grafting is basically a second order reaction kinetics model;

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}t} = kn_\mathrm{B}n_\mathrm{A}$$

where n_i is the number density of reactive end functionalised polymer i. The end functionalised polymers are dispersed in polymer A or B that is identical with respect to molecular weight but without the reactive ends, the relaxation properties of functionalised and unfunctionalised polymers are thus identical. The influencing factors are contained within the expressions derived for the rate constant, k. In deriving the expressions the molecular weights, frictional and relaxational properties of both polymers (functionalised and non-functionalised) are assumed to be identical. The rate constant expressions incorporate such aspects as local reactivity of the functional groups, their residence time in the interfacial region and the probability of two functional groups encountering each other. The melt dynamics of the polymers have a significant influence on the observed time dependence of Σ and the statistical step length defines a critical local reactivity, other factors incorporated are the time taken to diffuse a statistical step length (τ_a) and the ratio of the degree of polymerisation to the entanglement value. Thus if the local reactivity Q is less than the critical value Q_c (mean field situation) then

$$k = Qa^3\xi \tag{5}$$

if $Q > Q_\mathrm{c}$ diffusion control is evident and

$$k = a^4/(\tau_\mathrm{b}(N/N_\mathrm{e})\ln(N/N_\mathrm{e})) \tag{6}$$

where N_e is the entanglement degree of polymerisation of the polymer.

However, like the extended Kramer model, these equations only pertain to low values of Σ. For high values we have

$$k = \frac{Qa^3\delta(Na^4\Sigma^2)\exp(-9Na^4\Sigma^2)}{1 + Q\tau_\mathrm{a}(\delta/a)\ln(1/(\Sigma_\mathrm{a}\delta))} \tag{7}$$

The model developed by O'Shaugnessy accounts for different concentrations of end groups in the two layers but assumes that the relaxational properties at all time scales are equal for each polymer. For polymers above the entanglement molecular weight (a situation that prevails here), the model can be summarised. In the early stages of the reaction mean field conditions apply, the reaction kinetics are second order and $\Sigma(t) \propto t$. If the functional groups are sufficiently reactive, a depletion region may form and the time dependence of Σ now depends on the spatial extent of this depletion zone relative to the distance explored by the chain in the various dynamic modes inherent in the tube model of polymer dynamics. Predicted dependences of Σ on reaction time are obtained by integrating the second order rate equation using the appropriate expression for k dependent on Q and the time regime relevant to the dynamics of entangled polymer melts. For time scales where Rouse or tube diffusion are the dominant dynamics, the time dependence of the grafting rate follows $\Sigma(t) \sim t/\ln t$. For the time regime between these two modes ('breathing modes' dominant) then $\Sigma(t) \sim t^{1/2}$. At sufficiently long times, greater than the terminal relaxation time (reptation time) of the polymer, the kinetics of grafting are controlled by the Fickian diffusion to the interface of the end-reactive polymer present at the lower concentration and $\Sigma(t) \sim t^{1/2}$. When the interface becomes grafted by block copolymer formation to such an extent that the grafted molecules are separated by distances of R_g or less, then increases in Σ becomes increasingly exponentially suppressed with the growth of Σ, i.e. the rate of grafting slows down. From a consideration of typical reactivities and interface saturation times, O'Shaugnessy and Vavylonis [20] predict that only mean field kinetics should be observed up to interface saturation i.e. diffusion control of the grafting reaction never intervenes. For low values of the grafting density k is constant over the range of ξ but for high values of Σ, a numerical integration is required using Eq. (7) as the expression for k.

The final model for the kinetics of interfacial grafting in polymer melts is due to Fredrickson and Milner [14,15] and is similar to that of O'Shaugnessy et al. except that identical concentrations of the end functionalised polymer in each phase either side of the interface are presumed. This is a condition that is not met by our experiments and hence we do not consider this model in detail. In the very early stages the growth in Σ is approximately linear with time. This causes a depletion region near the interface and the growth in Σ is controlled by the diffusion of polymer into the interfacial region and $\Sigma(t) \propto t^{1/2}$ in this region. The final region is where the brush like layer at the interface has been formed and the growth in Σ becomes very slow due to the barriers to be overcome in penetrating the brush layer.

3. Experimental

3.1. Materials

Amine end group functionalised deutero polystyrene ($DPSNH_2$) was prepared by the reaction of living polystyrene with an α-bromo-ω-aminopropane. A protected amine was prepared by adding 2.5 equiv. of trimethyl chlorosilane to a rapidly stirred mixture of 3-bromopropylamine hydrobromide (0.1 mol) in dichloromethane with 3.5 equiv. of triethylamine added. The reaction was carried out in a flask that had been thoroughly purged with dry nitrogen and an atmosphere of dry nitrogen was maintained during the overnight stirring of the reactant mixture. After this time, dichloromethane and unreacted trimethyl chlorosilane were distilled off and after adding 100 ml of hexane the mixture was filtered. The filtrate was twice washed with 100 ml portions of 5% w/w aqueous sodium bicarbonate and finally with distilled water. Rotary evaporation removed the hexane to leave the crude product in about 75% yield. This was distilled under vacuum (< 1 mm Hg) and the distillate collected over the range 307–309 K. ^1H NMR in deuterochloroform gave resonances at 0.05 ppm ($Si\text{-}CH_3$), 1.9 ppm (CH_2), 2.95 ppm ($N\text{-}CH_2$) and 3.3 ppm ($BrCH_2$), all consistent with the structure of the protected amine.

