Segregation of SEBS Triblock Copolymers to the Interface between Immiscible Homopolymers

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Abstract

Segregation of poly(styrene-*b*-[ethylene-butylene]-*b*-styrene) (SEBS) triblock copolymer to the interface between immiscible homopolymers was investigated. The homopolymers used were polystyrene (PS) and low density polyethylene (LDPE). Polymer-polymer interfaces samples were prepared by spin coating thin polymer films from solution onto silicon substrates. The contrast between layers of polymer films investigated using the neutron reflectivity (NR) technique was enhanced by means of isotopic substitution. The segregation behavior of the SEBS triblock copolymer was investigated using bilayer and trilayer sample arrangements. Interpretation of the reflectivity of the samples was carried out by comparing the scattering length density profile which provides a best fit to reflectivity data, to the one estimated at 150^{o}C for the polymers used. The interpretation of these NR results indicated that the SEBS triblock copolymers segregated to the interface between PS and LDPE, where the blocks of the copolymer penetrate into the respective homopolymer phases. Miscibility between the blocks of the copolymer and the respective homopolymer layers was also observed.

Keywords: Copolymer, interfacial segregation, neutron reflectivity technique, SEBS

1. Introduction

The use of a compatibilizer, normally a block copolymer, is necessary to improve the interface when an immiscible polymer blend exhibits poor mechanical properties due to weak adhesion between the phases. Preferably, the block copolymer chosen should have not only a good emulsifying ability (reduction of the interfacial tension leading to a finer morphology) but also a good interfacial activity (penetration of the segments of a block copolymer into its respective homopolymer leading to an improvement in the adhesion between the phases). When an A-B copolymer capable of phase segregation is added to an immiscible blend of homopolymers A and B, it will try to reduce the number of unfavorable contacts between the homopolymer and the dissimilar copolymer blocks thus reducing the interaction energy. This results in localization of the copolymer at the interface between the two homopolymers. In so doing it causes a decrease in the interfacial tension between the homopolymers [1]. Note that for thermodynamic reasons the copolymer segregates from the bulk phases to the interfaces and then aggregates into layers or multilayers. This whole process is often referred to as “segregating to an interface” and this convention has been adopted when describing the process.

Over the years, the poly(styrene-*b*-[ethylene-butylene]-*b*-styrene) (SEBS) triblock copolymers have been intensively studied as compatibilizers for many immiscible polymer blends and commonly reported that the main function of the SEBS during processing lies in reducing the interfacial tension between two immiscible polymer phases resulting in a finer distribution of the minor phase of the blends studied. However, the improvement in the adhesion between the phases has not been fully achieved as expected especially for the case of relatively high molecular weight SEBS [2-6]. Therefore, well understanding the segregation of SEBS into the interface between immiscible homopolymers would help reducing this problem.

For a diblock copolymer segregating at the interface between two highly immiscible polymers, the junction points between the copolymer segments are expected to be found in a thin interfacial layer with extension of the block into the respective bulk phases creating two brushes [7-8]. Depending on the ratio of copolymer to homopolymer molecular weights, two extreme cases of wet and dry brushes could exist. However, under certain circumstances not only does interfacial segregation occur, but also segregation of the copolymer to the free surface [9-11]. Thermodynamically, two driving forces are responsible for surface segregation [12]. Firstly, the system tries to reduce the number of sharp interfaces that are present. With sharp interfaces present the number of available polymer conformations is greatly reduced, resulting in an entropic increase to the Gibbs free energy. Such sharp interfaces exist between the micellar corona and the surrounding homopolymer [8]. By placing the copolymer micelles at the free surface, the corona-homopolymer interfacial area is reduced, leading to a reduction in the overall free energy of the system. The second driving force for surface segregation arises if labeled species are used as is normally the case in NR studies. Deuterated copolymer micelles may segregate because of the enthalpic interaction between normal (hydrogenous) and deuterated molecules which mix in a non-ideal way and are influenced by the small difference in polarizability between the C-H and the C-D bonds [13]. Note that in the NR technique the deuterated polymer is normally used in order to enhance contrast between two otherwise indistinguishable species. The difference in polarizability produces an unfavorable interaction between the two species and a slightly lower surface tension for the deuterated component. The resulting tendency of the deuterated chains to segregate to the free surface is in competition with a decrease in entropic mixing. However, polymers have relatively low entropies of mixing and isotopic segregation has been observed [14-15].

The NR technique allows for determination of the composition profile of a sample normal to its surface. It provides detailed information about layer thickness, density and interfacial profile of the sample. Typically, NR has a resolution normal to the surface of 0.2 nm at 100 nm depth [16] and is capable of resolving the movement of chain segments across the interface between two polymer layers [17]. No information is obtained about the lateral structure because the measured reflectivity is an average obtained over a large area of illumination.

A series of layers as illustrated in Fig. 1 is usually studied using NR technique. An equation describing the interaction between the waves reflected from each surface can also be built up using Fresnel's law. The detailed mathematics of this are complex and described in various forms by Russell [18-19] and Bucknall and Higgins [20]. In order to be able to differentiate between different layers, their reflective indices clearly need to be

different; i.e. there must be contrast between them. If the neutron wavelength is constant, the refractive index of a layer, n, can be expressed as the following equation:

$$n = 1 - \frac{\lambda^2}{2\pi} Nb \qquad (1)$$

where N is the atomic number density per cm^3, b is the coherent scattering length and λ is the neutron wavelength.

