

# Structural Comparison of Langmuir–Blodgett and Spin-Coated Films of Poly(*tert*-butyl methacrylate) by External Reflection FTIR Spectroscopy and Two-Dimensional Correlation Analysis

Hyeon Suk Shin<sup>†,‡</sup> Young Mee Jung<sup>†,‡</sup> Jungmin Lee,<sup>‡</sup> Taihyun Chang,<sup>‡</sup>  
Yukihiro Ozaki,<sup>§</sup> and Seung Bin Kim<sup>\*,†,‡</sup>

Laboratory for Vibrational Spectroscopy and Department of Chemistry, Pohang University of Science & Technology, Pohang 790-784, Republic of Korea, and Department of Chemistry, School of Science, Kwansei Gakuin University, Sanda 669-1337, Japan

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The structures of Langmuir–Blodgett (LB) and spin-coated films of poly(*tert*-butyl methacrylate) (PtBMA) were investigated by means of external reflection Fourier transform infrared (FTIR) spectroscopy and two-dimensional correlation analysis. In addition, the structural relaxation of the films during heating was studied. At room temperature, the intensity ratio of the band at 1728 cm<sup>-1</sup> (assigned to the C=O stretching mode) and the band at 1147 cm<sup>-1</sup> (assigned to the C–O stretching modes of the *tert*-butoxy group) in the external reflection infrared spectrum of the LB film was greater than that in the spectrum of the spin-coated film. However, the values of this intensity ratio for the LB and spin-coated films converged with increasing temperature. The results suggest that the structural difference between the two types of film is primarily due to strain in the *tert*-butoxy group in the LB film. The same trend was observed in the intensity ratio of the bands at 1255 and 1274 cm<sup>-1</sup> assigned to the C–C–O stretching mode. Two-dimensional (2D) correlation analysis was applied to the external reflection FTIR spectral data of the LB and spin-coated films of PtBMA to analyze the relaxation of the films during heating. In the synchronous spectra of both film types, the strongest autopeak corresponded to the C–O stretching mode, appearing at 1151 and 1168 cm<sup>-1</sup> for the LB and spin-coated films, respectively. This suggests that the conformation of the *tert*-butoxy group changes significantly with increasing temperature. The intensity of the autopeak at 1151 cm<sup>-1</sup> in the synchronous 2D spectrum of the LB film is much higher than the intensities of the other autopeaks, indicating that the C–O group in the LB film undergoes mainly local reorientation, which in turn indicates that the *tert*-butoxy group is greatly strained in the room-temperature LB film. On the other hand, the *tert*-butoxy group of the spin-coated film is less strained than that of the LB film because the intensity of the autopeak at 1168 cm<sup>-1</sup> in the synchronous 2D spectrum of the spin-coated film is slightly higher than the intensities of the other autopeaks. Furthermore, the analysis of the signs of asynchronous cross-peaks revealed that the following sequence of spectral changes is induced as the temperature increases: 1131 (bending of <sup>bb</sup>C–C–O and <sup>bb</sup>C–C=O) → [1393 (CH<sub>3</sub> bending of  $\alpha$ -methyl), 1151 (C–O stretching)] cm<sup>-1</sup> and 1133 → 1393 → 1168 (C–O stretching) cm<sup>-1</sup> for the LB and spin-coated films, respectively. This suggests that in both film types the first event is associated with reorientation in both the chain backbone and the side chain. During heating, the  $\alpha$ -methyl group relaxes along with the C–O bond in the LB film but prior to the C–O bond in the spin-coated film.

## Introduction

Polymer thin films have received much recent attention due to their potential applications in nonlinear optical devices,<sup>1</sup> lubricants,<sup>2–4</sup> biosensors,<sup>5</sup> and dielectric layers.<sup>6</sup> When searching for a polymer film suitable for a particular application, it is very important to understand the relation between the structure and physical properties of polymer thin films.

Poly(*tert*-butyl methacrylate) (PtBMA) forms polymer Langmuir–Blodgett (LB) films<sup>7–10</sup> and has recently been employed as a buffer layer in nonlinear optics applications.<sup>11,12</sup> Esker et al.<sup>8</sup> used PtBMA as a precursor for poly(methacrylic acid) (PMAA), which is too hydrophilic to form pure LB multilayers. PMAA provides a hydrophilic surface with high carboxylic acid density, making PMAA a desirable material for the study of superabsorbing polymer networks and bioadsorption and as a precursor for subsequent chemical modification.<sup>8</sup> Prucker et al.<sup>13</sup> found that an LB film of poly(methyl methacrylate) (PMMA) shows a glass transition temperature ( $T_g$ ) similar to the  $T_g$  values characteristic of spin-coated and grafted

\* Corresponding author. Telephone: +82-54-279-2106. Fax: +82-54-279-3399. E-mail: sbkim@postech.ac.kr.

<sup>†</sup> Laboratory for Vibrational Spectroscopy, Pohang University of Science & Technology.

