Two-Dimensional Gradient Mapping Technique Useful for Detailed Spectral Analysis of Polymer Transition Temperatures

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This paper demonstrates the potential of a two-dimensional (2D) gradient mapping technique that utilized the eigenvalue manipulating transformation (EMT) of the spectral data set. The EMT technique, by lowering the power of a set of eigenvalues associated with the original data, enhances the contributions of minor principle components (PCs). The operation converts the original spectral data set to the one with subtle differences among the responses of the system being exaggerated. Small shoulders and obscure minor features may become much more visible, because such small differentiating features are often captured only by the minor PCs enlarged by the EMT treatment. This improvement for 2D mapping is potentially very important to determine the transition temperatures, which are not readily detected in convention spectral analysis.

Introduction

Study of thermal properties of polymers is of great importance due to a broad range of temperatures they are subjected to in applications. Thus, a number of methods have been developed to measure the transition temperatures of polymers by using optical probes such as X-ray reflectivity,[1,2] ellipsometry,[2−5] positron lifetime spectroscopy,[6] Brillouin light scattering,[7,8] optical waveguide spectroscopy,[9] and FTIR spectroscopy.[10,11] FTIR spectroscopy is an important technique to determine the glass temperature of polymers. In general, abrupt changes in the intensity of bands in FTIR spectra, which contain information of the polymer conformation, are often observed below and above the glass transition temperature. Such intensity changes are generally attributed to a large change in polymer chain mobility around the glass transition. However, the exact temperature at which the intensities of pertinent bands sensitive to the polymer conformation change most rapidly is not obvious from the conventional FTIR spectra. It is often difficult to estimate the extent of the intensity change of a specific band in a certain temperature range.

We have recently proposed a new two-dimensional (2D) data display scheme to determine transition temperature of polymers.[12,13] In this scheme, a set of spectra $A(\nu, T)$, where ν is the wavenumber and T is the temperature, are differentiated with respect to T to create a new data set corresponding to the first derivatives of the form dA/dT. This 2D gradient mapping representation that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature versus wavenumber provides a surprisingly simple and direct method for detecting the transition temperatures.[12−14] The construction of such a plot helps to directly visualize the entirety of complex spectral events occurring during a transition phenomenon. Most importantly, it exploits the selectivity of individual IR bands to allow the observer to easily and quickly draw connections between the macroscopic transition phenomenon and the molecular-scale responses. The location of the minima or maxima in a 2D gradient map enables us to observe changes in molecular environment experienced by different chemical moieties associated with the IR absorption at specific wavenumbers which are undergoing the transition process.[12−14]

However, this technique often suffers from the limitation of somewhat lower resolution power. Typical 2D gradient plots, compared to the conventional 2D correlation spectra[14−19] or moving window 2D map,[20,21] have a higher level of feature overlap which makes the differentiation of peaks more difficult. To overcome the shortcoming of the traditional 2D gradient mapping, we propose a new approach of the 2D mapping technique that utilizes the eigenvalue manipulating transformation (EMT) of the spectral data set.

Generalized 2D correlation spectroscopy is a well-established analytical technique that provides considerable utility and benefit in various spectroscopic studies of polymers.[14−19] We have recently proposed a very powerful modification of generalized 2D correlation spectroscopy to improve the data quality for 2D correlation analysis, which is the incorporation of multivariate chemometrics techniques.[22−26] The principal component analysis based 2D correlation spectroscopy (PCA2D) is one of the effective methods to improve the data quality for 2D correlation analysis. It shows, for example, a great advantage of the noise suppression for the generalized 2D correlation spectroscopy.[22,26] We formulated the reconstructed data matrix $\mathbf{A^*}$ ($\mathbf{A^* = WV^T}$), which no longer contains the residual (i.e., noise) contributions, from a few selected significant scores and loadings derived from PCA of the original set of perturbation-dependent spectra $\mathbf{A}$. Here, $\mathbf{W}$ and $\mathbf{V}$ are, respectively, the matrices of score and loading vectors. The notation $\mathbf{V^T}$ stands for the transpose of $\mathbf{V}$. The reconstructed data matrix, $\mathbf{A^*}$, obtained by the product of score and loading vectors of a few selected principal components, is used instead of the original raw spectral data matrix, $\mathbf{A}$, for a subsequent 2D correlation analysis.

Recently, we have proposed an idea of *eigenvalue manipulating transformation* for further improving the generalized PCA2D correlation analysis.[15,19,23−25] The PCA-reconstructed data matrix

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A* can be expressed by a singular value decomposition (SVD) as $\mathbf{A^*} = \mathbf{USV^T}$. Here, **U**, **S**, and **V** are, respectively, the orthonormal matrix of left singular vectors (i.e., eigenvectors of $\mathbf{A^*A^{*T}}$), the diagonal singular value matrix, and the matrix of right singular vectors (i.e., eigenvectors of $\mathbf{A^{*T}A^*}$), which are equivalent to the loading vectors. $\mathbf{S} = (\mathbf{W^TW})^{1/2}$ is a diagonal matrix, where each diagonal element corresponds to the positive square root of a principal component eigenvalue. In EMT, a new reconstructed data matrix $\mathbf{A^{**}} = \mathbf{US^{**}V^T}$, which is obtained by manipulating and replacing eigenvalues of **A***, is used instead of **A*** for the calculation of enhanced 2D correlation spectra. Here, **S**** is given by varying the corresponding eigenvalues in S by raising or lowering them to the power of *m*, as $\mathbf{S^{**}} = \mathbf{S}^m$.

