

COMMUNICATION

Precise structural investigation of symmetric diblock copolymer thin films with resonant soft X-ray reflectivity†

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Symmetric diblock copolymers are known to form lamellar structures in the bulk of an organic thin film. Polymer/polymer and polymer/substrate interfaces play a critical role in this application. Here, we report the investigation of multiple buried interfaces by using a novel technique resonant soft X-ray reflectivity which benefits from enhanced contrast between different polymers near the carbon K-edge. This allows us to obtain a precise interface structure. We also present an alternative method to determine optical constants of polymers by fitting X-ray reflectivity of polymers with known structural parameters at specific soft X-ray energies. This approach is compared with the way of obtaining β by NEXAFS and calculating δ via the Kramers–Kronig relationship. Finally, by using the determined index of refraction, the precise structure of a multilayer formed by a diblock copolymer is obtained by successfully fitting the resonant soft X-ray reflectivity profile.

Introduction

Diblock copolymers are widely used copolymers in science as well as in technological applications, including composite materials, adhesives and fibers.^{1–4} Depending on their relative length they form a large variety of self-assembled structures, which are of particular interest in the context of thin polymer films.^{1,5} Thin film surface and interface properties play a key role in applications listed above. Although it is recognized that

the surface and interfaces of block copolymers are critical to their performance, precise measurements with extremely low uncertainty of the film thickness and buried interface roughness are often lacking. Characterization techniques to probe the surface and interface include both real space and reciprocal space methods. Common real space methods such as scanning probe microscopy and transmission electron microscopy (TEM) elucidate the surface or interface only qualitatively.^{6–9} X-ray microscopy has also been successfully used in a number of systems that have large enough domains to quantify the composition. However, the spatial resolution is limited to 50 nm and the complex modulation transfer function only provides upper composition limits in many cases.¹⁰ In terms of reciprocal space methods, studies using X-ray and neutron scattering have successfully quantified the surface and interface structure with high statistical accuracy.^{11,12}

For equal volume fractions of a block copolymer, the two blocks have a tendency to auto-organize in a lamellar structure of alternating polymer blocks (a periodic multilayer of type ABBAABBA...).^{5,13,14} For symmetric diblock copolymer thin films deposited on silicon substrates with a native oxide layer, if the film thickness $h = (n + \frac{1}{2})L_0$ (where n is an integer and L_0 is the periodic thickness of ABBA), it will form a perfect lamellar structure with a smooth surface on the top.^{5,13,14} The widely used characterization techniques to probe surface and interface information of this multilayer structure are X-ray or neutron reflectivity techniques. They are well-established complementary research tools for the characterization of important structural parameters for polymer thin films such as film thickness, and surface and buried interface roughness. Neutron reflectivity measurements are widely utilized in the polymer science field because the scattering length density (SLD) of polymers can be easily manipulated by replacing hydrogens atoms with deuterium, adjusting the polymer thin film contrast without significantly altering physical properties.^{14–20} However, neutron reflectivity has some known limitations for example the high S/N ratio, small q -range achievable and chemical modification.

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On the other hand, for traditional hard X-ray reflectivity, the contrast depends on the relative electron density of materials. Hence, it is difficult to characterize polymers that usually contain just low- Z elements such as carbon, hydrogen, oxygen, *etc.* This leads to small contrast between different polymers and consequently it is difficult to obtain precise surface and interface information.^{21–23}

Resonant soft X-ray reflectivity (RSoXR) has been developed and successfully applied in the field of magnetic materials.²⁴ In the field of polymers, Wang *et al.*^{25,26} have extended the resonant principles to the carbon K-edge characterizing a PS/PMMA bilayer. Because the complex index of refraction, $n = 1 - \delta - i\beta$, changes rapidly as a function of photon energy in the soft X-ray region, the contrast between PS and PMMA was highly enhanced. In addition, through utilization of specific energies, the sensitivity to the polymer/polymer or polymer/vacuum interface can be selectively enhanced.²⁶ Benefiting from the enhanced contrast between different polymers, RSoXR provides a possible method to carefully examine the PS/PMMA buried interface in the case of the step-by-step spin cast bilayer structure. In many cases, the structure is much more complicated than a bilayer structure which contains only one buried polymer/polymer interface. For example, the precise investigation of a periodic multilayer formed by a diblock copolymer with more than two buried interfaces is always difficult and often a technique limitation. Furthermore, complex and numerous optical parameters and structural parameters of each layer lead to a big challenge for data interpretation. In particular, as the optical constants (δ and β) show strong sensitivity as a function of photon energy in the soft X-ray region, it is not always easy to obtain optical constants with high energy resolution, *i.e.* <0.1 eV. In addition, optical constants are usually obtained by measuring β with the Near Edge X-ray Absorption Fine Structure (NEXAFS) method and calculating δ *via* the Kramers–Kronig relationship.^{27–29} Scattering or reflectivity measurements are usually carried out at different beamlines. Energy calibration offsets from beamline to beamline lead to mismatched optical constants. And, for converting β to δ with the Kramers–Kronig relationship, the polymer density is needed, which is always difficult to measure directly. Due to these difficulties, precise measurements of the multilayer buried interface structure are truly a challenge.