<sup>‡</sup> Department of Chemistry, Pohang University of Science & Technology.

<sup>§</sup> Department of Chemistry, Kwansei Gakuin University.

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PMMA films. This observation led them to conclude that the  $T_g$  of the three films is independent of the intramolecular architecture and the organization of the macromolecular chains. However, See et al.<sup>7</sup> observed in ellipsometric studies that the transition temperature of LB films of PtBMA is approximately 80 °C, regardless of film thickness, whereas that of a spin-coated film of PtBMA increases with film thickness. Therefore, close investigation of the structural differences between the two kinds of films is important to understanding the link between molecular structure and transition temperature. The transition temperature of polymer thin films has been investigated by ellipsometry<sup>7,13–17</sup> and X-ray reflectometry.<sup>18–20</sup> These techniques provide no information on the molecular structure, orientation, or conformation in the thin films, whereas Fourier transform infrared (FTIR) spectroscopy has been used to probe the conformation of poly(methyl methacrylate) thin film and bulk.<sup>21,22</sup> However, no previous study has used FTIR spectroscopy to probe the structural differences between LB and spin-coated films of polymer.

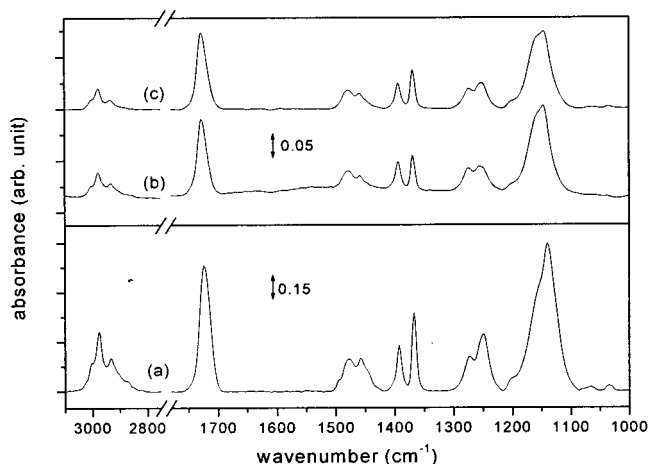
Generalized two-dimensional (2D) correlation spectroscopy is now a well-established technique that is known to provide new possibilities for the interpretation of spectroscopic data from polymers and polymer blends.<sup>23–26</sup> Two-dimensional correlation spectroscopy gives enhanced resolution of individual component bands in the vibrational spectra of polymers. Moreover, it permits us to probe intra- and intermolecular interactions in polymers and polymer blends. To date, however, 2D correlation studies of polymers have concentrated on bulk polymers; the present study is the first time this method has been applied to polymer films.

The purpose of the present study is to elucidate the structural differences between the LB and spin-coated films of PtBMA and their temperature-dependent structural variations by using external reflection (reflection–absorption) FTIR spectroscopy and 2D correlation analysis. Although the temperature dependencies of some bands in the external reflection spectra of the two types of films are easily distinguished, analysis of the temperature dependencies of many bands is hampered by problems associated with band overlap and the presence of bands with similar temperature dependencies. To avoid some of these problems, 2D correlation analysis was applied to analyze the temperature-dependent relaxation in more detail. This technique often provides additional useful information that is not readily available from one-dimensional spectra.

## Experimental Section

**Film Preparation.** PtBMA [ $M_w = 175K$ ,  $M_w/M_n = 2.33$ ,  $T_g = 107$  °C] was purchased from Aldrich Chemical Co. Ltd. and

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**Figure 1.** (a) FTIR transmission spectrum of a film of PtBMA cast on a ZnSe window; (b and c) external reflection spectra of a 50-layer LB film and a spin-coated film of PtBMA, respectively, at room temperature.

used without further purification. The tacticity of PtBMA was determined from the <sup>1</sup>H NMR spectrum as isotactic/heterotactic/syndiotactic = 11:37:52. An Au-coated silicon wafer from Lance Goddard Associates was used as a substrate. All substrates were cleaned in fresh piranha solution (30% H<sub>2</sub>O<sub>2</sub> mixed in a 1:5 ratio with concentrated H<sub>2</sub>SO<sub>4</sub>) prior to the deposition of the LB film. Langmuir films of PtBMA were prepared by spreading a 0.5 mg/mL chloroform solution of PtBMA onto a deionized water subphase at 20 °C. The Y-type PtBMA LB films consisting of 50 layers were fabricated by using a minitrough (KSV) and transferred at a surface pressure of 10 mN/m and rate of 5 mm/min onto an Au-coated silicon wafer. To prepare spin-coated films, a 1.44 wt % PtBMA solution dissolved in toluene was spun onto an Au-coated silicon wafer at 2000 rpm for 30 s. The thickness of the LB and spin-coated films measured by ellipsometry is 449 and 475 Å, respectively.

