Characterization of Transition Temperatures of a Langmuir–Blodgett Film of Poly(*tert*-butyl methacrylate) by Two-Dimensional Correlation Spectroscopy and Principal Component Analysis

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External reflection FT-IR spectra of a Langmuir–Blodgett (LB) film of poly(*tert*-butyl methacrylate) (PtBMA) were measured at temperatures ranging from 26 to 136 °C. The glass transition temperature (T_g) was determined from a two-dimensional (2D) mapping of the first derivative spectra of absorbance values against temperature over the wavenumber range 1100–1300 cm^{-1}, which contains spectral features that are very sensitive to conformational changes. This mapping provides a surprisingly simple and direct method for detecting the value of T_g. The glass transition temperature determined from the 2D map was approximately 84 °C. Another transition at 103 °C, corresponding to the glass transition temperature of bulk PtBMA, was also detected from the 2D map. Principal component analysis (PCA) was employed to analyze the temperature-dependent FT-IR spectra. The glass transition temperatures (80 °C; 100 °C) of the PtBMA LB film determined by the score plot of PCA are consistent with those determined by the 2D map. Additionally, the loading vectors of PCA were found to give valuable insight into the molecular-level phenomena associated with the glass transition process. To gain more details about the polymer chain mobility, two-dimensional (2D) correlation analysis was performed on two sets of FT-IR spectra collected above and below T_g. In the synchronous 2D correlation spectrum obtained below the glass transition temperature (26–66 °C), the observation that the strongest intensity change occurs at 1137 cm^{-1} indicates that the reorganization of the bending mode of the ^{bb}C–C–O and ^{bb}C–C=O bonds connected to the backbone (bb) chain and coupled to the C–O stretching mode of the *tert*-butoxy group is potentially the mechanism underlying the β-transition. This result is in good agreement with the presence of a transition (β-transition) at approximately 43 °C obtained from the band around at 1137 cm^{-1} in the 2D mapping data.

Index Headings: **Two-dimensional (2D) correlation spectroscopy; Principal component analysis; Glass transition temperature; Langmuir–Blodgett film; Poly(*tert*-butyl methacrylate); PtBMA.**

INTRODUCTION

Polymer thin films have recently received much attention due to their potential applications in various fields.[1–9] In particular, elucidating the thermal properties of polymer thin films is of great importance due to the broad range of temperatures they are subjected to in these applications. The thermal behavior of polymer thin films, including the glass transition temperature (T_g), has been examined by waveguide spectroscopy,[5] ellipsometry,[7,10–13] and X-ray reflectometry.[14–16] For example, Prucker et al.[5] used waveguide spectroscopy to show that the T_g of three different films of poly(methyl methacrylate) (PMMA) is independent of the intramolecular architecture and organization of the macromolecular chains. See et al.[7] used ellipsometry and X-ray reflectivity to study Langmuir–Blodgett (LB) and spin-coated films of poly(*tert*-butyl methacrylate) (PtBMA) and found that the value of T_g depended on the structure of the thin film. In addition, FT-IR spectroscopy has been used to investigate the T_g of polymer bulk and thin films.[17–20] In a study of spin-coated films of PMMA on aluminum using IR spectroscopy, Grohens et al.[20] reported conformational changes in PMMA chains at the polymer–metal interface and determined T_g from their conformational energy.

Generalized two-dimensional (2D) correlation spectroscopy is now a well-established technique and has proved very useful in the interpretation of spectroscopic data from various polymers and polymer blends.[21–24] The details of this technique are described elsewhere.[23,24] Previously, we have studied the structural difference between LB and spin-coated films of PtBMA by means of 2D FT-IR correlation analysis.[25,26] These results showed that the C–O bond of the *tert*-butoxy group is more strained in the LB film than in the spin-coated film. Examination of the sequence of spectral changes induced by increasing temperature revealed that as the LB film is heated, the reorientation of the backbone chain occurs first, followed by reorganization of the side chains. However, conventional 2D correlation analysis does not enable one to pick out the transition temperature at which the intensities of almost all IR bands sensitive to conformational forms change most abruptly.