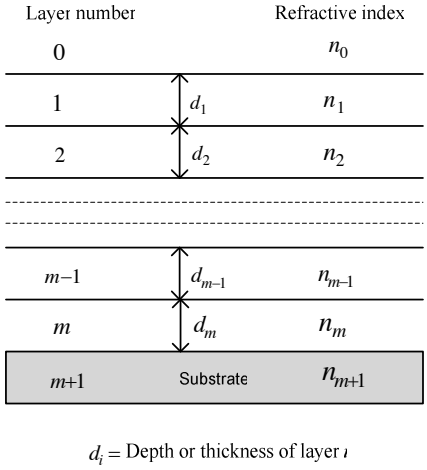

Fig. 1 Typical conformation of a neutron reflectivity polymer multi-layers sample

The refractive index of a layer is dependent upon the value of the so-called scattering length density, Nb, which can be calculated for a particular polymer using the following equation:

$$Nb = \frac{\sum n_i b_i}{M_o} \rho N_A \qquad (2)$$

where n_i is the number of atoms of element i in the monomer, b_i is the neutron scattering length of atom i (cm), M_o is the monomer molecular weight ($gmol^{-1}$), ρ is the density (g/cm^3), N_A is Avogadro's number (mol^{-1}).

As aforementioned, one of the greatest assets available to neutron reflectivity is the use of isotopic substitution for contrast enhancement. By substituting hydrogen with deuterium, a vastly different scattering length density can be produced. The variations in contrast used for the samples investigated here are discussed in the following section. Over the years, segregation of diblock copolymers into the interface between immiscible homopolymers has been widely discussed in the literature but not on triblock copolymers. The aim of this work is to investigate segregation of the SEBS triblock copolymers into the interface between polystyrene (PS) and low density polyethylene (LDPE) homopolymers. PS is a glassy polymer having properties which are adequate for many applications. However, it is normally used in service below its glass transition temperatures, T_g. In general, the PS is prone to brittle fracture. Because of such problem, LDPE which is a rubbery polymer above its T_g, is incorporated into PS matrix phase. As aforementioned, introducing small amount of the SEBS into the PS/LDPE blend system would enhance a finer morphology and increase in the adhesion between PS and LDPE phases. This can lead to significant improvements in the mechanical behavior of the PS.

2. Materials and Methods

The PS used was supplied by BP Chemical company (M_w = 250,000, polydispersity = 2.2). The LDPE (Stamylan LD2100 TN00) is a commercial product of DSM, (M_w = 121,000, polydispersity = 12.3). The molecular weights of the homopolymers were determined using the gel permeation chromatography (GPC) technique performed by RAPRA Technology Ltd., UK. All homopolymers were obtained in pellet form. The SEBS triblock copolymers used are commercial products of Shell

Development Company: Kraton G1651 and Kraton G1652. The number average molecular weight (M_n) values of the SEBS were obtained from the supplier and are shown in Table 1.

Table 1 Molecular characteristics of SEBS

SEBS	Total M_n	Mid-Block M_n	End-Block M_n	PS (%)
G1651	240,000	160,000	39,000	33
G1652	55,000	39,000	8,000	29

Typically, for the investigations of polymer-polymer interfaces samples are prepared by spin coating thin polymer films from solution onto optically flat substrates such as silicon or quartz. The first layer is deposited upon the substrate by spin coating from solution. In this study, the solvent used was toluene and the spin speed of 2000 rpm was used. The effect of the spin speed on the thickness of the films prepared was studied by Hermes [21-23]. The thickness of the film was determined by using an ellipsometer. If another layer is required, the substrate with the first layer on it is first dried overnight in a vacuum oven. The further layer is then spin coated onto a clean glass slide, larger than the substrate. The film on the slide is allowed to dry for a sufficient length of time. For the PS, the films prepared were dried approximately 1 hour at 40^{o}C in a vacuum oven. Once sufficiently dried, the edge of the film is loosened from the slide by either wiping the edges with acetone or scratching the edges with a scalpel. The film can then be carefully floated off the glass slide on the surface of water. The substrate with the first film is then placed under the film and then either the water level reduced or the substrate carefully lifted until the film attaches to the substrate. The substrate with the two layers is then dried, initially on the bench until all traces of water have disappeared, and then fully dried in the vacuum oven. The process can then be repeated if further layers are required. In order to prevent the layers already on the substrate from floating off, it is essential that they are dried well before attempting to pick up another film. This method of sample preparation was also used for the SEBS triblock copolymer films.

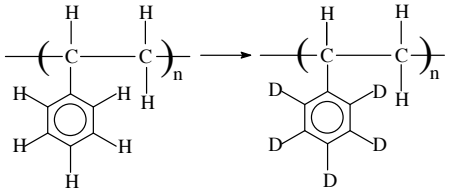

Fig. 2 ^{1}H - ^{2}H exchanges for benzene ring of PS block (hard segment) of SEBS (H and D denote ^{1}H and ^{2}H respectively)

The contrast between layers of polymer films investigated using the NR technique is normally enhanced by means of isotopic substitution. In this study, hydrogen atoms (^{1}H) of benzene rings of PS blocks of SEBS were substituted by deuterium atoms (^{2}H) as illustrated in Fig. 2. The best conditions used for the partial deuteration of the benzene ring of SEBS were found to be similar to a method reported by Willenberg [24]. The procedure to obtain PS-d_5 of the hard segments of SEBS triblock copolymer was as follows:

The SEBS triblock copolymer was dissolved in benzene-d_6 at a concentration of 10 wt/vol.%, under N_2 with stirring. After approximately 40 minutes, ethyl aluminium dichloride was added (200 μl of a 1M solution in hexane). The solution was stirred for 2 hours and the reaction was quenched with water (1 ml). The polymer was then precipitated by addition of methanol (15 ml). The deuterated polymer was then obtained by filtering the product, washing with methanol and drying under vacuum. The SEBS samples were characterized before and after the deuteration using the nuclear magnetic resonance (NMR) technique. The NMR results revealed that the proton-deuteron

exchange in the benzene ring of hard segments of the SEBS samples was higher than 95%.

