

# X-Ray Reflectivity Study of Polyimide Thin Films Swollen by 1,3-Butadiene and *n*-Butane

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**ABSTRACT:** X-ray reflectivity measurements were performed on two different polyimide thin films synthesized from 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) in 1,3-butadiene and *n*-butane. In 1,3-butadiene at 2.3 atm, the film thickness increased by 24–30%. However, the film thickness increased by only 10% in *n*-butane at 2.3 atm. Excessive increases in film thickness were shown in 1,3-butadiene, but the decreases in film density were minor. The probability of the condensation of 1,3-butadiene in the films is indicated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1818–1825, 2000

**Key words:** X-ray reflectivity; polyimide; swelling

## INTRODUCTION

Polyimides are well known as membrane materials for separating gases. In particular, polyimides with 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) have been reported to be a promising membrane material for some gas separations because they exhibit high separation performance for different gases.<sup>1–4</sup> 6FDA-based polyimides reportedly exhibit good performance for the separation of olefin gases from paraffin gases compared with other conventional polymers.<sup>5–8</sup> However, there have been very few studies on this subject.

Recently, in the 1,3-butadiene/*n*-butane separation system we found that some of the 6FDA-based polyimide films showed very high 1,3-butadiene permeability compared with *n*-butane or other inorganic gases, such as oxygen or nitrogen.<sup>9</sup> The ideal separation factors for 1,3-butadiene versus *n*-butane for the 6FDA-based polyimides that we

studied were 220–24,000 at 25°C. The sorption amount of 1,3-butadiene in the films was larger than that of *n*-butane for all polyimides. The solubility selectivities were 1.1–7.7. The 1,3-butadiene diffusion coefficients were 30–22,000 times larger than that of *n*-butane. However, the separation factors in the mixed gas system were 3–80. The swelling of the film induced by 1,3-butadiene was considered.<sup>9</sup>

We investigated the swelling behavior of 6FDA-based polyimides by X-ray reflectivity measurements. This method is generally used for measurement of the thickness of thin polymer films (~300 nm).<sup>10–12</sup> The thickness determination accuracy is very high. The estimated error is within a few angstroms.<sup>12–15</sup>

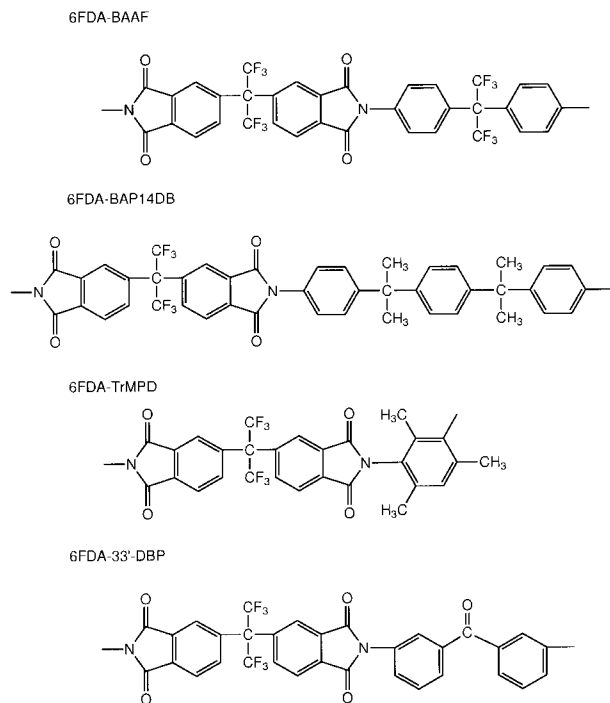
The density of four kinds of 6FDA-based polyimide thin films determined by X-ray reflectivity measurements agrees with the density of their regular thick dense films determined by floating methods. This shows that an X-ray reflectivity measurement provides an accurate density determination of a 6FDA-based polyimide thin film.

We describe the effects of 1,3-butadiene and *n*-butane pressure on the film density and the thickness of two different 6FDA-based polyimide

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**Figure 1** The chemical structures of the polyimides.

thin films. As a result, we indicate that polyimide thin films are swollen more by 1,3-butadiene than by *n*-butane and show the probability of a high density of 1,3-butadiene in the films.