**FTIR Spectroscopy.** FTIR spectra were measured at a spectral resolution of 4 cm<sup>−1</sup> with a Bomem DA8 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The Seagull attachment (Harrick Scientific Corp.), which includes a heating block attachment, was used in this study. All external reflection FTIR spectra were obtained with p-polarized radiation at an angle of incidence of 82°. To ensure a high signal-to-noise ratio, 1024 scans were added. Sample and source compartments were evacuated to 0.5 Torr. The external reflection FTIR spectra of the as-deposited LB and as-spun films of PtBMA were measured at 25 °C (room temperature) and 50, 60, 70, 85, 100, 115, and 130 °C. Spectra were measured after the sample was equilibrated for 5 min at the measurement temperature.

**2D Correlation Analysis.** Baseline correction and smoothing were performed for all the external reflection FTIR spectra before calculation of the 2D correlation spectra. The 2D software used in this study is the same as that described previously.<sup>27</sup>

## Results and Discussion

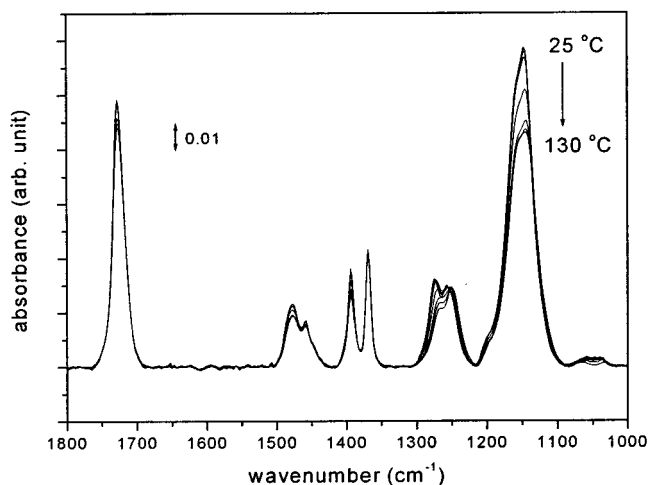
**Comparison of FTIR Spectra of Bulk and Thin Films of PtBMA.** LB films of PtBMA were efficiently fabricated using the method reported previously.<sup>7–10</sup> Figure 1a shows the IR transmission spectrum of PtBMA (a cast film on a ZnSe window) at room temperature, and Figure 1b and Figure 1c show external reflection spectra of an LB film and a spin-coated film of PtBMA, respectively. The thin films are anisotropic, whereas the cast film of PtBMA is isotropic. The orientations of specific functional groups in the thin films can, therefore, be estimated by comparing the relative intensities of the absorption bands in the transmission spectrum with those

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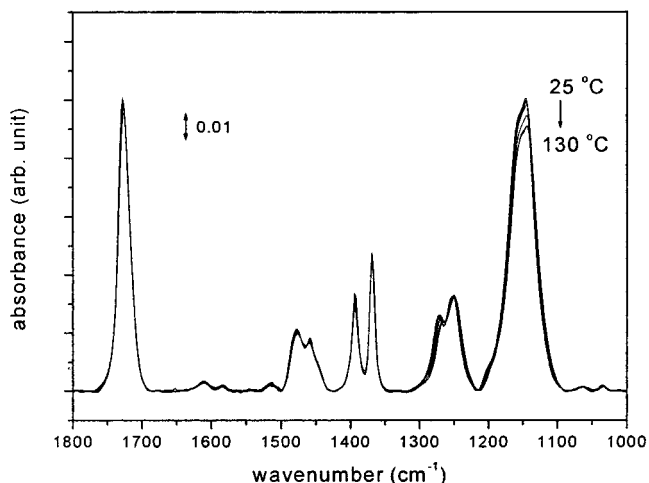
**Table 1. Normalized Intensities and Assignments for PtBMA at Room Temperature<sup>a</sup>**

wavenumber (cm <sup>-1</sup> )			
cast film on ZnSe	LB film	spin-coated film	assignments
2976 (0.81)	2980 (0.74)	2978 (0.69)	$\nu(\text{CH}_3)$
1724 (1.72)	1728 (2.69)	1728 (2.49)	$\nu(\text{C}=\text{O})$
1396	1395	1395	$\text{CH}_3$ bending of <i>tert</i> -butyl <sup>b</sup>
1393	1393	1393	$\text{CH}_3$ bending of $\alpha$ -methyl <sup>c</sup>
1367 (1.00)	1369 (1.00)	1369 (1.00)	$\text{CH}_3$ bending of <i>tert</i> -butyl <sup>b</sup>
1272	1274	1273	$\nu(\text{C}-\text{C}-\text{O})$
1250	1255	1252	$\nu(\text{C}-\text{C}-\text{O})$
	(1151) <sup>d</sup>	(1168) <sup>d</sup>	$\nu(\text{C}-\text{O})$
1140 (2.00)	1147 (3.43)	1146 (2.67)	$\nu(\text{C}-\text{O})^e$
	(1131) <sup>d</sup>	(1133) <sup>d</sup>	Bending of <sup>bb</sup> C-C-O and <sup>bb</sup> C-C=O <sup>f</sup>