At temperatures well below the crystalline melt temperature of crystalline and semi-crystalline polymers, such as LDPE, the crystallinity causes the surface of films of such polymers to be molecularly rough, which leads to a loss of specular reflection. To overcome this problem, a sample cell illustrated in Fig. 3 was used. The cell consists of a brass trough in which a thick layer of the LDPE was held. On top a silicon block is placed after coating with one or two polymer layers and held in place with a retaining plate (see Fig. 3). The cell is heated via heating cartridges in the brass base. Silicon is essentially transparent to neutrons with a transmission efficiency of approximately 90%, enabling the neutrons to pass through the Silicon to the polymer layers beneath. In this study, the bulk LDPE was pressed into a mould using a hot press at 150°C. After cooling, the bulk LDPE layer was carefully removed from the mould and stored in a dry place until required.

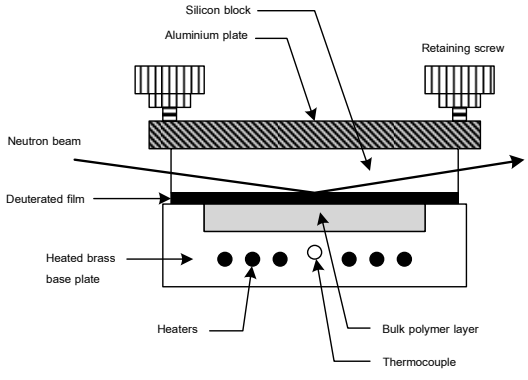

Fig. 3 Schematic diagram of the heating cell used to measure NR reflectivity profiles from polymer in the melt

When assembled, the cell was covered with a box and purged continuously with nitrogen, thus maintaining a nitrogen blanket around the cell for the duration of the experiment. This is to protect the polymers from degradation. Each experiment including the neutron alignment procedure took approximately 4 hours and was performed at a temperature of 150°C. The NR measurements were carried out on the CRISP time-of-flight (TOF) spectrometer at the ISIS Facility of the Rutherford Appleton Laboratory (RAL), Oxon, UK. The general layout of these instrument has been described in detail elsewhere [13], [20]. Generally, three angles were measured per sample in order to provide the required neutron momentum transfer range, Q. The area of illumination and the instrumental resolution were kept constant for all the angles. Once the raw data had been collected they were reduced and normalized to reflectivity profiles, $R(Q)$, as a function of Q. The data were then fitted as described below.

Reflectivity data obtained from a NR experiment cannot be directly translated into a scattering length density, Nb, profile (from which the composition profile can be deduced). This is because there is a loss of phase information incurred due to the squared term in the reflectivity coefficients [12], [20]. Instead, NR data are usually analyzed by proposing models for Nb and using these to calculate the reflectivity, which can then be compared with the experimental profile. By varying the parameters of the model the differences between the experimental and calculated reflectivity profile can be minimized. In order to achieve this, a combination of maximum entropy fitting and model fitting using matrix formalism methods [25] has been used. The maximum entropy fitting methods have an added advantage in that they make very few initial assumptions about the sample; i.e. it is almost a model free fitting procedure. The maximum entropy fitting method of Sivia et al. [26] has been used here. The results obtained from the maximum

entropy model were checked for physical meaningfulness and then refined using a standard matrix model fitting.

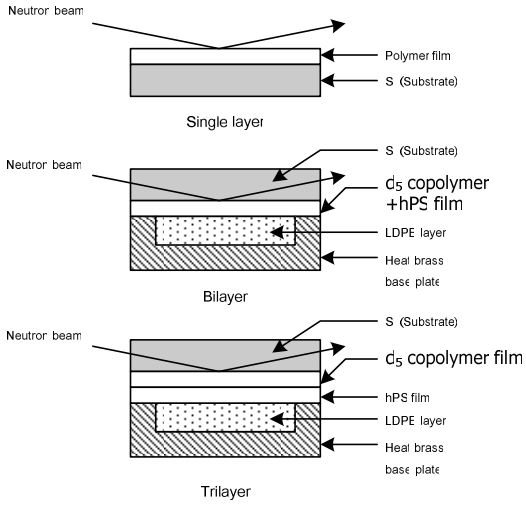

Fig. 4 Sample arrangements for neutron reflectivity measurements

3. Results and discussion

The bulk scattering length densities, Nb, of the polymers used in this study estimated using equation (2) are listed in Table 2. These values will be used to compare with those of thin film polymers obtained from fitting results of NR experiments and evaluate segregation behavior of SEBS into the interface between PS and LDPE layers. Films of polymers were prepared using the method described in the previous section. For single layer samples, a film was directly spun onto a Si wafer. For bilayer samples, a film of d_5SEBS copolymer (G1651 or G1652) was first coated onto the Si wafer. After the film was sufficiently dry, a film of hPS was placed on the top of the copolymer layer. Samples arrangements for NR measurements are illustrated in Fig. 4. In this set of experiments, the structure and thickness of d_5SEBS(G1651), d_5SEBS(G1652), d_5SEBS(G1651)+hPS, d_5SEBS(G1652)+hPS and hPS films were first determined at room temperature. This was necessary in order to reduce the number of variables when fitting the complicated profiles obtained from bilayer and trilayer samples.