Deuteropolystyrene was prepared by anionic polymerisation of deuterostyrene in benzene solution under high vacuum using *sec*-butyl lithium as initiator. Polymerisation was carried out overnight and then dry THF was added (20% by volume) and the solution of living polymer cooled to 273 K before adding 5 equiv. of the protected amine. The now colourless solution was poured into a large excess of methanol and the precipitated polymer filtered off, washed with methanol and dried under vacuum. Deprotection of the amine end group was achieved by refluxing a THF solution of the dried polymer to which a small volume of dilute hydrochloric acid had been added. Thin layer chromatography of the resulting polymer using toluene/hexane (80:20) as the eluting solvent indicated that end functionalisation was quantitative. Three different molecular weight polymers were synthesised by this means, $DPSNH_2250$, $DPSNH_2100$, $DPSNH_250$ the numbers indicating the approximate molecular weight (in units of 10^3 g mol^{-1}).

Polymethyl methacrylate was prepared by the anionic polymerisation of methyl methacrylate in THF solution under high vacuum. The initiator was 1,1-diphenylhexyl lithium and 10 M equiv. of lithium chloride were added to control molecular weight and molecular weight polydispersity and the reaction carried out at ~195 K. On completion of polymerisation, high purity carbon dioxide was admitted to the reaction flask until atmospheric pressure was reached. The solution was left overnight with constant stirring at 195 K, thereafter the polymer was precipitated by pouring the solution into a large excess of hexane, filtered off, washed and dried in vacuum. The polymer produced had a carboxylic acid group at one end and is indicated as HPMMACOOH.

Hydrogenous polystyrene (HPS) with no functional end groups was prepared by exactly the same procedure as for the deuteropolystyrene except that the reaction was terminated by addition of methanol rather than the protected aminopropane. Polymethacrylic acid (PMAA) was purchased from Polysciences, molecular weights and polydispersities of all polymers used are given in Table 1.

3.2. Neutron reflectometry

Three series of experiments were carried out; (i) effect of concentration on the grafting reaction of $DPSNH_2250$ with PMAA; (ii) influence of concentration of $DPSNH_2250$ on the grafting kinetics for the reaction with HPMMACOOH; (iii) dependence of grafting kinetics on the molecular weight of DPS-NH_2 reacting with HPMMACOOH. For all three experimental series, the samples consisted of bilayers of the two polymers on polished silicon blocks that were 5 mm thick. The methacrylic layer was spun on to the silicon block to form a film circa 700 Å thick. For HPMMA-COOH the solvent used was toluene, water being used as the spin coating medium for PMAA. The thin films were then held at 313 K under vacuum overnight to relax any stresses due to spin coating. Upper layers of mixed HPS/$DPSNH_2$ polymers were spin coated directly on to the acrylic layer using 1,2,4-trimethyl benzene as the solvent. Ellipsometry showed that the polystyrene layer thicknesses were circa 700–800 Å, each bilayer specimen was then held at 453 K under vacuum for defined times. Separate experiments where 1,2,4-trimethyl benzene alone was spin coated on to the acrylic polymer film showed that there was no change in either thickness or surface roughness of the acrylic layer, these latter parameters being determined by X-ray reflectometry.

Neutron reflectometry data for each polymer couple were obtained using the CRISP reflectometer on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Chilton, UK. The neutron beam was collimated by slits defined by translatable sheets of cadmium, the slit height immediately before the specimen being 2 mm. By using three different grazing angles of incidence the range of momentum transfer, Q, normal to the sample surface explored was $\sim 10^{-3} \leq Q/\text{Å}^{-1} \leq 0.2$ and the resolution in Q, over all Q ranges was 4%. The lowest Q values were in the region of total reflection ($R(Q) = 1$), and all data at higher Q values was placed on an absolute scale using this region of total reflectivity as calibration. For $Q > 0.1$ Å^{-1}, the reflectivity was essentially constant at the background value mainly due to incoherent scattering from the polymer couple. Reflectivity data were analysed using Abeles modification of the optical matrix method [33] that calculates exactly the reflectivity from a model of the polymer couple and where possible roughness at the air-film and film substrate can be incorporated as Gaussian broadening. The total thickness of the bilayer was simulated by a series of layers of constant composition. In the region of the interface between the polystyrene and acrylic layers, a functional form (Eq. (8) below) was used to describe the region where an excess of deuterated polymer was formed due to reaction at the interface.

Table 1
Molecular weights and polydispersity of polymers

Polymer	M_w (10^3 g mol^{-1})	M_w/M_n
$DPSNH_2250$	230	1.02
$DPSNH_2100$	95.1	1.04
$DPSNH_250$	43.4	1.03
HPS250	228.7	1.08
HPS100	102.5	1.03
HPS50	46.0	1.03
HPMMACOOH	124	1.04
PMAA	100	~2

4. Results

The variation of the scattering length density (SLD) normal to the polymer bilayer surface was modelled as a series of stacked lamellae with the SLD of each lamellar layer being calculated from its volume fraction composition [21,22,34]. Near the interface between the two polymers, the interfacial excess layer due to grafting was approximated by a hyperbolic tangent distribution in which the volume fraction distribution of $DPSNH_2$ was described by

$$\phi(z) = \phi_{\text{bulk}} + \left(\frac{\phi_{\text{int}} - \phi_{\text{bulk}}}{2}\right)\tanh[(z + z_{\text{off}} - t_{\text{PS}})/w] \quad (8)$$

where ϕ_{bulk} is the volume fraction of DPS-NH_2 in the polystyrene top layer, ϕ_{int} the value at the interface with the acrylic layer. The shape of the distribution is controlled by z_{off} and w, the former being the thickness of the distribution at $(\phi_{\text{int}} - \phi_{\text{bulk}})/2$ and w is a measure of the overlap between the grafted layer and the bulk polystyrene layer which has a thickness, t_{PS}. A schematic of a SLD distribution for this model is shown in Fig. 2. Reflectivity profiles were calculated for this model and fitted to the experimental data by adjusting ϕ_{int}, z_{off} and w using a non-linear least squares fitting algorithm. The thickness of the upper polystyrene layer and the total thickness of the bilayer were allowed to vary to a small extent (± 10% of measured thickness) as part of the fitting process to account for any physical relaxation of the polymers at the elevated temperatures where reaction took place. The interface between the two polymers before annealing at elevated temperatures has a small intrinsic roughness of circa 1.5 nm from the bilayer preparation. Typical examples of the fits to the data are shown in Fig. 3(a) and the corresponding volume fraction distributions of $DPSNH_2$ resulting from the best fit the reflectometry data are shown in Fig. 3(b), the small variation in the bulk concentration of $DPSNH_2$ is within the error of the fitting to the reflectivity data. From the volume fraction distribution, the interfacial excess of