To overcome this problem, we devised a new 2D data presentation method that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature vs. wavenumber on a single map. In comparison to the conventional 2D correlation plot, the new 2D mapping technique is conceptually much simpler and easier to construct, yet often offers equally powerful and useful features. The proposed approach retains one of the most attractive features of other 2D representation methods: the ability to directly visualize the entirety of complex spectral events occurring during a transition phenomenon. Most importantly, the 2D mapping technique exploits the selectivity of individual IR bands to allow the observer to easily and quickly draw connections between the macroscopic transition

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phenomenon and the molecular-scale responses. The location of the minima or maxima in this 2D mapping enables us to determine the transition temperature of the thin film of polymer, which is based on changes in molecular environment experienced by different chemical moieties associated with the IR absorption at specific wavenumbers.

Principal component analysis (PCA) is a data compression technique that is well established in many fields of spectroscopy.[27–30] PCA can be used not only to compare object clusters, but also to display relationships among variables as well as among variables and objects. Furthermore, a number of recent spectroscopic studies have employed a combination of 2D correlation spectroscopy and PCA, which has proved a powerful spectral analysis method in various areas.[31–34] However, the use of PCA in the determination and characterization of transition temperatures of polymer thin films has not been commonly practiced.

The purpose of the present study is to determine the transition temperature of an LB film of PtBMA probed at the molecular level and to investigate the overall reorientation of functional groups sensitive to conformational changes over two temperature ranges, one above and the other below the glass transition temperature. This goal is accomplished by taking advantage of two novel analysis techniques introduced in the present study. The first of these is a new type of 2D IR data mapping, which shows great potential for determining transition temperatures. The second novel approach is the use of PCA to examine the glass transition process in the polymer thin film during the heating process. Furthermore, the present study provides new insight into the use of a combination of 2D correlation spectroscopy and PCA.

EXPERIMENTAL

Film Preparation. Poly(*tert*-butyl methacrylate) (PtBMA) [M_w = 175K, M_w/M_n = 2.33, T_g = 107 °C] was purchased from Aldrich Chemical Co. Ltd. and used without further purification. A Au-coated silicon wafer from Lance Goddard Associates was used as a substrate. All substrates were cleaned in fresh piranha solution (30% H_2O_2 mixed in a 1:5 ratio with concentrated H_2SO_4) 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. Y-type PtBMA LB films consisting of 50 layers were fabricated using a minitrough (KSV) and transferred at a surface pressure of 10 mN/m and a rate of 5 mm/min onto a Au-coated silicon wafer.

FT-IR Spectroscopy. Fourier transform infrared spectra were measured at a spectral resolution of 4 cm^{-1} with a Bomem DA8 FT-IR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. A seagull accessory of Harrick Scientific Corporation, which includes a heating block attachment, was used in this study. All external reflection absorption FT-IR spectra were obtained using *p*-polarized radiation at an angle of incidence of 82°. To ensure a high signal-to-noise ratio, 1024 scans were coadded. Sample and source compartments were both evacuated to 0.5 torr. External reflection FT-IR spectra of the LB film of PtBMA were measured at intervals of 3 °C over the temperature range 26–136 °C. To attain thermal equilibrium, samples were maintained for 5 min at the measurement temperature before the spectra were measured. The first derivatives of the FT-IR spectra with respect to temperature over the space of temperature vs. wavenumber were calculated using the software MATLAB (Version 6, The Math Works Inc.).

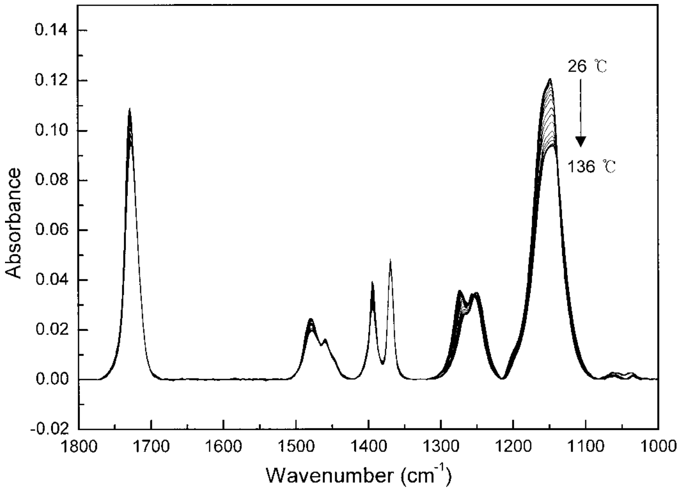

FIG. 1. Reflection absorption FT-IR spectra of a 50-layer LB film of PtBMA at various temperatures (26–136 °C).