Table 2 Estimated values of Nb of polymers used

Polymers	Nb at room temp. ($Å^{-2}$)	Nb at 150°C ($Å^{-2}$)
hPS *	1.50×10^{-6}	1.33×10^{-6}
d_5PS †	4.57×10^{-6}	4.31×10^{-6}
LDPE	-3.32×10^{-6}	-0.28×10^{-6}
d_5SEBS(G1651) §	1.09×10^{-6}	1.01×10^{-6}
d_5SEBS(G1652) §	0.84×10^{-6}	0.78×10^{-6}
d_5SEBS(G1651)/hPS (10/90 wt%)	1.37×10^{-6}	1.30×10^{-6}
d_5SEBS(G1652)/hPS (10/90 wt%)	1.34×19^{-6}	1.27×10^{-6}

* undeuterated PS

† deuterated PS having 5 deuterium atoms in benzene ring

§ deuterated SEBS having 5 deuterium atoms in benzene ring of PS blocks

Fig. 5-9 illustrate the neutron reflectivity data obtained for single layers of hPS, d_5SEBS(G1651), d_5SEBS(G1652), d_5SEBS(G1651)+hPS and d_5SEBS(G1652)+hPS films respectively. The inset illustrates the scattering length density profile corresponding to the fit to the data. The thickness of hPS film is approximately 2000 Å while that of d_5SEBS(G1651), d_5SEBS(G1651)+hPS and d_5SEBS(G1652)+hPS films is approximately 1500 Å. The small difference in scattering length density found for the hPS and d_5SEBS(G1651)+hPS and d_5SEBS(G1652)+hPS films compared to the bulk values shown in Table 2 (i.e. for hPS Nb(film) $\approx 1.27\times10^{-6}$ $Å^{-2}$ c.f. and Nb(bulk) $\approx 1.50\times10^{-6}Å^{-2}$, for d_5SEBS(G1651) Nb(film) $\approx 0.86\times10^{-6}$ $Å^{-2}$ c.f. and Nb(bulk) $\approx 1.09\times10^{-6}$ $Å^{-2}$) may be an indication that the thin films have slightly different densities from the bulk PS and the blends of d_5SEBS/hPS. For the case of hPS and d_5SEBS(G1651) films, the densities of these films are expected to be lower than that of the bulk. Such an effect has been reported by, among others, Fernandez and co-workers [27].

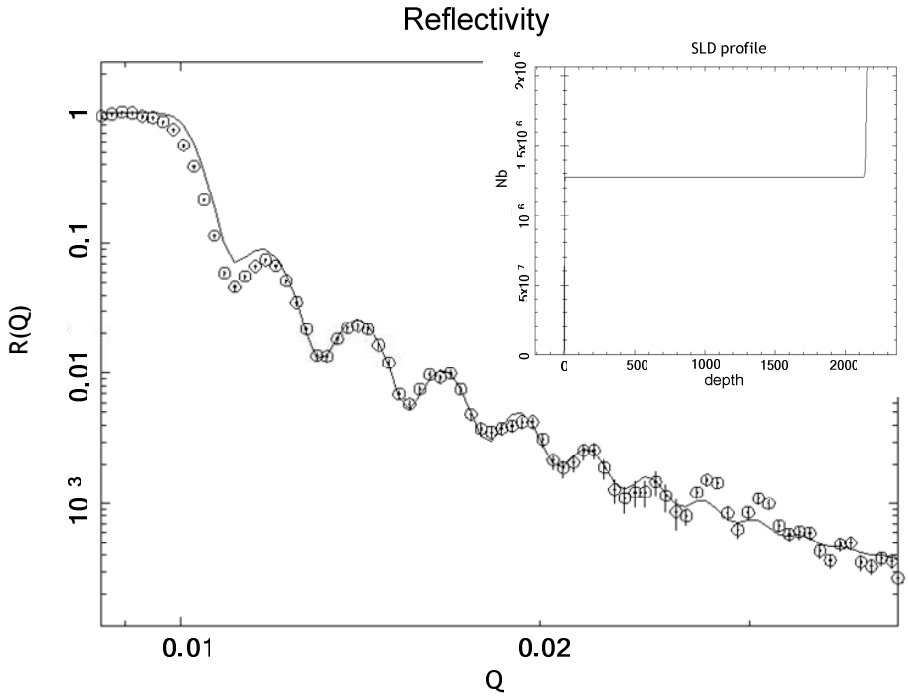

Fig. 5 Reflectivity profile and corresponding scattering length density profile (insert) for hPS at room temperature