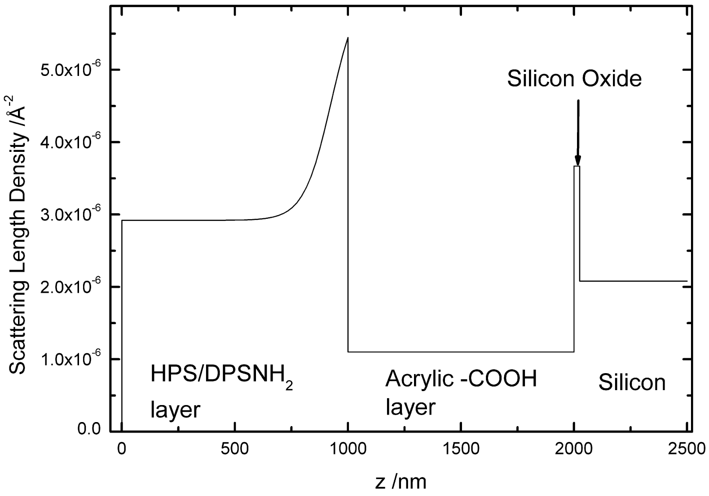

Fig. 2. Scattering length density over the polymer bilayer at a point where a finite extent of reaction is evident.

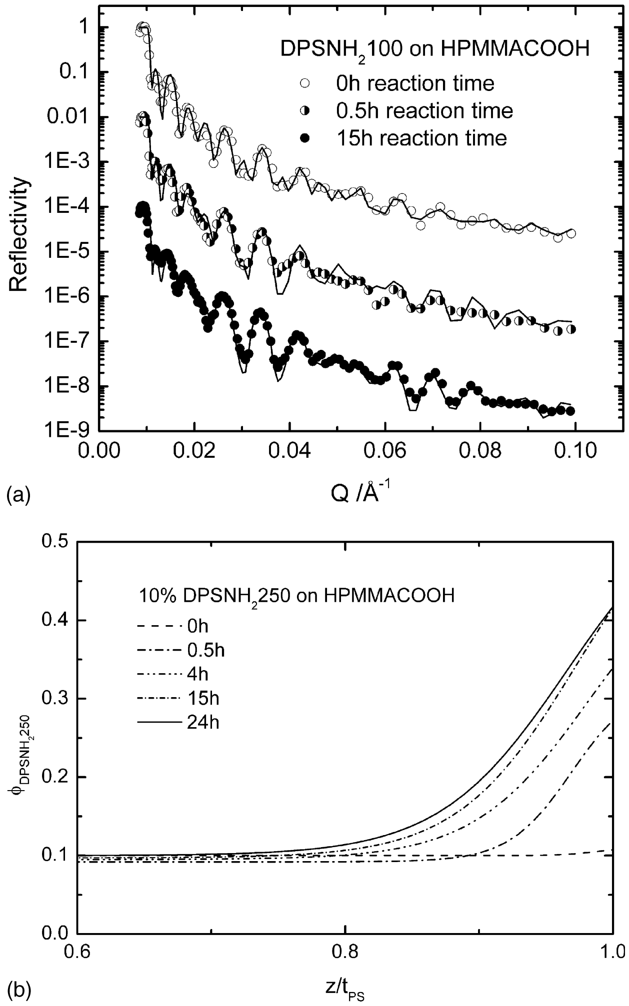

Fig. 3. (a) Typical fits (solid line) to neutron reflectivity data. For zero time the data are absolute, longer reaction times are artificially displaced by two decades to lower reflectivity to aid clarity. (b) Volume fraction distribution of $DPSNH_2$ obtained from fits to reflectivity data.

$DPSNH_2$ was obtained from

$$z^* = \int_0^\infty (\phi(z) - \phi_{\text{bulk}})\mathrm{d}z \tag{9}$$

and the ellipsometric thickness, L, of the interfacial excess layer formed by reaction was calculated from

$$L = \frac{1}{z^*}\int_0^\infty z(\phi(z) - \phi_{\text{bulk}})\mathrm{d}z \tag{10}$$

4.1. $DPSNH_2$—polymethacrylic acid combination

This pairing corresponds most closely to the situation for which the original Kramer model was developed, i.e. the presence of an essentially infinite number of one reactive group (–COOH) and a finite number of the second ($-NH_2$). Using the bulk density of PMAA and the known molecular weight of the polymer, the average number of –COOH groups per nm^2 at the interface with the $DPSNH_2$/HPS layer is circa 3.5. Using an average upper layer thickness of 100 nm and considering the range of the $DPSNH_2$ concentrations in the upper layer, the number of amine ends available ranges from circa 5×10^{-2} to 10×10^{-2} nm^{-2}, far smaller than the number of –COOH groups. Grafting densities obtained from the variation of z^* with time are shown in Fig. 4(a) for all three concentrations of $DPSNH_2250$ used. For each of these the data are rather similar, a rapid increase in Σ to values of circa 2×10^{-2}–2.5×10^{-2} nm^{-2}, thereafter Σ remains constant at these values. The layer thickness (Fig. 4(b)) qualitatively shows the same behaviour but with a larger variation in the actual values, although an asymptotic interfacial excess layer thickness of ~13 nm at long reaction times seems to be approached for the 10 and 30% $DPSNH_2$ systems.