Principal Component Analysis (PCA). Fourier transform infrared spectra were mean centered prior to the PCA calculation. However, other steps commonly used in PCA such as normalization scaling of data according to the standard deviation were not carried out because of the need to preserve the amplitude information of the variation of spectral intensities, which is important for the 2D correlation analysis. PCA calculations were performed using the software Pirouette (Infometrix Inc.).

Two-Dimensional Correlation Analysis. Baseline correction and smoothing were performed on all external reflection FT-IR spectra before carrying out the 2D correlation analysis. The software used for the 2D correlation analysis was the same as that described previously.[35]

RESULTS AND DISCUSSION

Figure 1 shows external reflection FT-IR spectra measured from a 50-layer LB film of PtBMA over the temperature range of 26 to 136 °C. In these spectra, the band at 1147 cm^{-1} assigned to a C–O stretching mode undergoes the largest intensity change with increasing temperature. In addition, the relative intensity of the bands at 1256 and 1274 cm^{-1} due to the C–C–O stretching mode changes significantly with increasing temperature. The temperature dependencies of the bands at 1147, 1256, and 1274 cm^{-1} indicate that the properties of the C–O bond next to the *tert*-butyl group change considerably with increasing temperature. The glass transition temperature of the LB film of PtBMA determined from the change in the relative intensity of the bands at 1147 and 1728 cm^{-1} is approximately 74 °C.[25] To more accurately identify the transition temperature of the LB film of PtBMA, we implemented a 2D mapping representation of the absorption

TABLE I. Half temperatures of the temperature range at which the minimum and maximum of the first derivative value of each peak in the range between 1100 and 1300 cm^{-1} appear.

Peak wavenumber	Half temp.	Peak wavenumber	Half temp.
1276	83 °C	1276	103 °C
1150	84 °C	1150	104 °C
1137	84 °C	1137	103 °C
Average temp.	84 °C	Average temp.	103 °C

variations against both wavenumber and temperature as described below.

A set of spectra $A(\nu, T)$, where ν is the wavenumber and T is the temperature, was differentiated with respect to T to create the set of first derivatives of form dA/dT. The plot of these first derivatives as functions of both wavenumber and temperature has the appearance of a 2D map. The position of the maxima and minima of the first derivative value of each band on this map might be closely involved with the transition temperature since the reorientation of polymer at the glass temperature is expected to result in large changes in the IR intensities of almost all bands sensitive to the polymer conformation with respect to temperature.

Figure 2a shows the 2D map constructed from the first derivatives of A with respect to T in the region 1100–1300 cm^{-1}, which contains bands that are very sensitive to conformational changes.[17–20,25] In the 2D map, the glass transition temperature would be determined by locating the line parallel to the wavenumber axis at which the first derivatives of almost all pertinent bands sensitive to the polymer conformation change most rapidly with temperature.[36] Indeed, however, the transition does not occur at a specific temperature, but in a temperature range. Figure 2b depicts the first derivative values as a function of temperature for peaks at 1276, 1150, and 1137 cm^{-1} as extracted from Fig. 2a. Temperatures indicated with arrows in Fig. 2b are maximum and minimum of the first derivative values. The glass transition temperature is determined as the average of the middle temperatures between temperatures at minimum and maximum of the first derivative values of each peak. The results for the PtBMA LB film are summarized in Table I.