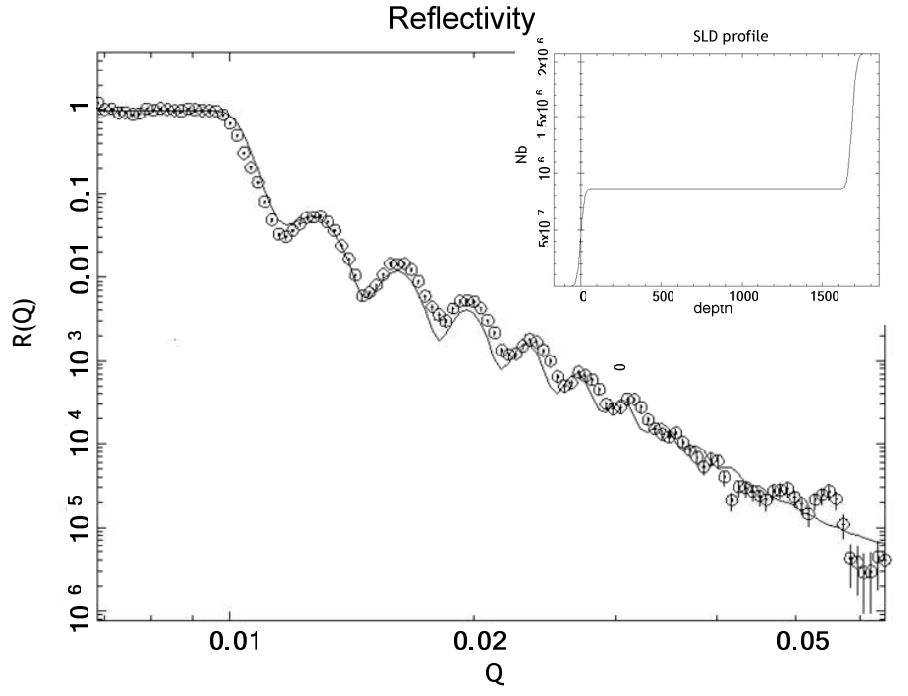

Fig. 6 Reflectivity profile and corresponding scattering length density profile (insert) for d_5SEBS(G1651) at room temperature

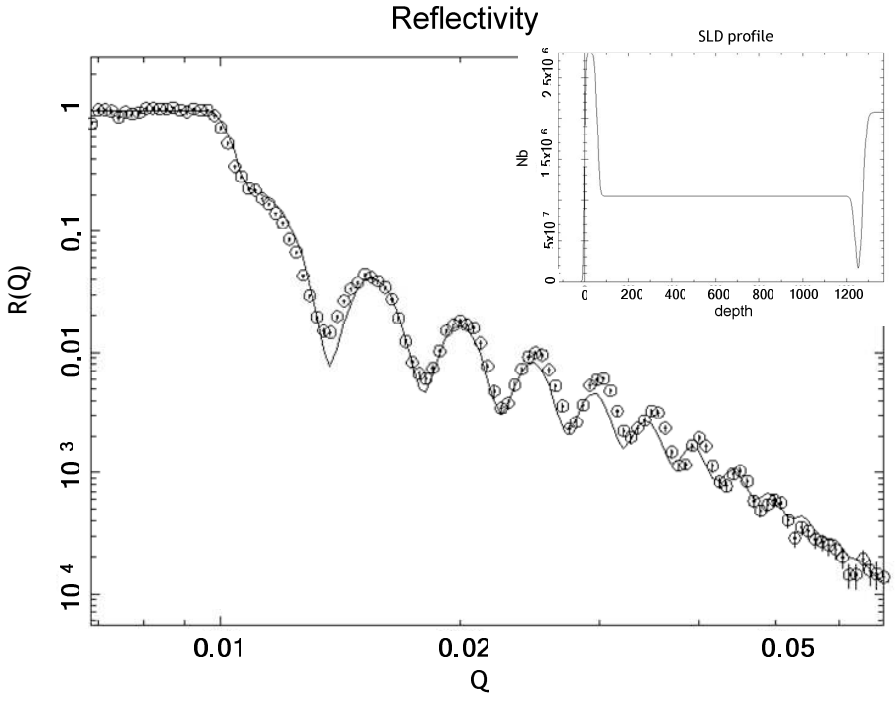

Fig. 7 Reflectivity profile and corresponding scattering length density profile (insert) for d_5SEBS(G1652) at room temperature

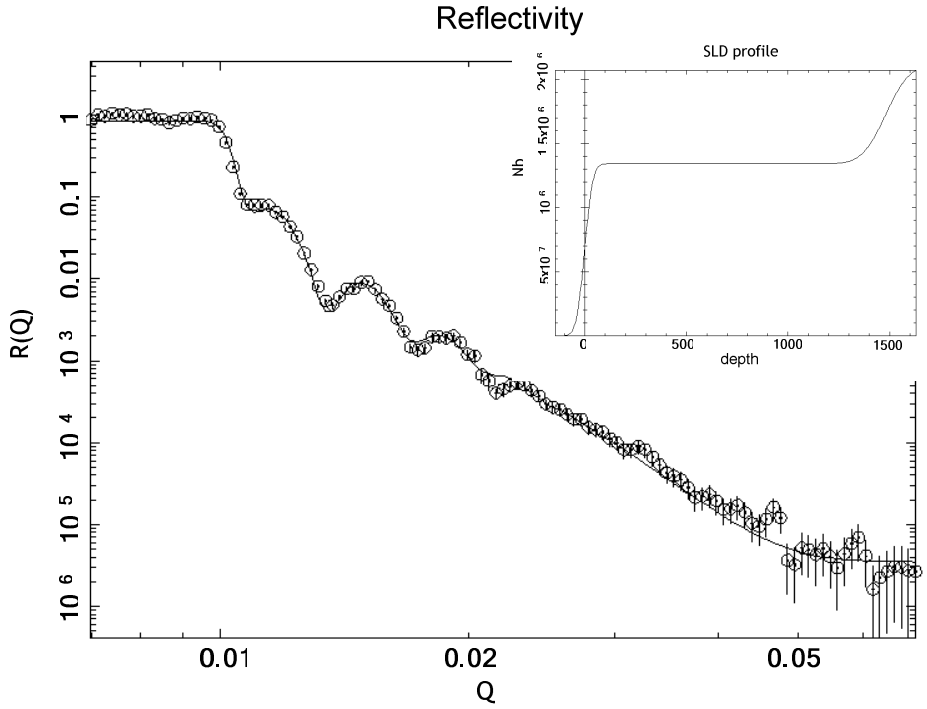

Fig. 8 Reflectivity profile and corresponding scattering length density profile (insert) for d_5SEBS(G1651)+hPS at room temperature