4.2. $DPSNH_2$–HPMMACOOH combination

4.2.1. Concentration dependence

For the molecular weight of HPMMACOOH employed,

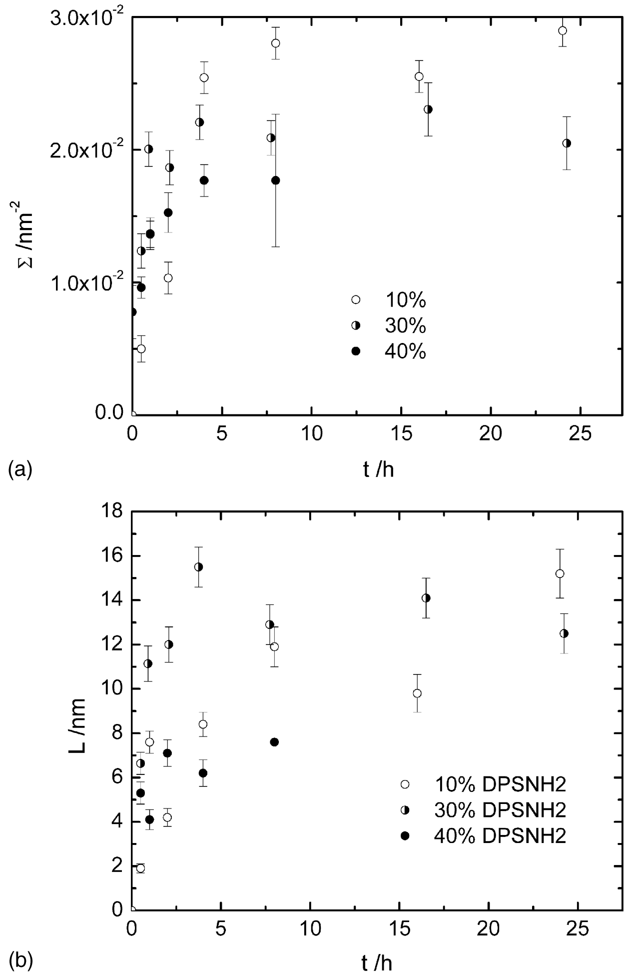

Fig. 4. (a) Grafting density of DPSNH$_2$250 at the interface with PMAA as a function of reaction time. (b) DPSNH$_2$250 layer thickness changes as a function of the reaction time at the HPMAA interface.

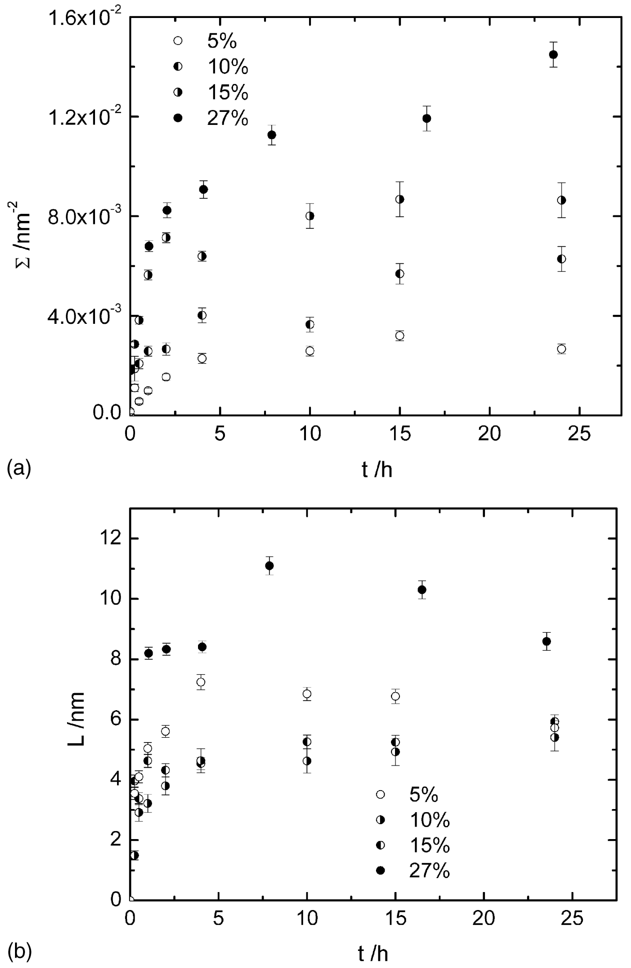

Fig. 5. (a) Grafting density as a function of reaction time for DPSNH$_2$250 at the interface with HPMMACOOH. (b) DPSNH$_2$250 layer thickness dependence with reaction time at the HPMMACOOH interface.

the average number of end carboxyl groups available at the interface is $\sim 2.8 \times 10^{-2}$ nm^{-2}, assuming that all the carboxyl groups are available for reaction, i.e. they have the correct orientation and proximity to the interface. A 10% concentration of DPSNH$_2$250 in the upper layer has an approximately equal number of NH$_2$ end groups available in the total thickness of the polystyrene upper layer. The actual time dependence of the grafting density obtained for the four concentrations used is shown in Fig. 5(a). For all concentrations the grafting curves are similar, a rapid increase in the early stages but after circa 7 h the rate of grafting is considerably reduced but not to zero for concentrations of DPSNH$_2$ of 10% w/w and greater. Over the reaction times investigated here, the nominal maximum value of Σ possible (= number of –COOH groups nm^{-2} calculated above) is approaching twice the actual maximum value of Σ observed experimentally even though for the 27% DPSNH$_2$ in HPS the –NH$_2$ ends far exceeds the number of –COOH groups available. Values of the layer thickness, Fig. 5(b), are much less regular in their variation with reaction time although the largest values of L observed are associated with the highest values of Σ, a possible indication of some stretching of the grafted chains. The interfacial layer thickness for the 5% DPSNH$_2$ is larger than that for the 10% concentration but the grafting density is lower. We can only attribute this anomalous result to the possibility that the –COOH groups at the interface have regions where their concentration is higher and thus the local grafting density is much higher than the average leading to a more highly stretched configuration. Additionally, reaction would be probable for such regions of high concentration. Higher concentrations of DPSNH$_2$ lead to the interface becoming more evenly covered with reacted polymer molecules.