In this paper, we successfully extend resonant soft X-ray reflectivity to investigate surface and buried interfaces in an auto-assembled multilayer structure formed by symmetric diblock copolymer polystyrene (PS)-*block*-poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PAEES) with high precision. The optical constants of PS and PAEES were obtained by fitting the X-ray reflectivity profile of a homopolymer at specific photon energies near the carbon K-edge. The X-ray reflectivity profile is governed by the optical and structural parameters of the thin film. If the structural parameters are known, the optical parameters can be extracted by fitting reflectivity profiles. With this novel approach, it is possible to obtain optical constants directly. As X-ray reflectivity on homopolymers and block copolymers is carried out on the same beamline, the photon energy offset issue mentioned above has been avoided. The optical constants

revealed by this new method and traditional NEXAFS methods are compared. Subsequently, we perform resonant soft X-ray reflectivity on the PS-*b*-PAEES diblock copolymer thin films. With the δ and β values obtained by the new method, the soft X-ray reflectivity profile was successfully fit. Our results demonstrate that resonant soft X-ray reflectivity is a particularly powerful technique to precisely characterize the multilayer structure and its numerous buried interfaces. Precise surface and interface information of block copolymers is important for both the scientific and engineering community.

Experimental

PS was purchased from Polymer Source with $M_n = 90\,000$ g mol⁻¹, $M_w/M_n = 1.05$. PAEES was synthesized by nitroxide-mediated radical polymerization with $M_n = 19\,000$ g mol⁻¹ and

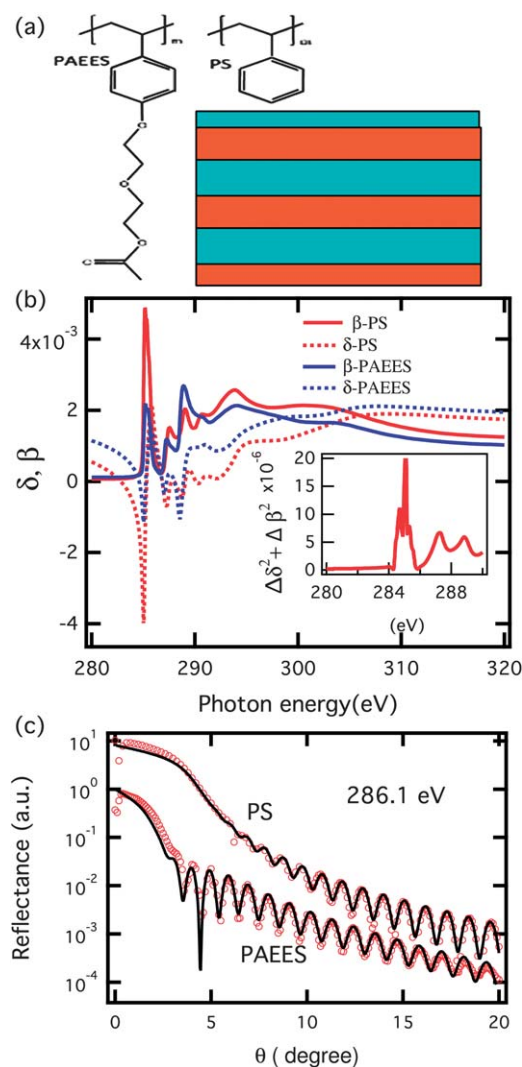


Fig. 1 (a) Chemical structures of PAEES and PS and lamellar schema formed by this block copolymer, (b) β and δ for PS and PAEES (the blue dotted line is the real part in the PAEES index of refraction. The blue solid line is the imaginary part of the PAEES index of refraction. The red dotted line is the real part of the PS index of refraction. The red solid line is the imaginary part of the PS index of refraction. The inset figure is a depiction of the contrast between PS and PAEES); (c) experimental and fit results for PS and PAEES thin films at the resonant energy of 286.1 eV.