The glass temperature in the LB film of PtBMA appears at 84 °C in the 2D map shown in Fig. 2, which is inconsistent with the glass transition temperature (74 °C) we reported previously.[25] In this study, the glass transition temperature was comprehensively determined from the 2D map of the first derivatives of almost all pertinent bands very sensitive to the polymer conformational changes, while that in our previous study was determined from the relative intensity change of the band at 1147

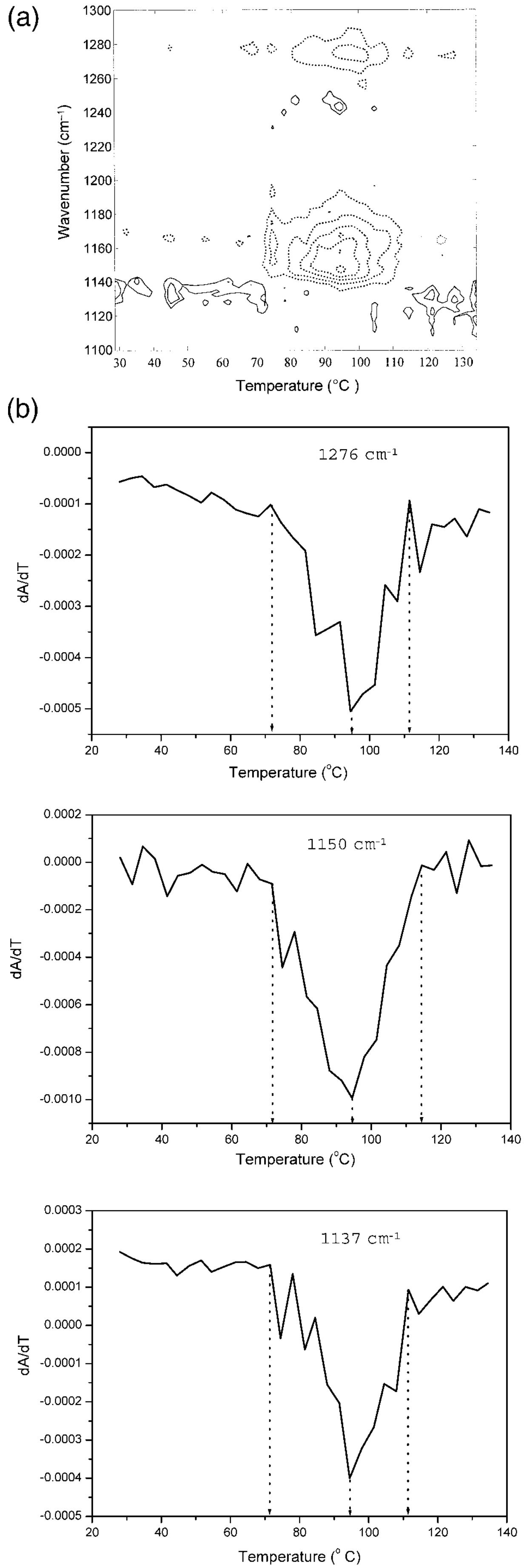

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FIG. 2. (**a**) 2D map of the first derivatives of a set of spectra $A(\nu, T)$ calculated with respect to T, where ν is the wavenumber and T is the temperature. Solid and dotted lines represent positive and negative peaks, respectively. (**b**) The first derivative values as a function of temperature for peaks at 1276, 1150, and 1137 cm^{-1} can be extracted from Fig. 2a. Temperatures indicated with arrows are maximum and minimum of the first derivative values.

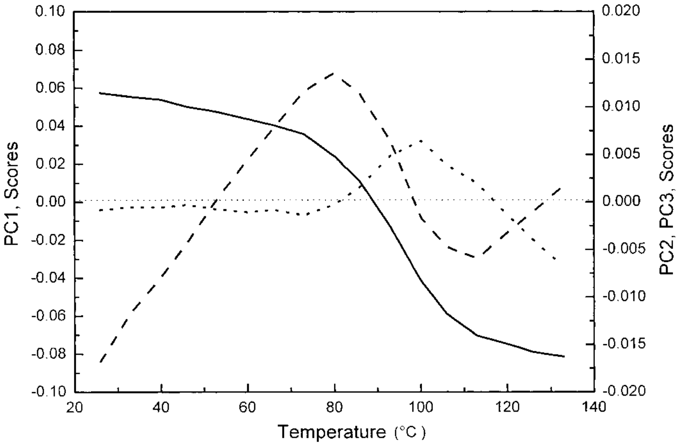

FIG. 3. Score plots vs. temperature for the temperature-dependent FT-IR spectra of an LB film of PtBMA. Solid, dashed, and dotted lines represent the PC1, PC2, and PC3 scores, respectively.

cm^{-1} using the C=O mode at 1728 cm^{-1} as an internal reference band in the FT-IR spectra.