4.2.2. *Influence of molecular weight of DPSNH$_2$*

To investigate the role of molecular weight on the interfacial grafting kinetics, DPSNH$_2$100 and DPSNH$_2$50 were mixed with HPS of equivalent degrees of polymerisation. Additionally, the concentration of each DPSNH$_2$ was adjusted so that the molar concentration of –NH$_2$ end groups was the same for all the molecular weights of the

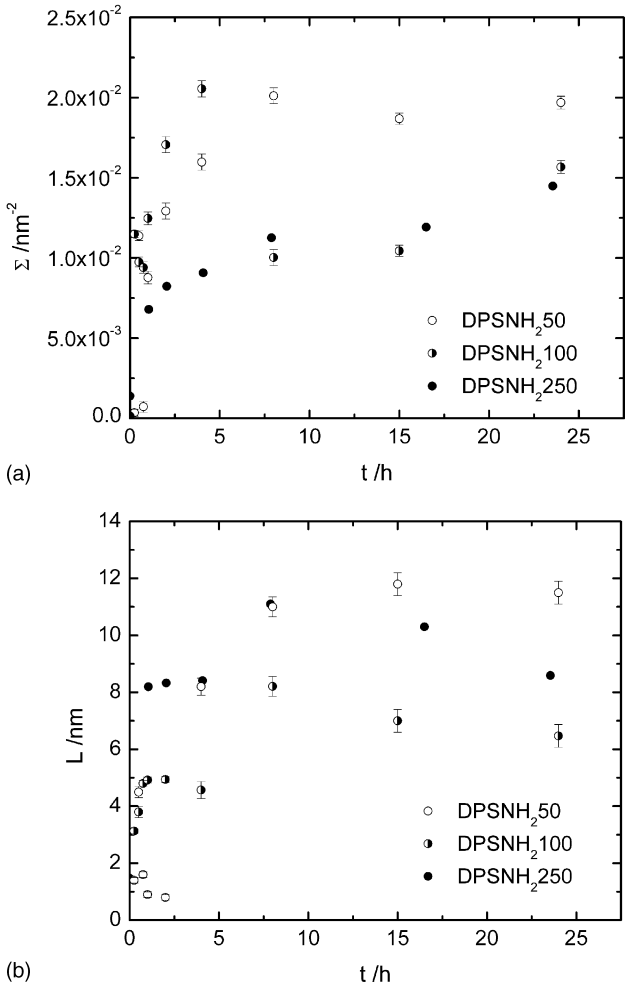

Fig. 6. Molecular weight dependence of grafting density (a) and layer thickness (b) for DPSNH$_2$ reacting with HPMMACOOH whilst the concentration of amine end groups is maintained constant.

deutero polymer used. For the lowest molecular weight DPSNH$_2$, the values of Σ are significantly larger than for the two higher molecular weights but grafting densities for DPSNH$_2$100 are of the same magnitude as those of DPSNH$_2$250, (Fig. 6(a)), however, we note the large scatter in the values of Σ at short reaction times for the DPSNH$_2$100 for which we can attribute no physical cause but may reflect insensitivity in the model used to describe the interfacial layer formed by reaction. Layer thicknesses, Fig. 6(b), are again somewhat scattered with no discernible trend in even the asymptotic layer thickness at long reaction times except that the largest layer thickness is observed for the lowest molecular weight polymer.

5. Discussion

Of the small amount of other experimental data [13,16, 29,35–38] available on the grafting kinetics at the interface between immiscible polymer melts, none conform exactly to the systems investigated here. In the earlier studies, the reactive polymers were of much lower molecular weight than those used here and were usually mixed in an unreactive host of considerably higher molecular weight. Such combinations are very different to the conditions presumed in the models for interfacial grafting described by O'Shaugnessy and Fredrickson and Milner, wherein, the intrinsic polymer melt dynamics play a significant role. Experimental data obtained for polymers with lower molecular weights than used here gave values of Σ up to an order of magnitude larger than observed by us and in one case larger by two orders of magnitude. However, in the last case the high value of z^* was attributed to a very rough interface being produced as a result of the reduction of the interfacial tension and eventual 'pinch out' of polymer from the interface. Nonetheless, all earlier experimental data shows the same dependence of Σ with time as that exhibited by all the combinations that we have investigated. At low reaction times, the rate of grafting is constant and a linear increase in Σ is noted, the rate of grafting then decreases rapidly over a short time span to a significantly smaller rate of grafting that approaches zero.

All of the theoretical models developed for interfacial grafting kinetics include many factors influencing the value and dependence of Σ on time. Some factors are common to all theories, e.g. concentration of reactive polymer, rate constant of the second order reaction, thickness of the interfacial region, where some small degree of mixing takes place in the absence of any interfacial grafting. However, individual theories incorporate additional specific factors. For example, the theory due to O'Shaugnessy includes the entanglement degree of polymerisation and the relaxation time of a monomer unit for the purpose of accurately describing the polymer melt dynamics. The value of this latter parameter has some uncertainty. The two theories that originate from Kramer require values for the chemical potential of a grafted brush-like layer at each value of Σ to define the resistance to approaching reactive polymer. In all theories, the major uncertainty is the concentration at the interface of reactive groups, both fixed i.e. groups with an essentially fixed concentration, the carboxylic acid groups here, and mobile, i.e. those groups whose concentration will be significantly influenced by reaction, the DPSNH$_2$ units for the combination discussed here. To provide quantitative comparison for the influence of the bulk concentration of reacting species a phenomenological equation can be used to provide parameters for comparison. The equation employed is [38]