$M_w/M_n = 1.19$ (the chemical structure is shown in Fig. 1(a)). The glass temperature (T_g) of PS is about 100 °C, while the T_g of the PAEES block is -3 °C.³⁰ The block copolymer poly(deuterated-stryrene-*block*-4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PS-*b*-PAEES) was synthesized by a nitroxide-mediated radical polymerization.³¹ This block copolymer ($M_n = 68\,900$ g mol⁻¹, $M_w/M_n = 1.32$ with equal volume fraction) is well-suited for our investigation due to the symmetric block ratio. Thin polymer films were spin-coated from a toluene solution onto a silicon wafer. By tuning the solvent concentration and spin speed, we can finely control the thin diblock copolymer film thickness in order to obtain a thin film with a smooth surface ($h = 3.5L_0$ and $h = 4.5L_0$) after thermal annealing. The residual solvent was removed by post-deposition annealing. Furthermore, extended annealing in a vacuum at 170 °C for 24 h was used to obtain a vacuum equilibrium alignment of parallel lamellae throughout the thin film. Near edge X-ray absorption fine structure (NEXAFS) measurements were performed at the high-resolution soft X-ray beamline 10-1 of the Stanford Synchrotron Radiation Laboratory (USA) for the pure PS and PAEES polymers. Carbon K-edge absorption spectra are recorded with an energy resolution of 50 meV. The resonant soft X-ray reflectivity measurements were carried out at the UE56/2-PGM-1 beamline at BESSY (Germany) within the ALICE chamber. To avoid radiation damage of the polymers, the data were acquired in about 10 min per angular scan and the samples were translated occasionally to expose a fresh sample area. The fits were performed using the non-commercial program IMD,³² and reflex12 which is a MATLAB routine for the simulation of specular X-ray reflectivity data using the transfer matrix algorithm.

Results and discussion

The indices of refraction (or optical constants) of PS and PAEES were first determined by the traditional NEXAFS method. The absorptive part of the index of refraction β was obtained by

converting normalized AEY carbon K-edge NEXAFS spectra of the homopolymers PS and PAEES (shown in Fig. 1(b)). As the backbones of PS and PAEES are identical, they exhibit similar absorption spectra while the hydrophilic moiety in PAEES results in the differences. The dispersion δ is consequently obtained from β through the Kramers–Kronig integral equation, which is also shown in Fig. 1(b). We observe clearly that the complex index of refraction (δ and β) changes rapidly near the carbon K-edge. The contrast ($\Delta\delta^2 + \Delta\beta^2$) between PS and PAEES was calculated²⁶ and illustrated in the inset of Fig. 1. Indeed, the contrast between different polymers is highly enhanced near the carbon K-edge.

As a new approach, values for δ and β can also be obtained for specific photon energies by analyzing a reflectance profile recorded at particular photon energies. By modeling the reflectance of the material, the fit of the model to the experimental data will yield the desired values of the optical parameters once the structure is known. This approach is in particular advantageous in the resonant photon energy range, where the index of refraction varies rapidly. Uncertainties related to the particular photon energy used in an experiment can thus be avoided by determining δ and β for this photon energy specifically. We have followed this approach in our experiment and started out by recording reflectance curves at a set of photon energies of the homopolymer reference materials. Specifically, we used thin films of homopolymer PS (about 140 nm) and PAEES (about 121 nm) and the photon energies near the carbon K-edge, and carried out resonant soft X-ray reflectivity. In order to obtain the structural parameters of thin films, we first characterize the polymer thin films using a non-resonant energy, for example 275 eV, where the index of refraction matches well with the calculations using Henke's database.³³ By fitting reflectance profiles, parameters describing thin films' structure, such as thin film thickness, surface roughness and buried interface roughness can be determined. As all the measurements are performed with the same sample, those thin films' structural