## EXPERIMENTAL

### Sample Preparation

The chemical structures of the polyimides used in this study are shown in Figure 1. The diamines used were 2,2-bis(4-aminophenyl)hexafluoropropane (BAAF),  $\alpha$ - $\alpha'$ -bis(4-aminophenyl)-1,4-diisopropylbenzene (BAP14DB), 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD), 3,3'-diaminobenzophenone (33'DBP). All polyimides were prepared by chemical imidization methods in this laboratory. The precursor polyamic acids were prepared by the slow addition of equimolar amounts of 6FDA dianhydrides (Hoechst Chmikalien Co.) to solutions of the diamines in *N*-methyl-2-pyrrolidone (NMP) under nitrogen at room temperature. The polyamic acid solutions were diluted to less than 10% to prevent gelation. Imidizations were carried out by the addition of fourfold equimolar amounts of diamines of the acetic anhydrides with pyridine to the polyamic acid solutions under nitrogen at room temperature. The reaction

solutions were poured into methanol to precipitate the polyimide solids. The precipitated polyimides were washed several times with methanol and then dried at 80°C for 24 h under a vacuum. Their molecular characteristics are shown in Table I.

Polyimide thin films for X-ray reflectivity measurements were prepared on Si(111) wafers. The 2.5–5% by weight polymer solution in diethylene glycol dimethyl ether was filtered (2- $\mu$ m pore size) and spun cast at 2000 rpm on cleaned silicon wafers. Each sample was baked at 110°C for 1 h and then at 150°C for 3 h, and then the sample was air dried at 190°C for 12 h to remove any residual solvent.

Regular thick dense films were prepared by casting NMP solutions of polyimides on clean glass plates with an applicator. The films were dried in an oven at 110–190°C for 5 h under atmospheric pressure and then at 200°C for 72 h under a vacuum. Solutions were filtered through a 2- $\mu$ m filter prior to casting to remove any large particles or impurities. Films of 12–30  $\mu$ m thickness were obtained. These film densities were compared to the density of thin films determined by X-ray reflectivity measurements. The densities of the regular thick dense films were measured by floatation using zinc nitrate aqueous solutions.

We confirmed no residual solvent in the films used in this study using gas chromatography.

### X-Ray Reflectivity Measurements

The index of refraction at X-ray energies is slightly less than one and is typically written as  $n = 1 - \delta - i\beta$ , where

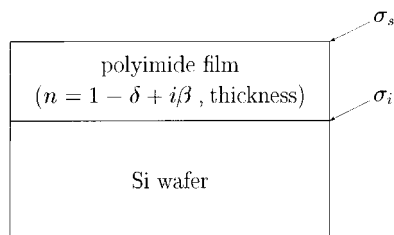
$$\delta = \frac{r_e \lambda^2}{2\pi} \frac{\rho}{M} N_0 \sum_{i=1}^n x_i f_{1i} \quad (1)$$

$$\beta = \frac{r_e \lambda^2}{2\pi} \frac{\rho}{M} N_0 \sum_{i=1}^n x_i f_{2i} \quad (2)$$

**Table I** Molecular Characteristics of Polyimides

Polyimide	$M_n$	$M_w$	$M_w/M_n$
6FDA-BAAF	15,100	27,600	1.83
6FDA-BAP14DB	21,400	42,400	1.98
6FDA-TrMPD	52,700	166,000	3.15
6FDA-33'DBP	14,600	31,200	2.14

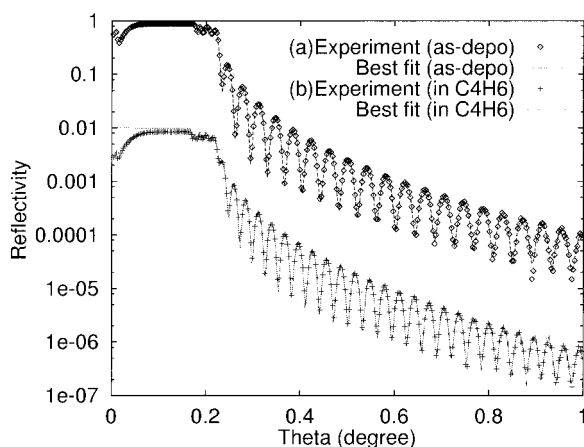
$M_n$ , the number-average molecular weight;  $M_w$ , the weight-average molecular weight.