Over the temperature range of approximately 73 to 113 °C, the three bands at 1276, 1150, and 1137 cm^{-1} in Fig. 2 displayed sets of peaks indicating that the values of the first derivatives of these bands change markedly with increasing temperature. The minima of the first derivatives of the three bands are located at approximately 95 °C. The behavior of these bands sensitive to the conformational changes may reflect changes associated with an additional transition process, which corresponds to the transition temperature of bulk PtBMA at 103 °C (Fig. 2 and Table I). Also, there may be an event of the physical change at approximately 113 °C. Above 113 °C, the intensities of two bands at 1276 and 1150 cm^{-1} are relatively constant, whereas that of the band at 1137 cm^{-1} changes in a limited temperature range (Fig. 2). Such behaviors of intensities of bands at 1276 and 1150 cm^{-1} mean that the strained side chains in the LB film are relaxed in the temperature range of 73 to 113 °C.[25] In contrast, the backbone chains of PtBMA (due to the band at 1137 cm^{-1}) have a slight mobility continuously above 113 °C.

Abrupt changes in the intensity of bands assigned to the ν(C–C–O) mode coupled to the ν(C–O) mode in the region 1100–1300 cm^{-1},[17–20,25] which reflect the segmental motion of the polymer, are expected at the glass transition temperature. To investigate the reorganizations occurring in the PtBMA at the glass transition temperature, PCA was applied. Figure 3 shows the score plots of PCA factor 1 (PC1), factor 2 (PC2), and factor 3 (PC3) for the temperature-dependent FT-IR spectra. The largest variances in PCA are typically captured by the first principal component, PC1. In our system, for the external reflection FT-IR spectra of an LB film of PtBMA, PC1 accounts for 97% of the total spectral intensity changes. The analysis of score plots has substantial merit in detecting the existence of changes. The presence of inflection points, maxima, and minima in the scores potentially indicates the presence of transitions and pinpoints the temperature at which the event takes place.

The score plot of PC1 in Fig. 3 (solid line) shows a monotonic decrease over the temperature region investigated. This reveals that PC1 reflects the overall intensity changes of ordinary character from the beginning to the end of the temperature range. We now consider the second principal component, PC2, which accounts for 2.3% of the total intensity variations. The score plot of PC2 (dashed line in Fig. 3) has a maximum at 80 °C and a minimum at 113 °C. As can be seen in Fig. 3 (dotted line), the third principal component, PC3, accounts for only about 0.32% of total intensity variations and has a maximum at approximately 100 °C. Very often, a large positive or negative score value of one object (e.g., temperature) compared to other objects points out an outlier; however, in the present case the two temperatures at 80 and 100 °C nearly coincide with the transition temperatures detected in the 2D map of the first derivatives. This reveals that both PCA and the 2D mapping are capable of detecting the transition temperatures. Thus, the score plot provides a convenient and sensitive indicator of the presence of the glass transitions at the curve maxima or minima.

Figure 4 shows plots of the loading vectors of PC1, PC2, and PC3 as a function of wavenumber. This representation plays a valuable role in the interpretation of the raw spectral data because a plot of the loading vectors against the corresponding wavenumbers highlights the spectral region which has the greatest influence on the principal component being analyzed. In our analysis of the loading vectors, we first consider the overlapped spectral features observed in the vicinity of the band located at 1147 cm^{-1} in the raw spectra. This region of the spectrum showed the greatest variation in intensity with increasing temperature, as shown in Fig. 1. The assignments and frequencies of bands in the region of 1100 to 1300 cm^{-1} observed by PCA and 2D correlation analysis are summarized in Table II. The loading vector of PC1 (Fig. 4a) has maximum values at 1160 and 1149 cm^{-1}, as expected. The corresponding loading vector for PC2 (Fig. 4b) reaches a maximum at around 1139 cm^{-1}. These show that the absorptions that are responsible for the discrimination by PCA are large and strongly overlapped. Thus, in the original spectra the major spectral variations that result from overall processes occurring during the temperature increase are observed in the vicinity of 1147 cm^{-1}, which is assigned to the C–O stretching mode.[25]