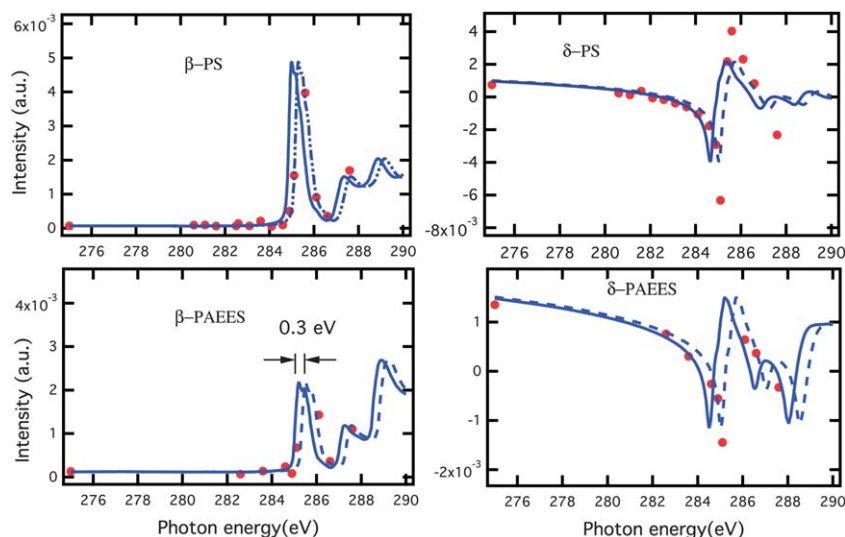


Fig. 2 Optical constants δ and β measured by two different approaches: calculated from NEXAFS spectra (solid line) and fitted from X-ray reflectivity (dot). The blue dashed lines are shifted, relative to the blue solid line, 0.3 eV to higher energy.

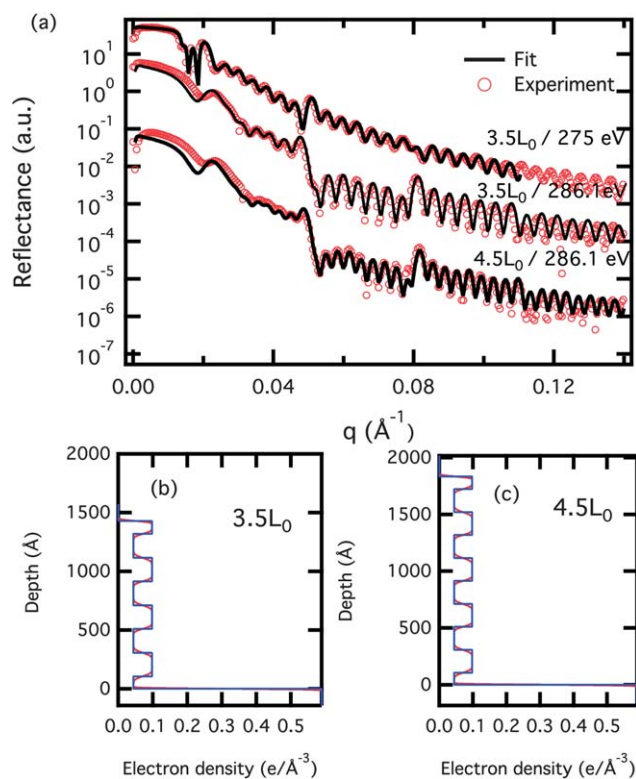


Fig. 3 (a) Resonant soft X-ray reflectivity results for PS-*b*-PAEES ($3.5L_0$, $4.5L_0$) at non-resonant energy and resonant energy of 275 eV; (b) and (c) represent the fitted electron density profiles for different thin film thicknesses ($3.5L_0$, $4.5L_0$). The red and blue lines represent the depth profile with and without considering the interface roughness, respectively.

parameters can be used to fit the reflectance profiles at other energies. The data acquired at the resonant energy of 286.1 eV are shown as an example in Fig. 1(c) (full results are shown in the ESI, Fig. S1 and S2†) for PS and PAEES, respectively. With the structural parameters determined at non-resonant energy, only two variables δ and β are left as free parameters to be determined by a least square fit.

The summarized δ and β values determined with the two different methods are displayed in Fig. 2. The red circles are the δ and β values obtained by the method of fitting the reflectance profile. The blue solid line represents the δ and β values obtained from the NEXAFS measurements. As those two datasets are obtained at two different synchrotron facilities, a small offset of 0.3 eV of photon energy is observed. The blue dashed lines are shifted 0.3 eV from blue solid lines toward higher energy. However, this small energy offset leads to a significant

difference of the δ and β value. The inaccurate optical constants will lead to problems of molding structural parameters. This emphasizes the importance of obtaining precise optical constants at the same beamline. Our new method overcomes the potential issue raised by energy calibration problems.