$$\Sigma = A(1 - \exp(-t/\tau)) \tag{11}$$

where A and τ are characteristic of the molecular weight and concentration of DPSNH$_2$ in the upper polystyrene layer and we anticipate

$$\tau \alpha 1/k[\mathrm{COOH}] \tag{12}$$

For DPSNH$_2$250 on PMAA the value of A is essentially constant at 0.022 ± 0.005 nm^{-2} for all the concentrations of DPSNH$_2$250 considered. When the same DPSNH$_2$250 is on the HPMMACOOH film, a definite, albeit weak, increase in A is observed with increasing concentration, c, of the deuteropolymer in the upper layer given by;

$$A = 5.4 \times 10^{-4} + 4.6 \times 10^{-4} c$$

with c in wt%. These different behaviours reflect the large differences in the concentration of –COOH groups available for reaction. In the PMAA, their large excess over the available $-NH_2$ groups results in no dependence on the concentration of these latter groups. Whereas, for the HPMMACOOH the carboxyl and amine group concentrations are of the same order of magnitude and any change in either will have an influence on the observed grafting rate and hence the value of A in Eq. (11). If Eq. (12) is a valid description of the characteristic time then values of τ for DPSNH$_2$250 on HPMMACOOH should be larger than when the lower layer is HPMAA. For the latter combination the average value of τ is $0.5 \pm 0.2\ h^{-1}$ whereas, when HPMMACOOH formed the lower polymer layer the values of τ observed for the four concentrations explored is $1.9 \pm 0.3\ h^{-1}$. Hence, the anticipated increase in magnitude is observed but not in proportion to the ratio of the surface concentrations of the –COOH groups nominally available based on the earlier figures given. The molecular weight of the DPSNH$_2$ influences both A and τ but the latter is essentially independent of molecular weight within experimental error, the scaling relations obtained from the data are;

$$A = 0.25\ M^{-0.25}, \quad \tau = 2.4\ M^{-0.02}$$

Evidently, the influence of molecular weight is primarily exercised through the parameter A, with a decrease in the ultimate extent of grafting with molecular weight being observed.

A qualitative comparison of the experimental data with the predictions of the various theories can be made if values are assumed for the various parameters that each theory uses. Thus for both theories that originate from Kramer's group a value for the rate constant is needed and we have assumed a value of $0.18\ l\ mol^{-1}\ s^{-1}$, a value that Kramer reported earlier on the basis of ion beam analysis between epoxide and amine groups, other parameters such as statistical step length, diffusion coefficients, extent of diffuse interfacial layer etc, are accessible from other sources. For the extended Kramer theory, the thickness of the polystyrene layer (which defines the ultimate number of reactive molecules available) has been fixed at 100 nm and the equilibrium coefficient for the reverse reaction that is incorporated in the full theory has been set to a value of unity on the assumption of a complete absence of reverse reactions. For the O'Shaugnessy model values of the unknowns Q and τ_a are even more uncertain, the only guidance provided being that their product has a magnitude of $\sim 10^{-11}$, we have used 0.1 as the value of Q and 10^{-10} s for the value of τ_a. Fig. 7(a)–(c) shows the dependence of Σ on reaction time for each of these models where the concentration of one of the reaction polymers has been varied whilst maintaining the degree of polymerisation of both polymers constant. All models predict that the extent of grafting should be reduced as the concentration of one of the reacting polymers is reduced. Comparing these predictions with the data of Fig. 5(a) the original Kramer model seems to be the most appropriate since it suggests an early approach to the saturation extent of grafting Σ_{sat} that is observed by experiment. The O'Shaugnessy model predictions appear to be very distant from approaching a Σ_{sat} value and changing the magnitude of the model's parameters to accelerate the approach to Σ_{sat} increases the rate of grafting in the early stages to values far larger than actually observed. The extended Kramer model is evidently approaching Σ_{sat} at longer reaction times. We note that the values of Σ predicted by all three models are of the same magnitude as the experimental data, but larger by a factor of two compared to the observed values of Σ. Fig. 7(d)–(f) shows the influence of varying the degree of polymerisation but keeping the molar concentration of reactive end constant. Clear differences are apparent now between the original Kramer model which predicts that the higher molecular weight polymer should have the larger values of Σ_{sat}, moreover, the initial rate of grafting is essentially identical for all molecular weights. This does not agree with the predictions of the O'Shaugnessy or extended Kramer models where now the highest molecular weight polymer should have the lower values of Σ_{sat} and the rate of grafting at the interface is also reduced as the molecular weight of the reacting polymer increases. The experimental data of Fig. 6(a) has the smaller values of Σ_{sat} associated with the higher molecular weight DPSNH$_2$, the data at earlier reaction times is too scattered to state with confidence that the rates of grafting also reduce as molecular weight increases, however, the initial rate for the DPSNH$_2$50 does appear to be larger than that of the DPSNH$_2$250 polymer.

Since the O'Shaughnessy model shows little sign of approaching a Σ_{sat} value within the reaction times used, only the extended Kramer model has been compared to our data. Initially, it is assumed that all the –COOH groups of the HPMMACOOH were available and the influence of the second order rate constant over the range $0.1 \leq k/l\ mol^{-1}\ s^{-1} \leq 0.2$ is shown in Fig. 8 together with some of our experimental values of Σ. Although, the initial rates of grafting observed and calculated are in reasonable agreement with each other, there is no agreement in Σ_{sat}, the predicted values of Σ continuing to increase long after the experimental values have saturated. The possibility that the available –COOH groups may be far smaller is shown in Fig. 8(c) where f_B is the fraction of these groups available for reaction. Values of f_B less than one have no effect on the time at which Σ_{sat} is reached and moreover the rate of grafting and the ultimate value of Σ_{sat} clearly falls below the