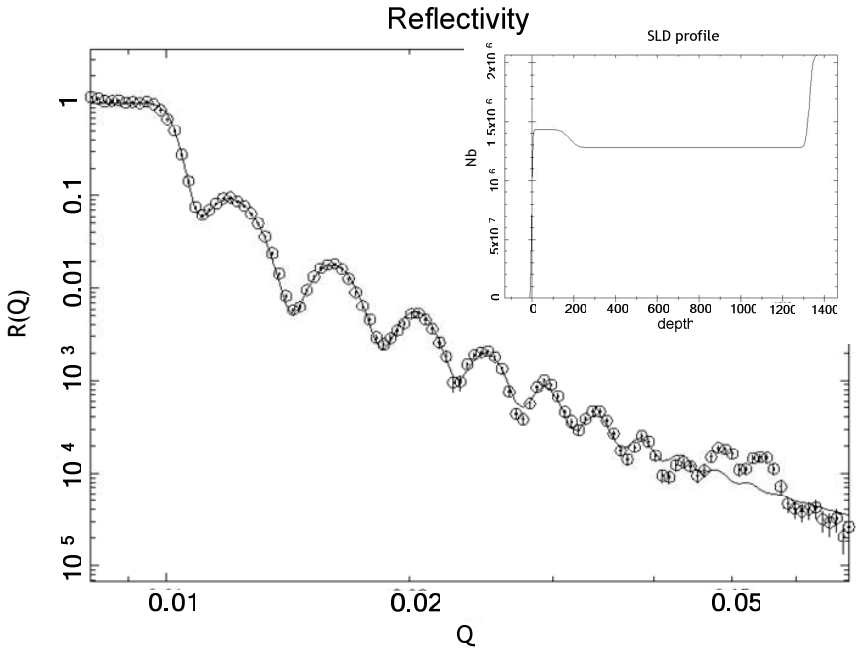

Fig. 9 Reflectivity profile and corresponding scattering length density profile (insert) for d_5SEBS(G1652)+hPS at room temperature

Table 3 Possible interpretation of Nb profile for (d_5SEBS(G1652)+hPS)/LDPE sample.

Layer *	Thickness (Å)	Nb ($Å^{-2}$)	Interfacial roughness § (Å)	Possible interpretation
Silicon	Block	1.780 x10^{-6}	18.71	
1	467.1	0.781 x10^{-6}	84.95	Micelles
2	1199.0	1.262 x10^{-6}	165.80	hPS mixed with micelles
LDPE	Substrate	-0.28 x10^{-6}		

* Start from left hand-side (0) to right hand-side of the depth axis of scattering length profile plot

§ Roughness between layers, i.e. the value of 18.71 is the roughness between Silicon and the first layer

Table 4 Possible interpretation of Nb profile for (d_5SEBS(G1651)/hPS)/LDPE sample.

Layer *	Thickness (Å)	Nb ($Å^{-2}$)	Interfacial roughness § (Å)	Possible interpretation
Silicon	Block	1.780 x10^{-6}	82.37	
1	255.90	1.366 x10^{-6}	43.87	d_5PS segments of d_5SEBS(1651)
2	1120.04	0.908 x10^{-6}	47.88	d_5SEBS(1651)
3	513.30	1.346 x10^{-6}	42.76	hPS mixed with d_5PS segments of d_5SEBS(1651) (total thickness ≈2016 Å)
4	1242.02	1.555 x10^{-6}	43.50	
5	198.60	1.899 x10^{-6}	41.88	
6	62.10	2.636 x10^{-6}	40.84	
7	20.19	0.809 x10^{-6}	11.08	hPS mixed with EB segments
LDPE	Substrate	-0.280 x10^{-6}		

* Start from left hand-side (0) to right hand-side of the depth axis of scattering length profile plot

§ Roughness between layers, i.e. the value of 82.37 is the roughness between Silicon and the first layer

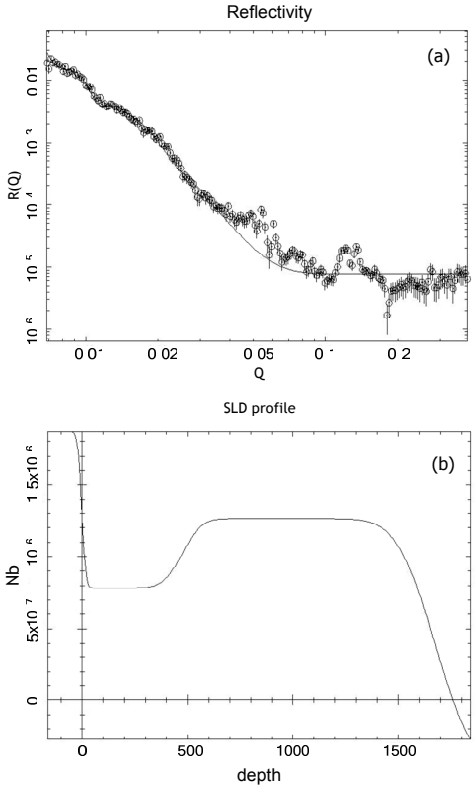

Fig. 10 (a) Reflectivity profile and (b) corresponding scattering length density profile for (d_5SEBS(G1652)+hPS)/LDPE at 150°C

For the d_5SEBS(G1652) film, many attempts to find a better model of single layer for these NR data have up until now proved unsuccessful. As seen in Fig. 7, the model with three layers was found to provide a better fit to the data. However, without complementary data from other techniques, this fit may not be unique. By using an ellipsometry technique, the thickness of the d_5SEBS(G1652) film is found to be approximately 1500 Å. Due to time constraints, the scattering length densities of deuterated copolymers at 150°C were not measured. However, the scattering length densities of Si and LDPE at room temperature and 150°C have been reported by Hermes [21] (see Table 2).