Resonant soft X-ray reflectivity is then applied to the multi-layer structure of the diblock copolymer thin film. The resonant soft X-ray reflectivity results for the symmetric diblock copolymer thin films composed of PS-*b*-PAEES with different thicknesses of $3.5L_0$ and $4.5L_0$ are recorded with 12 energies between 275 eV and 287.6 eV. The full energy results for $3.5L_0$ and $4.5L_0$ thicknesses are plotted in the ESI Fig. S3 and S4.† Among them, the reflectivity results at the resonant energy of 286.1 eV for $3.5L_0$ and $4.5L_0$ and non-resonant energy of 275 eV for $3.5L_0$ are plotted in Fig. 3 as examples. As we expected, different reflectivity profiles are readily seen with different photon energies. Those differences correspond to changes of the contrast between PS and PAEES by tuning of the photon energies. At the non-resonant energy, 275 eV, we find two Bragg peaks in the low- q range. When q is bigger than about 0.08 \AA^{-1} , the fringes become smooth and gives us less information. However, at the resonant energy of 286.1 eV, the contrast between two polymers is much more remarkable, and the fringes contain rich information through the whole q range. At this energy, the absorption is very high which makes the fringes slightly smooth particularly at low incident angles.

Experimental reflectivity profiles are then fitted to a model multilayer with a MATLAB program (reflex12). The optical constants (δ and β) for PS and PAEES are obtained from the fitted results of the homopolymer data as discussed in the previous part. As the reflectivity on homopolymers and block copolymers is carried out at the same beamline, the δ s and β s obtained by fitting the reflectance profiles of the homopolymers can be used directly. The modeling is done by fixing a multilayer model (antisymmetric wetting condition ABBAABBAAB)³⁴ and varying the structural parameters (*i.e.* thickness and roughness of each layer). The fitted results at different energies reveal structural information including surface roughness, interface roughness and thickness of each layer in the polymer thin film. The fitted profiles are plotted in Fig. 3 as a dark solid line and we note that the fitted profile is pretty close to the experimental results. A large source of error appears at high q (here the fitting results can not line up with the experiment results). The reason could be potentially the inhomogeneity of the film thickness. The fitted depth profiles are shown in Fig. 3(b) at 286.1 eV. The thickness and roughness of the surface and each buried interface are revealed. The fitted structural results are listed in Table 1 for only the non-resonant 275 eV and resonant 286.1 eV

Table 1 Fitting results for PS-*b*-PAEES thin films with $3.5L_0$ thickness

Model		3 repetitions				
		Caplayer (PS)	PAEES	PS	Buffer (PAEES)	Substrate (Si)
275 eV	Thickness (\AA)	99.3 ± 2.1	201.1 ± 2.3	195.9 ± 2.2	101.9 ± 2.2	**
	Roughness (\AA)	15.0 ± 2.0	18.6 ± 6.3	21.1 ± 6.8	14.0 ± 7.3	4.9 ± 0.5
286.1 eV	Thickness (\AA)	102.2 ± 0.9	202.1 ± 0.8	198.1 ± 0.8	107.3 ± 0.7	**
	Roughness (\AA)	9.9 ± 0.5	18.7 ± 0.6	21.7 ± 0.4	21.5 ± 0.6	3.7 ± 0.7

(all the fitted results are shown in the ESI†). We observe almost the same multilayer structure at both resonant and non-resonant energies. However, the uncertainty of the thickness and roughness at resonant energies is much smaller than that at the non-resonant energy. At resonant energies, the uncertainty of thickness is at least 2 times lower than that at non-resonant energies. The uncertainty of the surface roughness at resonant energy is 4 times lower than that at non-resonant energy. Impressively, buried interface roughnesses revealed at resonant energies are more than 10 times lower than those at non-resonant energies. This implies that resonant soft X-ray reflectivity is indeed a powerful characterization technique to probe more than two buried interfaces and it provides extremely precise structural information.

Conclusion

In this paper, we presented a novel approach to determine the optical constants of organic materials. It is based on fitting reflectivity profiles at specific energies near the carbon K-edge. This approach is then compared with the traditional method using NEXFAS, showing the advantages of obtaining optical constants directly without knowing the density of thin films at specific energies while also avoiding energy calibration offsets between beamlines. Then, we used resonant soft X-ray reflectivity to examine the multilayer structure formed by diblock copolymers. By using the optical constants determined with the novel approach, the precise structural parameters of thickness and roughness of the surface and numerous buried interfaces are successfully revealed. This first successful application of resonant soft X-ray reflectivity to investigate the complex morphology of a block copolymer with high precision is carried out and can also be used in other organic material systems. Our method of determination of optical constants can be also extended to all other organic materials.

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