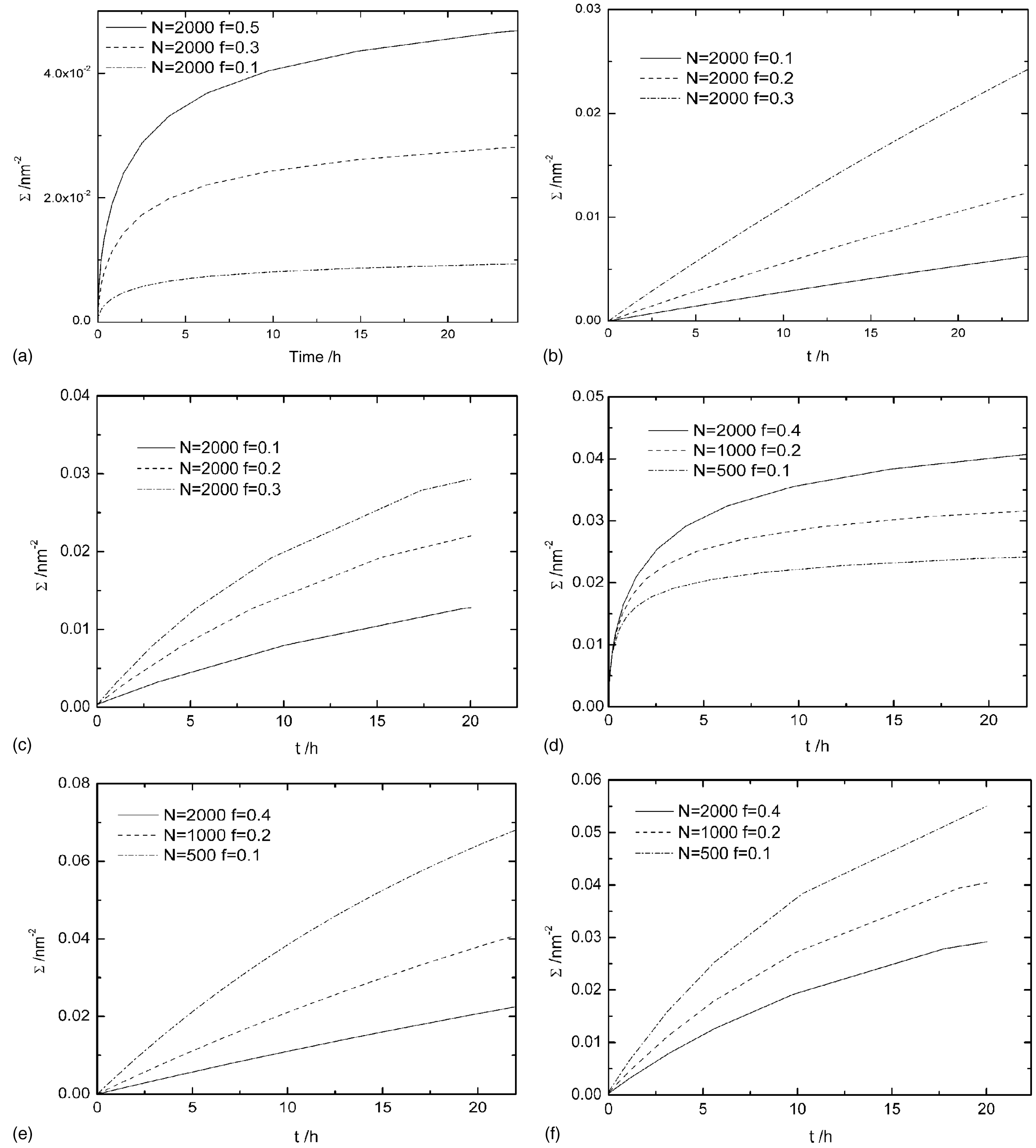

Fig. 7. Simulations of models for the kinetics of interfacial reactions between immiscible polymers, predicted influence of weight fraction (*f*) of reacting polymer for (a) original Kramer model; (b) O'Shaugnessy model; (c) extended Kramer model. Influence of degree of polymerisation of reacting polymer for (d) original Kramer model; (e) O'Shaugnessy model; (f) extended Kramer model.

experimental values and thus this cannot be the source of the observed behaviour.

The major difference between theory and experiment is the prediction of the value of Σ_{sat} and hence the time at which this value is reached. Two factors are cited as the source of the reduction in grafting rate, firstly, a depletion of unreacted chain ends in the neighbourhood of the interface and secondly saturation of the interface by grafted molecules preventing the approach of unreacted chains to within the reaction distance of the interface. The diffusion coefficient of DPSNH$_2$250 is anticipated to be little altered from that of unmodified polystyrene and a diffusion coefficient of $\sim 2.2 \times 10^{-14}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ is expected. This suggests that the time for a DPSNH$_2$ molecule to diffuse