<sup>a</sup> Normalized intensities are in parentheses. <sup>b</sup> See ref 30. <sup>c</sup> The assignment of  $\text{CH}_3$  bending of  $\alpha$ -methyl was determined by the substitution of the *tert*-butyl group with deuterium,  $[\text{CH}_2\text{CCH}_3\text{CO}-\text{OC}(\text{CD}_3)_3]_n$  (spectrum not shown). <sup>d</sup> Deconvoluted bands in 2D correlation analysis. <sup>e</sup> According to the IR frequency calculation, this band is coupled with various bands. <sup>f</sup> The bending mode of <sup>bb</sup>C-C-O and <sup>bb</sup>C-C=O bonds connected to the backbone and coupled with the C-O stretching mode.

**Figure 2.** FTIR spectra of a 50-layer LB film of PtBMA at various temperatures (room temperature to 130 °C).

in the external reflection spectra. The normalized intensities of selected bands of PtBMA in Figure 1 are shown in Table 1. The intensity of the band at 1369 cm<sup>-1</sup> due to the  $\text{CH}_3$  symmetric bending mode of the *tert*-butyl group was employed as an internal standard for comparing the relative intensity changes. This band was chosen because the orientations of the transition moments of the three methyl groups that comprise the *tert*-butyl group are expected to be the most isotropic, and the intensity of this band changes little with temperature (see Figures 2 and 3). The normalized intensities of the carbonyl stretching bands in the 1724 cm<sup>-1</sup> region are 1.72, 2.69, and 2.49 for the cast film on the ZnSe window, the LB film, and the spin-coated film, respectively. According to the selection rule of external reflection spectroscopy,<sup>28</sup> these intensities indicate that the carbonyl groups in the LB and spin-coated films are anisotropic compared to those in the cast film and perpendicular to the surface. The normalized intensities of the C-O stretching bands in the 1140 cm<sup>-1</sup> region show the same trend as those of the C=O stretching bands, although the C-O bands are highly overlapped. These findings indicate that the orientations of the C=O and C-O bonds are tilted to the surface normal. The band

**Figure 3.** FTIR spectra of a spin-coated film of PtBMA (1.44 wt %; 2000 rpm) at various temperatures (room temperature to 130 °C).

assignments of PtBMA in Table 1 were made by reference to reports of the band assignments of PMMA<sup>29-32</sup> and vibrational frequency calculations of a model compound.<sup>33</sup>

Comparison of the relative intensities in the reflection spectra of the LB and spin-coated films shows two distinctive features. First, the intensity ratio of the band at 1147 cm<sup>-1</sup> (assigned to a C-O stretching mode) to the band at 1728 cm<sup>-1</sup> (assigned to the C=O stretching mode) is higher in the LB film than in the spin-coated film. Second, the intensity ratio of the band around 1255 cm<sup>-1</sup> to the band around 1274 cm<sup>-1</sup> due to the C-C-O stretching modes also differs between the LB and spin-coated films (see Table 1). These observations will be addressed later in the discussion of Figures 4 and 5.

The method used to fabricate the LB film is quite different from that used for the spin-coated film. To create the LB film, a monolayer of PtBMA is formed at an air-water interface and then transferred to the Au substrate. At the air-water interface, the polar ester groups of PtBMA are in the water subphase, while the *tert*-butyl groups point into the air. Thus, the formation of an oriented structure in the monolayer at the air-water interface is the probable origin of the different conformations of the PtBMA in the LB and spin-coated films. The orientation of the C=O and C-O-C bonds of PtBMA that results from the fabrication process of the LB film can be relaxed by heating; thus, the LB film is expected to relax to a greater extent than the spin-coated film. Several research groups have proposed that the cast and spin-coated films of PMMA contain distinct two conformers, which differ by the rotation of the -OCH<sub>3</sub> bond.<sup>29,34,35</sup> However, Sundararajan reported that there exist two conformers by up and down orientations of the carbonyl group from the calcula-

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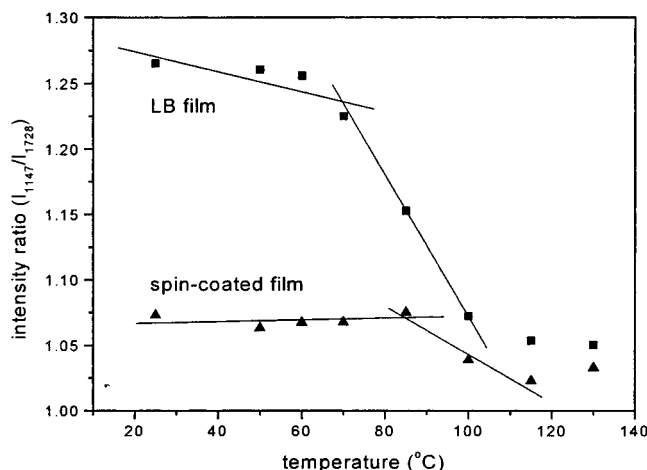
(33) To provide a guideline for the assignment of the observed bands of PtBMA, we carried out density functional theory (DFT) calculations using the nonlocal density function of Becke's three parameters employing the Lee-Yang-Parr functional (B3LYP) with 6-31G\* basis sets for a model compound,  $\text{CH}_3\text{CH}_2\text{CCH}_3[\text{COOC}(\text{CH}_3)_3]\text{CH}_3$ . All the calculations were carried out using the Gaussian 98 suite of programs. The geometries were fully optimized and found to be local minima from the vibrational frequency analysis.