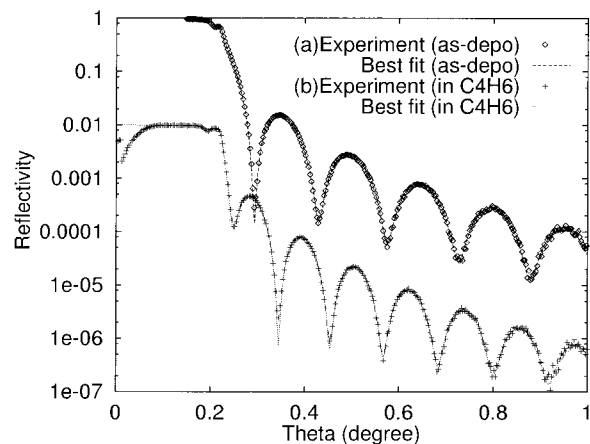
**Figure 2** A schematic diagram of the structure with the parameters used for the X-ray reflectivity simulations. The film thickness ( $\delta$ ) in the index of refraction of the polyimide, the surface roughness ( $\sigma_s$ ), and the film-substrate interface roughness ( $\sigma_i$ ) are adjustable parameters of the fitting process. One additional parameter is a scale factor that is shifted for the overall data. Another parameter is an offset angle that is needed to convert the experimental  $\theta$  into absolute  $\theta$ .

Here  $r_e$  is the classical electron radius,  $\lambda$  is the X-ray wavelength,  $M$  is the molecular weight,  $\rho$  is the mass density,  $N_0$  is Avogadro's number,  $x_i$  is the molar fraction of the  $i$ th atom of the atomic scattering factor  $f_i$  of real and imaginary components  $f_{1i}$  and  $f_{2i}$ , and  $n$  is the number of atoms in a molecule.

The reflection of X-rays from a layered medium was discussed by Parratt<sup>16</sup> who derived a recursion formula to calculate the reflected intensity



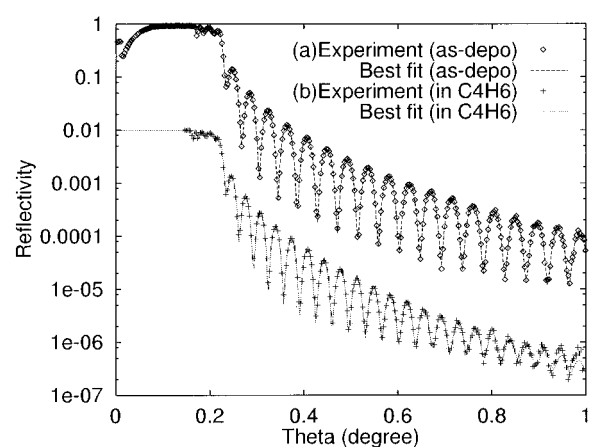
**Figure 3** The X-ray reflectivities of the 6FDA-BAAF(1) film in (a) a vacuum for the ( $\diamond$ ) experiment and (- - -) calculation and (b) 1,3-butadiene (2.3 atm) for the (+) experiment and (- - -) calculation. The thickness of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $103.5 \pm 0.1$  and  $135.5 \pm 0.1$  nm, respectively. The density of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $1.50 \pm 0.03$  and  $1.37 \pm 0.03$  g/mL, respectively.



**Figure 4** The X-ray reflectivities of 6FDA-BAAF(4) film (a) in a vacuum for the ( $\diamond$ ) experiment and (- - -) calculation and (b) in 1,3-butadiene (2.3 atm) for the (+) experiment and (- - -) calculation. The thickness of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $28.2 \pm 0.1$  and  $36.7 \pm 0.1$  nm, respectively. The density of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $1.44 \pm 0.03$  and  $1.30 \pm 0.03$  g/mL, respectively.

from successive interfaces. The theory was modified to include the effects of interface roughness.<sup>17</sup>

The calculated model spectra using the recursion formula were converted to the X-ray reflectivity data by the nonlinear least squares method.



**Figure 5** The X-ray reflectivities of 6FDA-BAP14DB(1) (a) in a vacuum for the ( $\diamond$ ) experiment and (- - -) calculation and (b) in 1,3-butadiene (2.3 atm) for the (+) experiment and (- - -) calculation. The thickness of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $95.3 \pm 0.1$  and  $118.0 \pm 0.1$  nm, respectively. The density of the as-deposited film and the swollen film by 2.3 atm of 1,3-butadiene is  $1.28 \pm 0.03$  and  $1.24 \pm 0.03$  g/mL, respectively.