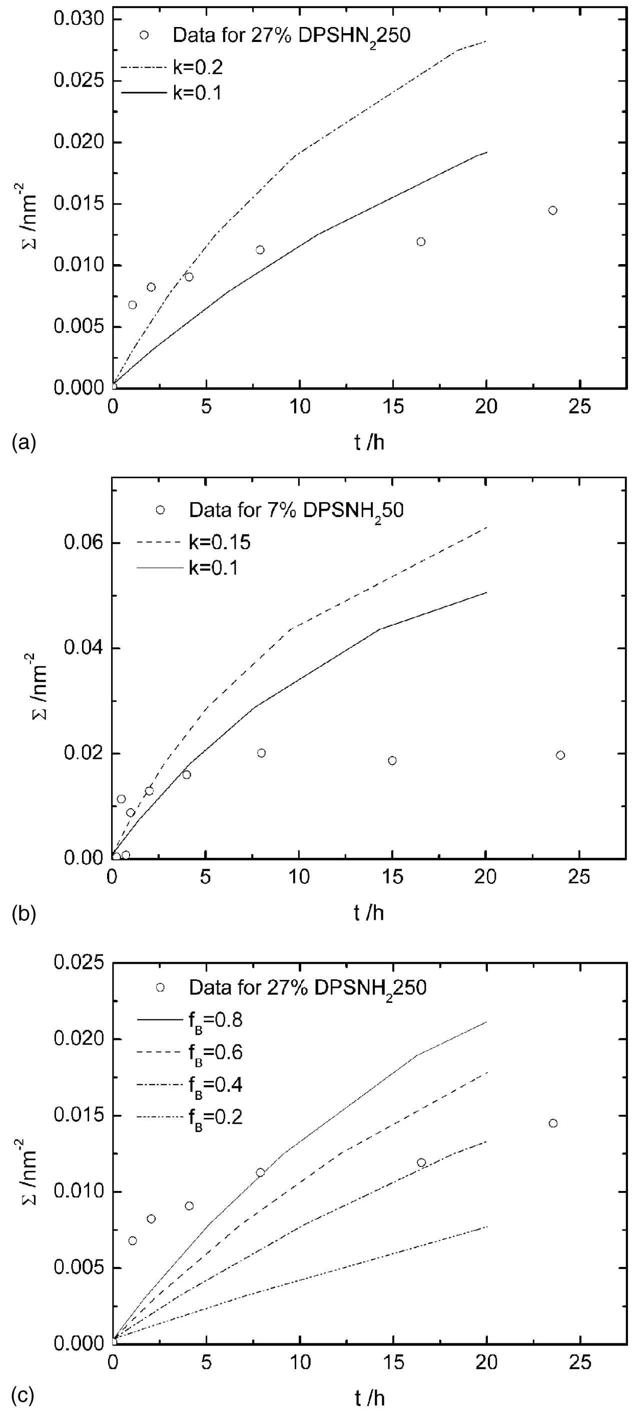

Fig. 8. Comparison of the predictions of extended Kramer theory with experimental data. Effect of varying the second order rate constant for the highest (a) and lowest (b) molecular weight DPSNH$_2$ polymers used. The role that the fraction of reactive end groups, f_B, in the acrylic layer is made evident in (c).

from one side of the 100 nm thick polystyrene layer to the interface is less than 20 min and consequently the DPSNH$_2$ chains are always in diffusion equilibrium with the interface and thus depletion of reactive polymer near the interface appears to be remote. When the interface becomes saturated, the grafted layer acquires a brush-like nature and incoming ungrafted chains have to stretch to traverse the brush layer and the entropic penalty entailed constitutes the barrier to reaction that slows the grafting reaction. Two methods of defining Σ_{sat} are quoted; firstly when the average distance between grafting points is equal to the radius of gyration of the grafting polymer, i.e. $\Sigma_{sat} = R_g^{-2}$, secondly $\Sigma_{sat} \sim (N^{1/2}a^2)^{-1}$ where a is the statistical step length of the polymer. Values of Σ_{sat} calculated by these two approaches are given in Table 2 together with the values observed experimentally for the three molecular weights of DPSNH$_2$. It is evident that the experimental values of Σ_{sat} are closer to the predictions based on Σ_{sat} being controlled by the radius of gyration possibly due to a 'masking' of reaction sites at the interface by segments of grafted polymer.

6. Conclusions

The extent of reaction at the interface between two end—functionalised immiscible polymers, polystyrene and polymethyl methacrylate, has been determined using neutron reflectometry. Aspects investigated include the concentration of 'fixed' reacting groups (–COOH), concentration of 'mobile' reacting groups (–NH$_2$) and the molecular weight of the polystyrene with a primary amine end function. The use of neutron reflectometry has provided a detailed description of the interfacial excess layer when the deuterated end functionalised polystyrene reacted with the carboxylic acid groups of the acrylic polymers, a modified hyperbolic tangent profile providing the best description of the volume fraction distribution of reacted polymer. From values of the interfacial excess calculated from these volume fraction profiles, the extent of grafting, Σ, as a function of reaction time has been calculated. All polymer combinations have a generic dependence of Σ on time, i.e. a rapid increase in Σ at short reaction times with Σ_{sat} also being reached quite early in the reaction and further increases in Σ being either very small or non-existent. When the concentration of fixed reacting groups is in large excess over that of the mobile groups, there is essentially negligible dependence of Σ on any changes in concentration of the mobile reacting groups. However, when both fixed and mobile reacting groups are present at concentration of the same, small magnitude, the values of Σ and Σ_{sat} are noticeably larger for higher concentrations of the mobile polymer when the concentration of the fixed reacting groups is held constant. Under the same circumstances of low concentrations of mobile reacting groups, changing the molecular weight of these mobile groups whilst maintaining a constant overall concentration of reactive end groups' results in the larger values of Σ being observed for the lower molecular weight polymer. This agrees with the predictions of two of the current theories that attempt a quantitative description of grafting kinetics at the interface between immiscible polymers. An exact coincidence between the

Table 2
Molecular weight dependence of calculated and experimental values of Σ_{sat} for $DPSNH_2$ reacting at the interface with HPMMACOOH

Polymer	Σ_{sat} from R_g (nm^{-2})	Σ_{sat} from $(N^{1/2}a^2)^{-1}$/nm^{-2}	Σ_{sat} observed/nm^{-2}
$DPSNH_2250$	5.7×10^{-3}	4.9×10^{-2}	1.1×10^{-2}
$DPSNH_2100$	1.4×10^{-2}	7.6×10^{-2}	1.4×10^{-2}
$DPSNH_250$	3.0×10^{-2}	11.3×10^{-2}	2×10^{-2}

most appropriate theory and experimental data is not obtained either by adjusting the second order rate constant or the effective concentration of fixed reacting groups. By varying the second order rate constant, reasonable agreement with the initial rate of grafting can be obtained but Σ_{sat} values are not reproduced. From the definitions of where the effects of Σ_{sat} should become evident it appears that the notion of brush-like layer formation being the source of the reduction in the rate of grafting is not upheld and other factors are at work in reducing the increase of Σ at long reaction times.

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