The segregation behavior of the SEBS triblock copolymer was investigated using bilayer and trilayer sample arrangements as illustrated in Fig. 4. For bilayer samples, a film of hPS blended with 10 wt% d_5SEBS was placed against bulk LDPE. The reflectivity profile of samples was measured at 150°C±2°C. Before conducting NR experiments, films of the blend samples were pre-annealed at 153°C in a vacuum oven for approximately 6.5 hours. Due to technical problems encountered during measurements, only reflectivity data of a (d_5SEBS(G1652)+hPS)/LDPE bilayer sample were obtained. The reflectivity and scattering length density profiles of this system are shown in Fig. 10. As the times required for collecting NR data were at least 4 hours and if the pre-annealing time is also taken into account, it is expected that the sample attained equilibrium. Table 3 shows a possible interpretation of the scattering length profile illustrated in Fig. 10(b) but is a very poor fit.

By comparing the scattering length densities of the film providing the best fit illustrated in Fig. 10(b) to the estimated ones (see Table 2), it can be expected that the first layer next to the Si wafer is formed by micelles of d_5SEBS(G1652) and the second layer is the blend of hPS and micelles of the deuterated copolymer. As seen in Table 3, the interfacial roughness between the second layer and LDPE layer is fairly broad (≈166 Å) and this indicates that there must be many micelles of d_5SEBS(G1652) located at this interface and the ethylene-butylene (EB) blocks of the copolymer are miscible with the LDPE bulk. If only hPS were located at the interface, the interfacial width between the hPS and LDPE layers would be very narrow (i.e. less than 10 Å) as hPS is highly immiscible with LDPE and this has been reported by Hermes [21]. As the concentration of the deuterated copolymer used was 10 wt% which is rather high, the interface between the film of d_5SEBS(G1652)+hPS blend and LDPE cannot accommodate all the micelles. Once the interface was saturated with certain amount of micelles, the rest of the micelles will have to

segregate upwards to the free surface (Si wafer). Note that segregation to the interface and to the free surface may occur simultaneously. For the system having a concentration of copolymer which is greater than the critical micelle concentration (CMC), segregation of the copolymer to both the polymer-polymer interface and free surface are likely to occur since the system tries to reduce the number of sharp interfaces that are present [19]. Moreover, deuterated polymer has a high potential to segregate to any free surface as this is a result of the difference in polarizability producing an unfavorable interaction between the two species and a slightly lower surface tension for the deuterated component. The slightly greater value of the film thickness of the annealed sample compared to the as-made sample may be due to small variations in solution concentration and/or spin speed.

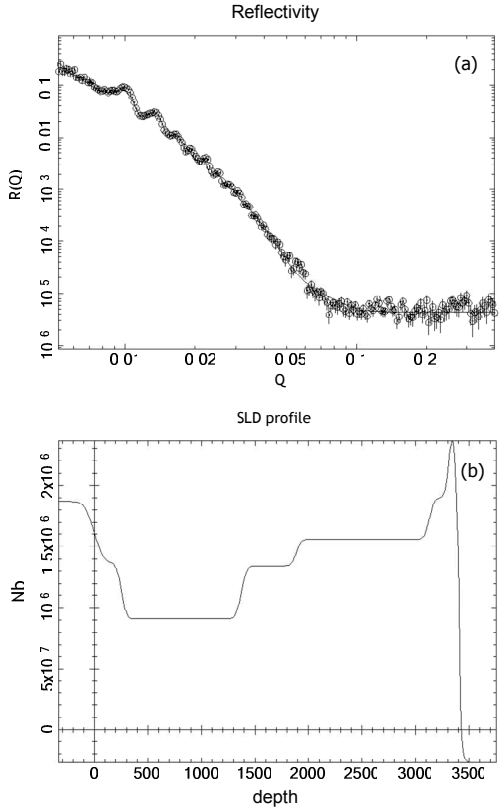

Fig. 11 (a) Reflectivity profile and (b) corresponding scattering length density profile for d_5SEBS(G1651)/hPS/LDPE trilayer sample at 150°C