**Table II Best Fitting Calculation Parameters for As-Deposited Films**

Sample	$\sigma_s$ (nm)	Density (g/mL)	Thickness (nm)	$\sigma_i$ (nm)	Density <sup>a</sup> (g/mL)
6FDA-BAAF(1)	$0.4 \pm 0.1$	$1.50 \pm 0.03$	$103.5 \pm 0.1$	$0.7 \pm 0.1$	1.47
6FDA-BAAF(2)	$0.4 \pm 0.1$	$1.46 \pm 0.03$	$64.8 \pm 0.1$	$0.6 \pm 0.1$	
6FDA-BAAF(3)	$0.3 \pm 0.1$	$1.49 \pm 0.03$	$62.6 \pm 0.1$	$0.5 \pm 0.1$	
6FDA-BAAF(4)	$0.5 \pm 0.1$	$1.44 \pm 0.03$	$28.2 \pm 0.1$	$0.7 \pm 0.1$	
6FDA-BAP14DB(1)	$0.3 \pm 0.1$	$1.28 \pm 0.03$	$95.3 \pm 0.1$	$0.7 \pm 0.1$	1.29
6FDA-BAP14DB(2)	$0.2 \pm 0.1$	$1.32 \pm 0.03$	$33.6 \pm 0.1$	$0.7 \pm 0.1$	
6FDA-TrMPD	$0.3 \pm 0.1$	$1.37 \pm 0.03$	$47.5 \pm 0.1$	$0.8 \pm 0.1$	1.34
6FDA-33'DBP	$0.4 \pm 0.1$	$1.43 \pm 0.03$	$65.5 \pm 0.1$	$1.3 \pm 0.1$	1.45

$\sigma_s$ , surface roughness;  $\sigma_i$ , film-substrate interface roughness.  
<sup>a</sup> For regular thick dense films.

The thin film structure is shown schematically in Figure 2. Each layer was described by four parameters:  $\delta$ ,  $\beta$ , thickness, and roughness. However, the absorption effect is very small for polymer systems, so we assumed  $\beta$  to be constant. One additional parameter was a scale factor that was shifted for the overall data. Another parameter was an offset angle that was needed to convert the experimental  $\theta$  into absolute  $\theta$  (e.g.,  $\theta = 0$  corresponding to the sample parallel to the incident beam). The calculated reflectivity was convoluted with a Gaussian function representing the instrumental resolution function.

The X-ray reflectivity experiments were performed using a two-circle goniometer based on a 2-kW standard X-ray tube.  $\text{CuK}\alpha_1$  X-rays were selected and collimated by reflection from the Si(111) monochromator. The monochromator was located 110 cm away from the X-ray generator. The monochromatic beam was then radiated on the sample after passing through a slit defined by the beam width. The width of the slit was fixed at 0.05 mm. The reflected intensity was measured by a scintillation counter after passing through a 0.12 mm wide slit.

The sample environment was maintained in a chamber with beryllium windows under a vacuum or with 1,3-butadiene or *n*-butane. The chamber was placed on the  $\theta$  axis of the goniometer. A  $\theta$ - $2\theta$  scan was taken to measure the specular reflection signal after completely aligning the sample. All measurements were performed at  $25 \pm 0.5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