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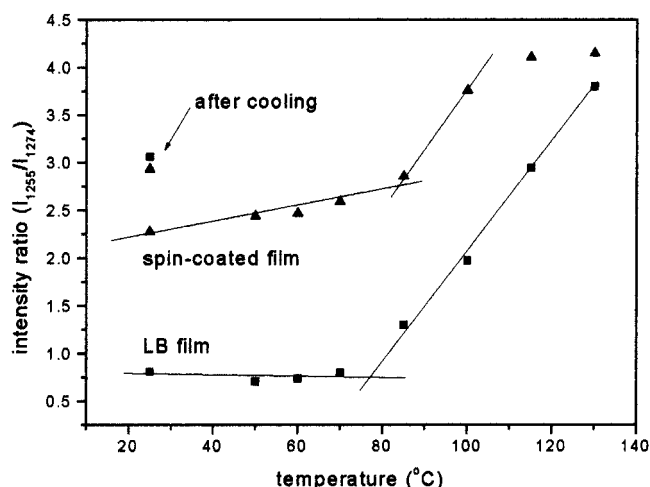
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**Figure 4.** Temperature dependence of the ratio of the intensity of a band near 1147  $\text{cm}^{-1}$  to the intensity at 1728  $\text{cm}^{-1}$  in 50-layer LB and spin-coated films.



**Figure 5.** Temperature dependence of the ratio of the intensity of a band near 1255  $\text{cm}^{-1}$  to the intensity at 1274  $\text{cm}^{-1}$  in 50-layer LB and spin-coated films.

tion of conformational energy of the side chain.<sup>36</sup> By analogy, it is expected that PtBMA will have different conformers, although the methyl group near the ester group in the side chain of PMMA is replaced by a *tert*-butyl group in PtBMA.

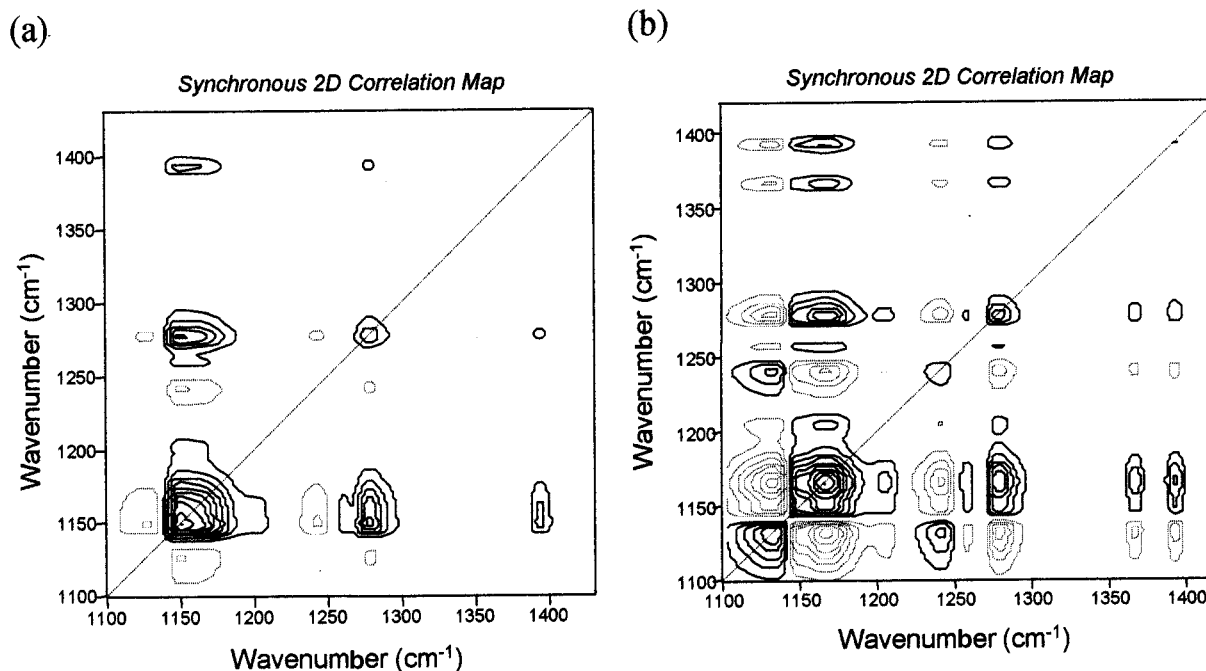
Figures 2 and 3 show the reflection spectra of the LB and spin-coated films of PtBMA, respectively, measured over a temperature range of 25–130 °C. Comparison of Figures 2 and 3 reveals that the temperature dependence in the relative intensity of the bands at 1147 and 1728  $\text{cm}^{-1}$  in the LB film is much greater than that in the spin-coated film. The bands at 1147 and 1728  $\text{cm}^{-1}$  are selected for two reasons: first, these bands have different orientations of the transition dipole moment, and second, consideration of these bands allows qualitative estimation of the relative orientation of the C–O bond with respect to the C=O bond. The temperature dependence of the intensity ratio of the two bands, plotted in Figure 4, shows that at room temperature the relative intensity in the LB film is higher than that in the spin-coated film, while at temperatures over 100 °C the relative intensities are approximately the same for the two films. As mentioned above, the *tert*-butyl group in the LB film of PtBMA is expected to be oriented toward the air due to its hydro-