As mentioned above, we can estimate the glass transition temperature from the scores of PC2. The transition process that takes place at 80 °C is indicated by a maximum value in the PC2 score plot (Fig. 3, dashed line). It is noted in the loading vector plot of PC2 (Fig. 4b) that the transition occurring at 80 °C is mainly correlated with absorptions due to the bending mode of the ^{bb}C–C–O and ^{bb}C–C=O bonds connected to the backbone (bb) chain and coupled to the C–O stretching mode of the *tert*-butoxy group at 1139 cm^{-1} as well as the stretching mode of C–C–O at 1268 cm^{-1}.[25] Therefore, plots of the loading vectors provide useful information about the transition processes occurring in the polymer thin films; they reveal hidden properties of the glass transition temperature. Furthermore, there is potentially another transition at around 100 °C characterized by a maximum in PC3. It is observed in the loading vector plot of PC2 (Fig. 4c) that the transition at 100 °C is also closely correlated to the three bands sensitive to the conformational changes. This

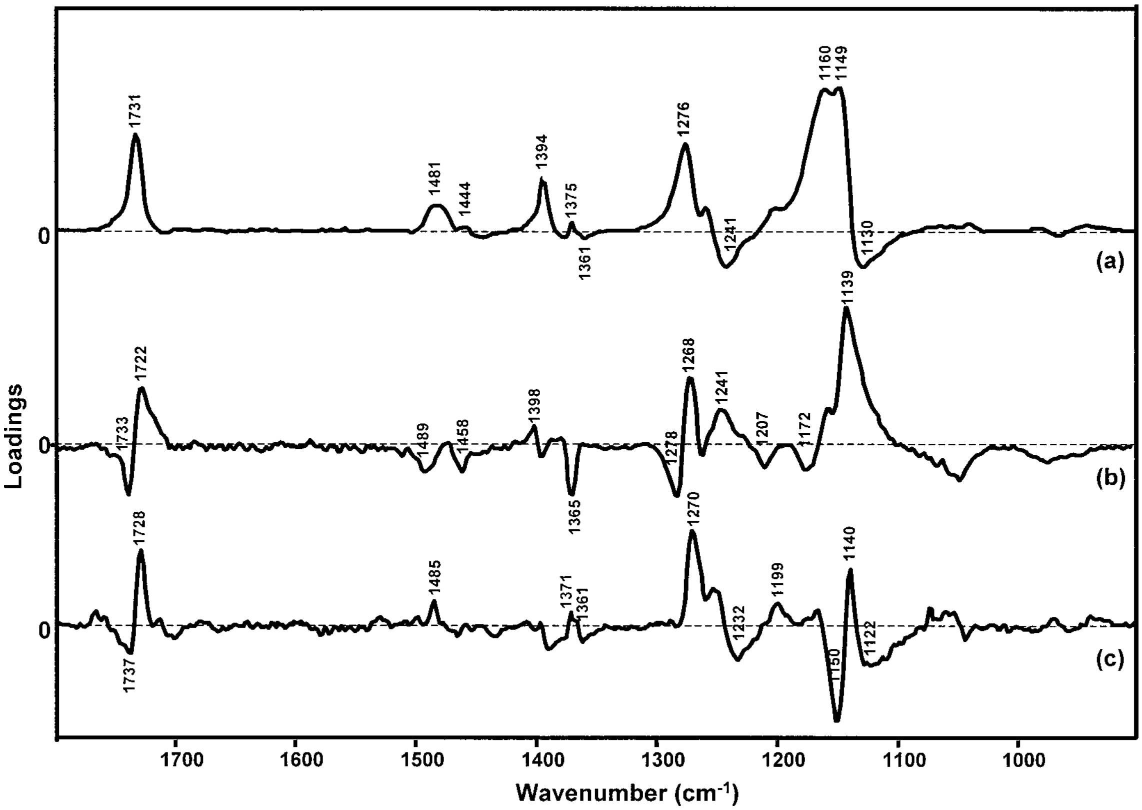

FIG. 4. Plots of (**a**) PC1, (**b**) PC2, and (**c**) PC3 loading vectors for the appropriate scores plotted in Fig. 3.