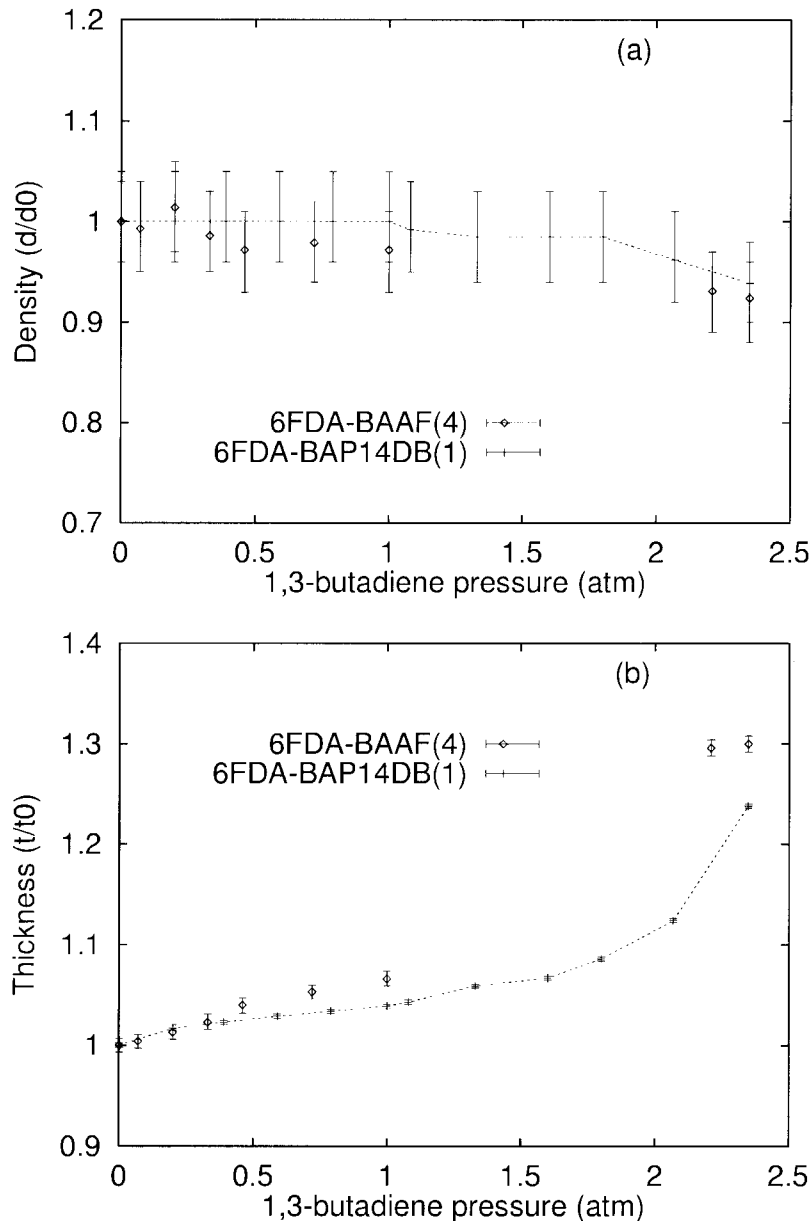
### As-Deposited Films

Figures 3(a), 4(a), and 5(a) show the reflectivity data for the as-deposited films in a vacuum. The

fits of the data are shown by the dashed lines in these figures according to the parameters in Table II. The sample names are also shown in Table II. The thicknesses of the films were 28–100 nm. The density of regular thick dense films are also indicated in Table II. The 6FDA-BAAF film exhibits the highest density. On the other hand, the 6FDA-BAP14DB film exhibits the lowest density. 6FDA-TrMPD and 6FDA-33'DBP have intermediate densities between those of 6FDA-BAAF and 6FDA-BAP14DB. All film densities agreed with the density of their regular thick dense films. An X-ray reflectivity measurement on 6FDA-based polyimide thin films in our study provided an accurate density determination. Four different thickness samples of 6FDA-BAAF and two different thickness samples of 6FDA-BAP14DB were prepared for investigation of the effects of film thickness on the density of the polyimide films. The densities of all films agreed with those of the regular thick dense films within experimental error.

### Swelling Behavior of 6FDA-BAAF and 6FDA-BAP14DB

Figures 6 and 7 show the changes in thickness and density in 1,3-butadiene and *n*-butane, respectively, for 6FDA-BAAF and 6FDA-BAP14DB. The measurements were performed at least 12 h after the samples were kept at a particular pressure. The measurements were repeated at the same pressure, and good reproducibility was found. Figures 3(b), 4(b), and 5(b) show the reflectivities of each sample in 1,3-butadiene at 2.3 atm. The data for the film in the gases are shifted down by 2 orders of magnitude for greater clarity. The results of the best fit are shown by the dotted lines in Figures 3(b), 4(b), and 5(b) and the parameters are shown in Table III. It can be seen



**Figure 6** The (a) density and (b) thickness of 6FDA-BAAF(4) and 6FDA-BAP14DB(1) in 1,3-butadiene (normalized by initial film density  $d_0$  and thickness  $t_0$ ).