phobicity, which may induce a confined molecular conformation of PtBMA in the LB film. If the orientation of the *tert*-butoxy group becomes slightly perpendicular to the surface, the intensity of the band at 1147  $\text{cm}^{-1}$  would increase. This phenomenon would explain why the relative intensity in the LB film is higher than that in the spin-coated film at room temperature. On heating, however, the structural relaxation of PtBMA in the LB film causes the relative intensity for the LB film to approach that of the spin-coated film, which shows slight change in relative intensity with increasing temperature. We, therefore, conclude from the data presented in Figure 4 that the PtBMA in the spin-coated film is unstrained and in an entropically favorable conformation, whereas the polymer molecules in the LB film are strained due to their prealignment at the air–water interface.

Careful inspection of Figures 2 and 3 reveals that the intensity ratio of the bands at 1255 and 1274  $\text{cm}^{-1}$  in the spectra of the LB film, due to the C–C–O stretching modes of PtBMA, also differs from the corresponding intensity ratio in the spin-coated film. The intensity ratio of these bands is plotted against temperature in Figure 5 for the LB and spin-coated films. It has been reported for PMMA that the relative intensity of these two bands is correlated with the conformation.<sup>34,35</sup> The same conclusion can be drawn from the results of the present study. At low temperatures, the relative intensity in the LB film is much weaker than that in the spin-coated film, but the relative intensities measured for the two film types converge at high temperature. This indicates that the population of the conformer that gives rise to the band at 1274  $\text{cm}^{-1}$  is higher in the LB film than in the spin-coated film and decreases gradually on heating. The convergence of the intensity ratios with increasing temperature indicates that at high temperature the relative populations of the two conformations are similar in the LB and spin-coated films of PtBMA. The increased population of the conformer with the band at 1274  $\text{cm}^{-1}$  at room temperature could be due to a strained structure within the LB film, and the trend depicted in Figure 5 is consistent with the result of Figure 4 in which a strained structure is relaxing during heating. We, therefore, conclude that the as-deposited layer structures of the two films are different, with the LB film having a more constrained structure than the spin-coated film.

Further inspection of Figure 5 reveals that the intensity ratio at room temperature after annealing is much higher than that before heating for both the LB and spin-coated films. This indicates that the thermal behavior of both the LB and spin-coated films is irreversible. Although the PtBMA in the spin-coated film is not strained, the ratio is not recovered. The hysteresis observed in the spin-coated film may be due to the thermal treatment above the glass transition temperature. Moreover, we can roughly determine the transition temperature from the slopes in Figures 4 and 5. The transition temperatures of PtBMA in the LB and spin-coated films are around 74 and 84 °C, respectively, and are consistent with the ellipsometric result reported by See et al.<sup>7</sup>

**Two-Dimensional Correlation Spectra.** Two-dimensional correlation analysis was performed in the spectral region of 1100–1430  $\text{cm}^{-1}$  to gain further insight into the differences between the structures of the LB and spin-coated films of PtBMA with changing temperature. This method makes it possible to monitor individual reorientational motions of the functional groups during thermal relaxation of the LB and spin-coated films of PtBMA. Figure 6 shows synchronous 2D correlation spectra in the region of 1100–1430  $\text{cm}^{-1}$ . These spectra