transition temperature possibly corresponds to the glass transition temperature of bulk PtBMA.[7]

To investigate the overall mobility of individual functional groups above and below the glass transition temperature, we applied 2D correlation analysis to two independent sets of data. The first set was constructed from spectra recorded at temperatures below the glass transition (26–66 °C), while the second set included only spectra measured above the glass transition temperature (93–136 °C). In this paper we focus on the autocorrelation peaks detected in synchronous 2D correlation spectra because the positions and intensities of these peaks reveal information about the overall chain mobility under a temperature perturbation.

Figure 5a shows the synchronous 2D correlation spectrum of the LB film of PtBMA obtained for the first set of data (26–66 °C). The power spectrum extracted along the diagonal line of the synchronous 2D correlation spectrum is shown at the top of Fig. 5a. The strongest autopeak appears at 1137 cm^{-1} and is correlated with peaks located at higher frequencies. The band at 1137 cm^{-1} is assigned to the bending mode of the ^{bb}C–C–O and ^{bb}C–C=O bonds connected to the backbone (bb) chain and coupled to the C–O stretching mode of the *tert*-butoxy group.[25] The C–O stretching mode gives rise to a moderate intensity change at 1162 cm^{-1} and a very weak change at 1148 cm^{-1} (Table II). Figure 5b shows the corresponding synchronous 2D correlation spectrum obtained from the second data set (93–136 °C). The power spectrum at the top of Fig. 5b reveals that the strongest autopeaks are at 1162 and 1148 cm^{-1}. This suggests 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 LB film.

TABLE II. Assignments for some interesting bands in the region of 1100–1300 cm^{-1}.

Wavenumber (cm^{-1})			
Previous report[a]	2D	PCA	Assignments
1274	· · ·	1268	ν(C–C–O)
1151	1162	1160	ν(C–O)
1147	1148	1149	ν(C–O)
1131	1137	1139	bending of ^{bb}C–C–O and ^{bb}C–C=O

[a] See Ref. 25. Frequencies of the bands obtained from 2D correlation calculation in this study differ from those in the previous study. This is due to the difference of the thermal treatments. FT-IR spectra in this study were measured at intervals of 3 °C, while those in the previous study were measured at interval of about 15 °C.

There are two popular hypotheses for the origin of the so-called β-transition of PMMA observed below the glass transition temperature.[37] One hypothesis links the β-transition only to the rotation of the alkoxycarbonyl group, while the other proposes that both rotation of the alkoxycarbonyl group and torsion of the main chain are responsible for the transition. In the synchronous 2D correlation spectrum (Fig. 5a) obtained below the glass transition temperature, the strongest intensity change is observed at 1137 cm^{-1}. As mentioned above, the band at 1137 cm^{-1} corresponds to a bending mode of the backbone chain coupled to a stretching mode of the *tert*-butoxy group. The observation that the strongest intensity change below the glass transition temperature occurs at 1137 cm^{-1}, therefore, indicates that the reorganization of