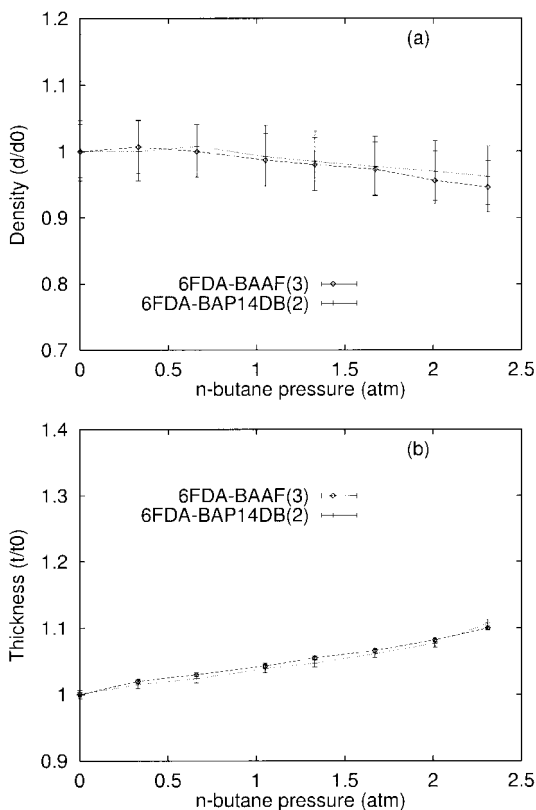
that the thickness of the 6FDA-BAAF films increases by 30% in 1,3-butadiene compared to that in a vacuum and that the rate of the thickness increase does not depend on the initial thickness.

The density of the as-deposited 6FDA-BAAF(1) film in a vacuum was 1.50 g/mL. The film density in 1,3-butadiene at 2.3 atm was 1.37 g/mL. Actually, this film contained the swelling gas. The  $\delta$  value determined by the fitting procedure was translated into the density using eq. (1). In the case of polyimide and a swelling gas mixture sys-

tem, we assumed that  $\sum_{i=1}^n x_i f_{1i} / M$  in eq. (1) was constant at the polyimide value.

The film thickness in 6FDA-BAAF(1) and 6FDA-BAP14DB(1) increased by 30.9 and 23.9%, respectively, in 1,3-butadiene at 2.3 atm compared to that in a vacuum. The fractional free volume of the bulk polymers was 0.185 for 6FDA-BAAF and 0.164 for 6FDA-BAP14DB. This suggests that the lowered packing structure of 6FDA-BAAF enhanced the swelling behavior. Table IV shows the film parameters in *n*-butane at 2.3 atm





**Figure 7** The (a) density and (b) thickness of 6FDA-BAAF(3) and 6FDA-BAP14DB(2) in *n*-butane (normalized by initial film density  $d_0$  and thickness  $t_0$ ).

for 6FDA-BAAF(3) and 6FDA-BAP14DB(2). The thickness increases only 10.5 and 9.9%, respectively, in *n*-butane at 2.3 atm. However, Figures 6 and 7 show that the thickness increases are nearly equal in both cases up to about 1.5 atm. Above that pressure, large expansions occurred on the introduction of 1,3-butadiene. Although the rate of increase in the thickness of 6FDA-BAAF(1) was 30.9% in 1,3-butadiene at 2.3 atm, the film density decreased by only 8.7%. We can conclude that the 6FDA-BAAF film resulted in swelling by 1,3-butadiene and that 1,3-butadiene condensed in the film.

The fractional free volume (FFV) of the polyimide film was calculated from the relation<sup>18</sup>

$$\text{FFV} = \frac{V - V_0}{V} = \frac{V - 1.3V_w}{V}$$

where  $V_w$  is the specific van der Waals volume;  $V_0$  is the specific occupied volume, which is  $1.3 \times V_w$ ; and  $V$  is the polymer specific volume. The van der Waals volume is calculated via the group contribution method of Bondi.<sup>19</sup> We assumed that the density of the swelling gas in polyimide thin films,  $\rho_b$ , is calculated from the following equation:

$$\rho_b = \frac{\rho_c \cdot t_c - \rho_0 \cdot t_0}{\text{FFV} \cdot t_0 + \Delta t}$$

where  $\rho_0$  and  $t_0$  are the density and the thickness of the as-deposited film, respectively;  $\rho_c$  and  $t_c$  are the results of the film in gases; and  $\Delta t$  is the increment of the film thickness in the gas.