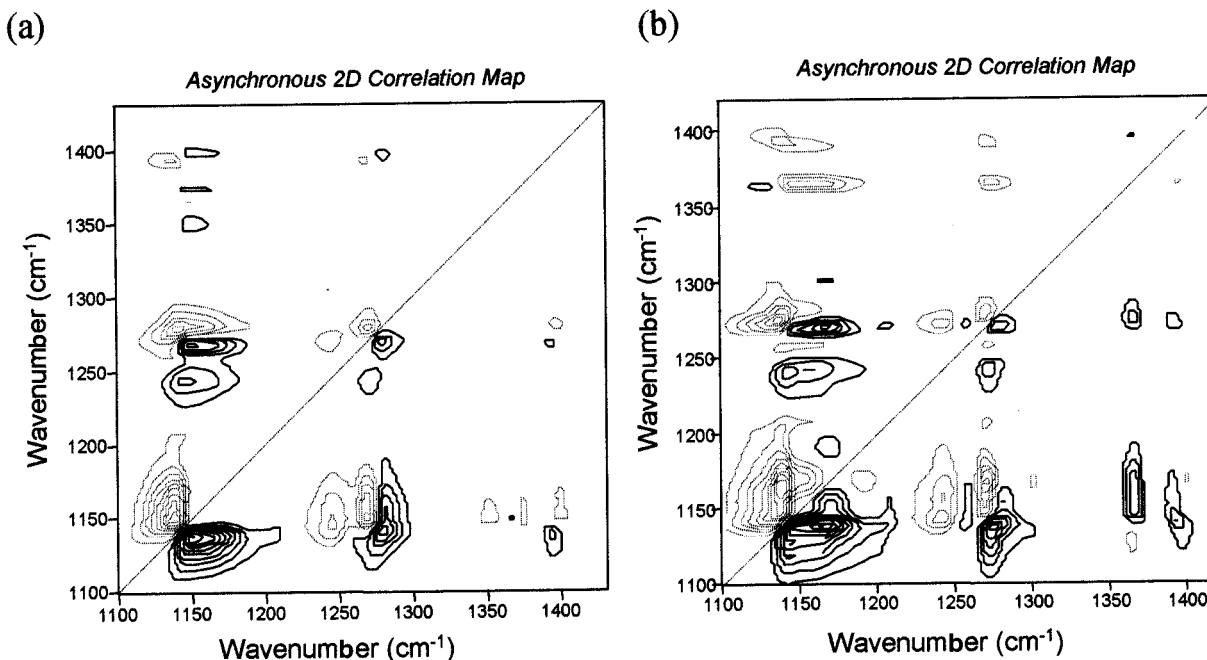
**Figure 6.** Synchronous 2D correlation spectra constructed from the temperature-dependent one-dimensional spectra of (a) LB and (b) spin-coated films of PtBMA in the region of 1100–1430  $\text{cm}^{-1}$ . Solid and dashed lines represent positive and negative cross-peaks, respectively.

were constructed from the temperature-dependent spectral changes of an LB film (Figure 6a) and a spin-coated film of PtBMA (Figure 6b). The 2D maps from both film types show strong autopeaks, located at 1151 and 1168  $\text{cm}^{-1}$  for the LB and spin-coated films, respectively. The position of the strongest autopeak is not the same for the LB and spin-coated films, which confirms that the PtBMA conformation is different in the two film types. This observation is consistent with the presence of two rotational isomers of the *tert*-butoxy group. In the synchronous spectrum of the LB film (Figure 6a), the band at 1131  $\text{cm}^{-1}$  correlates only with the band at 1151  $\text{cm}^{-1}$  within the range of 1100–1430  $\text{cm}^{-1}$ . According to the calculation of infrared frequencies,<sup>33</sup> the band at 1131  $\text{cm}^{-1}$  is assigned to the bending mode of  $^{bb}\text{C}-\text{C}-\text{O}$  and  $^{bb}\text{C}-\text{C}=\text{O}$  bonds connected to the backbone (*bb*) and coupled with the C–O stretching mode. The intensity change of the band at 1151  $\text{cm}^{-1}$  is only in-phase with those of other bands. However, in the synchronous spectrum of the spin-coated film (Figure 6b), most bands share cross-peaks. For example, the bands at 1168 and 1133  $\text{cm}^{-1}$  have cross-peaks with all of the bands in the region of 1100–1430  $\text{cm}^{-1}$ . The intensity changes of the bands at 1133 and 1168  $\text{cm}^{-1}$  are in-phase with those of all the bands in the region of 1100–1430  $\text{cm}^{-1}$ . In addition, the bands at 1133 and 1168  $\text{cm}^{-1}$  share negative cross-peaks in the synchronous spectrum of the spin-coated film, indicating that an increase in the intensity at 1133  $\text{cm}^{-1}$  is accompanied by a decrease in intensity at 1168  $\text{cm}^{-1}$ . Another feature of Figure 6a is the high intensity of the autopeak at 1151  $\text{cm}^{-1}$  relative to the intensities of the other autopeaks. This indicates that the C–O group in the LB film undergoes mainly local reorientation, which suggests that the *tert*-butoxy group is substantially strained. On the other hand, the *tert*-butoxy group of the spin-coated film is less strained than that of the LB film because the intensity of the autopeak at 1168  $\text{cm}^{-1}$  in Figure 6b is slightly higher than the intensities of the other autopeaks. These results collectively indicate that the polymer chains in the spin-coated film interpenetrate, whereas in the LB film the

C–O bonds of the ester groups on the side chains are greatly confined and the backbone chain is independent within a layer. Additionally, neither film type displays a significant autopeak for the band at 1393  $\text{cm}^{-1}$  assigned to the  $\alpha$ -methyl group attached to the main chain, indicating that this group does not contribute significantly to the reorientation in the two films.