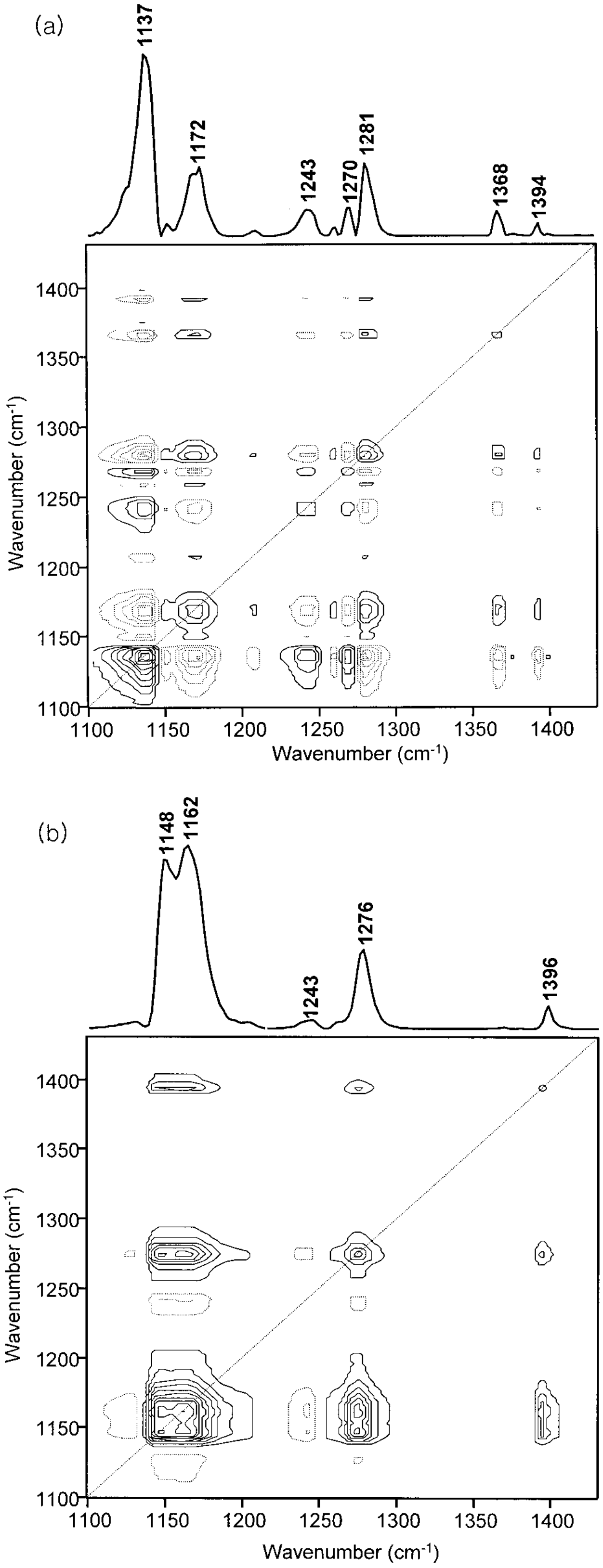

FIG. 5. Synchronous 2D correlation and power spectra of the LB film of PtBMA (**a**) below the glass transition temperature (26–66 °C) and (**b**) above the glass transition temperature (93–136 °C). Solid and dashed lines represent positive and negative cross peaks, respectively.

this band is potentially the mechanism underlying the β-transition. Thus, our results for PtBMA support the second of the two hypotheses given above.[26] This conclusion is also in good agreement with the presence of a transition (β-transition) at approximately 43 °C from the band at 1137 cm^{-1} in the 2D plot of the first derivative of A with respect to T (Fig. 2). Furthermore, the synchronous 2D correlation spectrum (Fig. 5b) constructed from the data set measured above the glass transition temperature is nearly identical to the previously reported spectrum that was created using all of the data (i.e., from 26 to 130 °C).[25] It reveals that overall intensity changes of all bands in the spectral region of 1100–1430 cm^{-1} with the temperature (26–130 °C) occur practically above the glass transition temperature.

CONCLUSION

This contribution gives a description of the application of two different methods to determine the glass transition temperature of an LB film of PtBMA from external reflection FT-IR spectra. The glass transition of a polymeric material is usually accompanied by considerable changes in the mobility of the polymer. From the viewpoint of FT-IR spectroscopy, these changes in mobility manifest as changes in the intensities of absorption bands, which can be analyzed to elucidate the molecular behavior at the glass transition temperature. The 2D map of the first derivative of absorbance with respect to temperature, which is plotted as a function of wavenumber and temperature, enabled us to determine the glass transition temperature. Glass transition temperature determined by the 2D map was approximately 84 °C. 2D mapping provides another transition at 103 °C, corresponding to the glass transition temperature of bulk PtBMA. PCA was successfully applied to determine the glass transition temperature by finding the point with the largest change from the PC2 and PC3 scores of the temperature-dependent FT-IR spectra that preserves almost all of the structural information of the original data. Plots of the loading vectors of PCA provided useful information about the transition processes occurring in the polymer thin film, suggesting hidden properties of the glass transition temperature.

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