Fig. 11 illustrates the reflectivity and scattering length density profiles of a trilayer sample of d_5SEBS(G1651)/hPS/LDPE system measured at 150°C±2°C. The bilayer of d_5SEBS(G1651)/hPS film coated onto the Si wafer was pre-annealed at temperature of approximately 155°C in the vacuum oven for 4 hours before conducting the NR measurement. Table 4 shows a possible interpretation of the scattering length density profile illustrated in Fig. 11(b). The first layer is expected to be d_5SEBS(G1651) with a few d_5PS segments migrated upwards to the Si wafer as the scattering length density of this region is greater than that of the d_5SEBS(G1651) itself. Undoubtedly, the second layer is the d_5SEBS(G1651) as the scattering density of this region is close to the estimated one (1.09×10^{-6} Å^{-2}). As mentioned before, the slightly lower value of Nb could be attributed to the slightly lower of the density of the thin film. According to the scattering length density profile of layers 3-6 illustrated in Fig. 11(b), small amounts of the copolymer segregated into the hPS layer and very small amounts of d_5PS segments had reached the interface between the hPS and LDPE. This is indicated by the scattering density of the sixth layer which is closed to the scattering length density of d_5PS itself (4.31×10^{-6} Å^{-2}). The seventh layer is expected to be a blend of hPS with relatively small amounts of EB segments of the copolymer as this is indicated by the scattering length density of this region. No sign of miscibility of the EB blocks with LDPE layer is observed. This is confirmed by the low roughness between the seventh layer and LDPE bulk which is a fairly sharp interface. There are two possible reasons why small amounts of the copolymer segregated into the hPS layer. The first reason is that the viscosity of the copolymer is relatively high at the measuring temperature. The second one is that the time scale used for collecting the reflectivity data was not long enough to allow the

copolymer to diffuse into the relatively thick layer of hPS (≈2000Å) although the sample was pre-annealed at the same temperature of approximately 150°C for about 4 hours before performing the NR experiment.

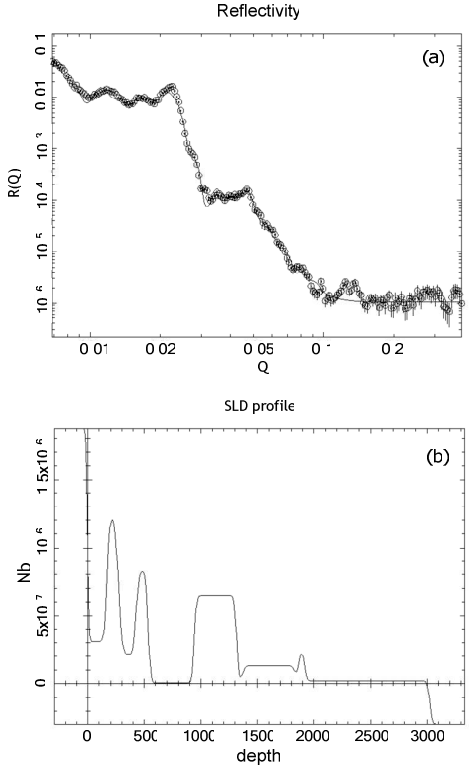

Fig. 12 (a) Reflectivity profile and (b) corresponding scattering length density profile for d_5SEBS(G1652)/hPS/LDPE trilayer sample at 150°C.

Fig. 12 shows the reflectivity and scattering length density profile of a trilayer sample of d_5SEBS(G1652)/hPS/LDPE system measured at 150°C±2°C. The bilayer of d_5SEBS(G1652)/hPS films coated onto the Si wafer was pre-annealed under the same conditions as those used for the case of the d_5SEBS(G1651)/hPS system. Unlike the case of d_5SEBS(G1651)/hPS/LDPE system, many attempts to find a better model of scattering length density profile for these NR data have up until now proved unsuccessful. The scattering length density profile shown in Fig. 12(b) is not the correct model as the total film thickness of d_5SEBS(G1652)/hPS which was selected is less than that of the real system which is about 3500 Å (the thickness of the copolymer film is of about 1500 Å and that of the hPS is of about 2000 Å) although it provides the best fit. Therefore, the results obtained from the fitting have no physical meaning. As found earlier, we have been unable to find a better model of the scattering length density for a single layer of the d_5SEBS(G1652) film measured at room temperature and the thickness of the film had to be estimated using an ellipsometer. The difficulty in finding a model of scattering length density profile to fit the reflectivity data of the trilayer sample of d_5SEBS(G1652) is likely to be associated with this same effect. The only information obtained from the reflectivity data illustrated in Fig. 12(a) is that the copolymer film may form a layer structure which is indicated by the two relatively broad peaks located at $Q \approx 0.02$ and ≈ 0.045.

Generally, the reflectivity data of the bilayer and trilayer samples should also be measured at room temperature. When these reflectivity data are compared to those measured at 150°C, the segregation behavior of the copolymer into the interface of homopolymers can be better understood. However, the LDPE layer has a high surface roughness at temperatures below its melting point due to the effect of crystallinity as already mentioned in the experimental section. Therefore, conducting NR experiments at room temperature has not been attempted. Interpretation of the reflectivity of the samples investigated in this study so far can only be done by comparing the scattering length density profile which provides a best fit to reflectivity data, to the one estimated at 150°C for the polymer used. The interpretation of these results gives some indication of how the copolymer segregates to the interface. For the cases of samples with a d_5SEBS(G1652) layer, other complementary

techniques, e.g. TEM, are required in order to obtain a scattering length density profile which provides a best fit to the reflectivity data with physical meaning. The main conclusions we can draw are the complexity possible when mixing such a three component system and the relative slowness of reaching equilibrium structures if diffusion of the copolymers were the only mechanism. Note that, from the practical point of view, the surface segregation is unlikely to occur during melt processing since the block copolymer used as a compatibilizer is normally not labeled with deuterium atoms, while segregation to the interface is expected to mainly occur as this is enhanced by the shear flow applied.

4. Conclusions

It has been shown that the SEBS triblock copolymers investigated segregate to the interface between PS and LDPE, where the blocks of the copolymer penetrate into the respective homopolymer phases. The NR results indicated that there would be miscibility between the blocks of the copolymer and the respective homopolymer layers. Presumably as a result of the penetration of the copolymer blocks into the respective homopolymers, the SEBS copolymers are expected to increase the strength between the interfaces of PS and LDPE.

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