The  $\rho_b$  values of each sample are also shown in Tables III and IV. The density of 1,3-butadiene at 2.3 atm in the film (0.58–0.63 g/mL) is compared with its liquid form  $d_{20}^4 = 0.62$  g/mL, although the saturated vapor pressure of 1,3-butadiene at the measurement temperature (25°C) is 2.76 atm. On the other hand, the density of *n*-butane in the film (0.22–0.30 g/mL) is lower than that of 1,3-butadiene in the film. Evidently, 1,3-butadiene is more concentrated than *n*-butane in the film. However, we do not discuss  $\rho_b$  in detail, because the values contain large errors. This is a case where neutron reflectivity would be far more informative.

The calculated curve does not match the observed intensity at large  $\theta$  in Figure 5 for 6FDA-BAP14DB(1) in 1,3-butadiene at 2.3 atm. The reflectivity measurement was performed over larger angular and more dynamic ranges (Fig. 8). Although the period of the oscillations in the curve in Figure 8 was matched using the mono-

**Table III** Best Fitting Calculation Parameters in 1,3-Butadiene at 2.3 atm

Sample	$\sigma_s$ (nm)	Density (g/mL)	Thickness (nm)	$\sigma_i$ (nm)	$\Delta t$ (%)	$\rho_b$ (g/mL)
6FDA-BAAF(1)	$0.5 \pm 0.1$	$1.37 \pm 0.03$	$135.5 \pm 0.1$	$0.9 \pm 0.1$	30.9	0.61
6FDA-BAAF(4)	$0.5 \pm 0.1$	$1.33 \pm 0.03$	$36.7 \pm 0.1$	$0.9 \pm 0.1$	30.1	0.58
6FDA-BAP14DB(1)	$0.4 \pm 0.1$	$1.24 \pm 0.03$	$118 \pm 0.1$	$1.4 \pm 0.1$	23.8	0.63

$\sigma_s$ , surface roughness;  $\sigma_i$ , film-substrate interface roughness;  $\Delta t$ , thickness increase;  $\rho_b$ , 1,3-butadiene density in the film.

**Table IV Best Fitting Calculation Parameters in *n*-Butane at 2.3 atm**

Sample	$\sigma_s$ (nm)	Density (g/mL)	Thickness (nm)	$\sigma_i$ (nm)	$\Delta t$ (%)	$\rho_b$ (g/mL)
6FDA-BAAF(3)	$0.6 \pm 0.1$	$1.41 \pm 0.03$	$68.8 \pm 0.1$	$0.9 \pm 0.1$	9.9	0.22
6FDA-BAP14DB(2)	$0.5 \pm 0.1$	$1.27 \pm 0.03$	$36.7 \pm 0.1$	$1.1 \pm 0.1$	10.5	0.30

$\sigma_s$ , surface roughness;  $\sigma_i$ , film–substrate interface roughness;  $\Delta t$ , thickness increase;  $\rho_b$ , *n*-butane density in the film.

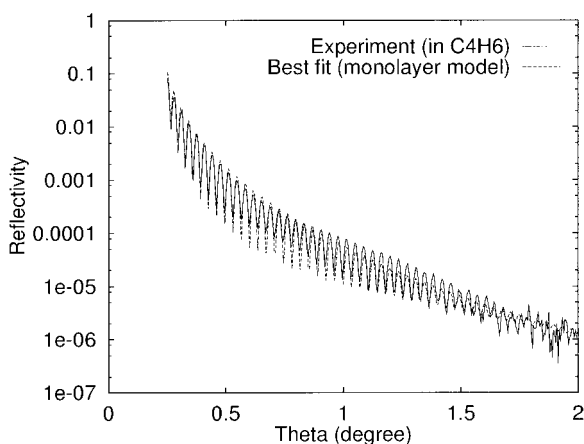
layer model with only a 6FDA-BAP14DB single film on silicon, the observed intensity was not reproduced. A good fit to the data was obtained only by the addition of a layer to the model at the 6FDA-BAP14DB surface (Fig. 9). The parameters to the fit in Figure 9 are shown in Table V. The density of the surface layer is 0.78 g/mL. The layer may be induced by the swelling or by X-ray radiation. However, the density of the layer was close to that of 1,3-butadiene liquid, and the layer immediately disappeared when the sample chamber was placed under a vacuum again. One possible explanation for the observed phenomenon was that the layer consisted of highly condensed 1,3-butadiene having nearly liquid density. We could not find the surface layer on the 6FDA-BAAF film in 1,3-butadiene. In *n*-butane we could not find the surface layer on either film. This may have been due to the extreme thinness of the surface layer.