Figure 7a and Figure 7b depict the asynchronous 2D correlation spectra constructed from the temperature-dependent spectral variations of the LB and spin-coated films of PtBMA, respectively. According to the rule proposed by Noda,<sup>25</sup> the signs of the asynchronous cross-peaks show the following sequence of spectral events as the temperature is increased: 1131  $\rightarrow$  (1393, 1151)  $\text{cm}^{-1}$  and 1133  $\rightarrow$  1393  $\rightarrow$  1168  $\text{cm}^{-1}$  for the LB and spin-coated films, respectively. This reveals that the intensity change of the band at 1131 or 1133  $\text{cm}^{-1}$  (the bending mode of  $^{bb}\text{C}-\text{C}-\text{O}$  and  $^{bb}\text{C}-\text{C}=\text{O}$  bonds connected to the backbone and coupled with the C–O stretching mode) occurs at a lower temperature than the intensity changes of the side chains at 1393  $\text{cm}^{-1}$  (the  $\text{CH}_3$  bending mode of the  $\alpha$ -methyl group) and 1151 or 1168  $\text{cm}^{-1}$  (the C–O stretching mode). The 2D correlation analysis provides the deconvoluted IR bands at 1131 or 1133  $\text{cm}^{-1}$ . Improved resolution is a strong point of the 2D correlation analysis. Noda<sup>37</sup> carried out IR dichroism measurements of mechanically perturbed PMMA and reported that the dynamic fluctuation, the local reorientational motion, of the IR dichroism signal of the  $\alpha$ -methyl group (i.e., reorientation of the main chain) precedes that of the ester-methyl groups. Interestingly, the present results show that the intensities of the bands at 1393 and 1151  $\text{cm}^{-1}$  in the LB film change simultaneously during thermal relaxation, as shown by the appearance of a cross-peak in the synchronous spectrum but not in the asynchronous spectrum. Thus, the two groups relax simultaneously as the temperature increases. This observation also confirms that the *tert*-butoxy group in the LB film is strained and relaxes together with the

(37) Noda, I. Ph.D. Dissertation, University of Tokyo, Tokyo, Japan, 1997.



**Figure 7.** Asynchronous 2D correlation spectra constructed from the temperature-dependent one-dimensional spectra of (a) LB and (b) spin-coated films of PtBMA in the region of 1100–1430  $\text{cm}^{-1}$ . Solid and dashed lines represent positive and negative cross-peaks, respectively.

$\alpha$ -methyl group during heating. For the spin-coated film, the band at 1393  $\text{cm}^{-1}$  associated with the  $\alpha$ -methyl group relaxes before the band at 1168  $\text{cm}^{-1}$  assigned to the C–O bond. Furthermore, the results from the 2D correlation analysis suggest that the intensity change of the band at 1131 or 1133  $\text{cm}^{-1}$  is associated with the  $\beta$ -transition and that this transition originates not only from the rotation of the alkoxy carbonyl group but also from the torsion of the main chain.<sup>38,39</sup>

### Conclusion

The external reflection FTIR spectra of the LB and spin-coated films of PtBMA, which are both anisotropic on the surface, were measured to compare the structure and thermal behavior of the two types of film. Analysis of the spectra showed that the *tert*-butoxy group in PtBMA is responsible for the structural differences between the two films.

In addition, a 2D correlation analysis of reflection spectra was performed over a range of temperatures to closely observe the structural relaxation. Calculation of the 2D correlations yielded additional useful information that is not readily available from one-dimensional spectra. Analysis of the synchronous and asynchronous spectra of

the LB and spin-coated films of PtBMA showed that the reorientational motion during heating is markedly different in the two films. Relaxation of the LB film is characterized by local reorientation of the *tert*-butoxy group. This indicates that the *tert*-butoxy group in the PtBMA in the LB film has a strained structure at room temperature. All bands in the spin-coated film share cross-peaks in the synchronous 2D spectrum, implying that the polymer chains in this film interpenetrate. The signs of the asynchronous cross-peaks show the following sequence of spectral events as the temperature is increased: 1131  $\rightarrow$  (1393, 1151)  $\text{cm}^{-1}$  and 1133  $\rightarrow$  1393  $\rightarrow$  1168  $\text{cm}^{-1}$  for the LB and spin-coated films, respectively. This suggests that in both film types the first event is associated with reorientation in both the chain backbone and the side chain, followed by reorientations of the side chains. During heating, the  $\alpha$ -methyl group relaxes along with the C–O bond in the LB film but prior to the C–O bond in the spin-coated film.

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**Supporting Information Available:** The transition temperature of PtBMA thin films determined by FTIR spectroscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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