Further work should be anticipated on the characterization of the surface layer, because this layer is considered to play an important role in the 1,3-butadiene and *n*-butane separation mech-

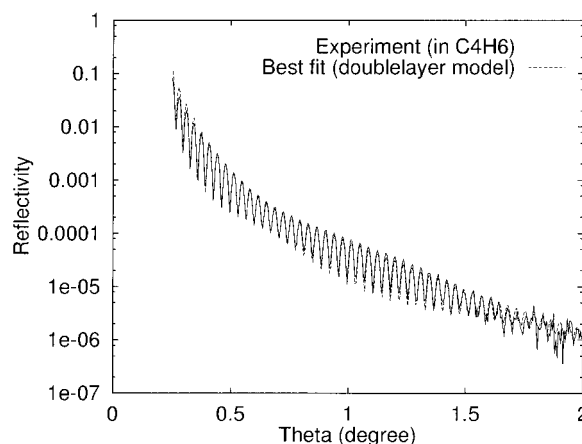
anism. We improved our reflectometer for larger dynamic range measurements, which has sufficient sensitivity for an ultrathin film. In order to obtain a more detailed characterization of the layer, other studies are needed using IR or Raman spectroscopy.

## CONCLUSION

We indicated the excessive thickness increases in 6FDA-based polyimide thin films in 1,3-butadiene and *n*-butane using X-ray reflectivity measurements. At 2.3 atm the rate of increase in the thickness in 1,3-butadiene (24–30%) was much larger than that in *n*-butane (about 10%). Furthermore, we indicated the probability of a more condensed state of 1,3-butadiene than *n*-butane in the films. The solubility selectivities of 1,3-butadiene versus *n*-butane were derived from the sorption measurements and were 1.1 for 6FDA-BAAF and 1.4 for 6FDA-BAP14DB, respectively.<sup>9</sup> This was qualitatively consistent with the results of the X-ray reflectivity measurements.



**Figure 8** The X-ray reflectivities of the 6FDA-BAP14DB(1) film in 1,3-butadiene at 2.3 atm for the (—) experiment and (---) calculation by the monolayer model. The monolayer model has a single 6FDA-BAP14DB film on the Si substrate.



**Figure 9** The X-ray reflectivities of the 6FDA-BAP14DB(1) film in 1,3-butadiene at 2.3 atm for the (—) experiment and (---) calculation by the double layer model. The double layer model has a surface layer on the 6FDA-BAP14DB film.

**Table V Best Fitting Calculation Parameters of 6FDA-BAP14DB(1) in 1,3-Butadiene at 2.3 atm Using Double Layer Model**

First Layer			Second Layer			
$\sigma_s$ (nm)	Density (g/mL)	Thickness (nm)	$\sigma_{12}$ (nm)	Density (g/mL)	Thickness (nm)	$\sigma_b$ (nm)
$0.7 \pm 0.2$	$0.78 \pm 0.1$	$3.3 \pm 0.3$	$1.1 \pm 0.2$	$1.31 \pm 0.1$	$115.4 \pm 0.3$	$0.3 \pm 0.2$

The double layer model has a surface layer on the 6FDA-BAP14DB film.  $\sigma_s$ , surface roughness;  $\sigma_{12}$ , first layer–second layer;  $\sigma_b$ , second layer–substrate.

We reported that the permeabilities of pure 1,3-butadiene in 6FDA-based polyimide films were very high. The permeabilities of 1,3-butadiene and *n*-butane increased, and the corresponding selectivity decreased in the 1,3-butadiene/*n*-butane mixed gas system at 25°C. This study was consistent with this phenomenon because 1,3-butadiene induced swelling of the polymer matrix and led to high permeability and low selectivity in the mixed gas system.

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