The EMT operation changes the emphasis of features contained in the original data set. For example, by uniformly raising the power of a set of original eigenvalues, the influence of factors associated with major eigenvalues becomes more prominent, whereas the minor eigenvectors primarily arising from the noise component are no longer strongly represented. Thus, this transformation of the data matrix becomes a gradual noise reduction scheme with attractive flexibility of continuously fine-tuning the balance between the desired noise suppression and retention of pertinent spectral information. The noise contributions, however, are already substantially suppressed by the original PCA-based data reconstruction using a limited number of principal components. By uniformly lowering the power of a set of eigenvalues associated with the original data, the smaller eigenvalues now becomes more prominent and the contributions of minor components become amplified. More subtle difference of spectral behavior for each component is now highlighted. Modification of 2D correlation spectra may be possible to selectively enhance certain correlational features, by systematically manipulating the eigenvalues which are nothing but weight factors of information contribution to the reconstructed data matrix.

In this contribution, we demonstrate a new approach to 2D gradient mapping that utilizes the EMT technique by lowering the power of a set of eigenvalues associated with the original data. To highlight the practical benefit of this new technique, we applied this technique to the FTIR spectra of spin-coated film of poly(methyl methacrylate) (PMMA) during the heating process. The EMT operation which enhances the contributions of minor principle components (PCs) will convert the original spectral data set to the one with subtle but important differences among the responses of the system being exaggerated. Small shoulders and obscure minor features may become much more visible, because such small differentiating features are often captured only by the minor PCs enlarged by the EMT treatment.

Experimental Section

We purchased atactic PMMA (tacticity: syndio 56%, hetero 38%, iso 6%; MW 120 000) from Aldrich Chemical Co. Ltd. Gold-coated silicon wafers from Lance Goddard Associate (U.S.A.) were used as the substrates for spin coating. 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 spin coating. To prepare the spin-coated films, about 1 wt % PMMA solution dissolved in toluene was spun onto a Au-coated silicon wafer at 1000 rpm for 30 s. The thickness of the PMMA thin film was 280 Å.

FTIR spectra were recorded at a spectral resolution of 4 cm^{-1} and at intervals of 10 °C in the range of 30−140 °C with a Bomem DA8 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector. The Seagull attachment (Harrick Scientific Corporation), 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 coadded. Although the FTIR spectra of the polymer thin films were recorded between 450 and 4000 cm^{-1}, only the region between 1100 and 1300 cm^{-1} is described in detail in this paper. The sample and source compartments were evacuated to 0.8 Torr. The first derivative of the spectral intensity with respect to temperature was calculated using the software of MATLAB (The Math Works Inc.).

Prior to PCA calculation, the mean centering operation was applied to the data matrix. To preserve the amplitude information of the variation of spectral intensities, which becomes important later for 2D correlation analysis, other steps commonly used in PCA, such as normalization scaling of data according to the standard deviation, were not carried out. PCA analysis was performed in the Pirouette software (Infometrix Inc.). Synchronous and asynchronous 2D correlation spectra were obtained using the same software as those described previously.[14,18,19,22−26] EMT-*reconstructed* spectral data and gradient 2D maps were also obtained using the software of MATLAB (The Math Works Inc.).

Results and Discussion

The temperature-dependent reflection−absorption FTIR spectra of atactic PMMA spin-coated film on the gold surface obtained during the heating process in the region of 1100−1300 cm^{-1} are shown in Figure 1. The absorption bands in that region are known to be assigned to the ν_a(C−C−O) mode coupled to the ν(C−O) mode and are believed to be very sensitive to conformational changes. Abrupt changes in the intensity of bands are observed below and above the glass transition and are generally attributed to a large change in polymer chain mobility at the glass transition, resulting in significant bond reorientation.[12] We have determined the glass transition temperature of the polymer thin films using a 2D gradient mapping representation that plots the values of the first derivatives of the absorbance with respect to temperature over the space of temperature versus wavenumber on a single map. Such 2D mapping representation indicates the exact temperature at which the intensities of pertinent bands sensitive to the polymer conformation change most rapidly. Such changes are not always obvious from the conventional 1D FTIR spectra. The glass transition temperature determined from 2D mapping representation of atactic PMMA thin film was 106 °C.[12]

To identify the thermal behavior of atactic PMMA thin film more closely, we applied PCA2D correlation spectroscopy to the temperature-dependent IR spectra of an atactic PMMA thin film. We formulated a PCA-reconstructed data set with only three significant PCs that have essentially all information needed to describe temperature-dependent IR spectra of atactic PMMA thin film. The reconstruction process successfully truncated the noise component from the original spectra. Figure 2, parts a and b, shows, respectively, the synchronous and asynchronous PCA2D correlation spectra generated from the PCA-reconstructed data. In the synchronous 2D correlation spectrum, we can mainly observe that intensities of bands at 1144, 1173, 1230, and 1262 cm^{-1} increase with the temperature, whereas those at 1157, 1201, and 1277 cm^{-1} decrease. The bands at 1201 and 1230 cm^{-1} are resolved into separate bands at 1189, 1204, 1227, and 1238 cm^{-1} in the asynchronous 2D correlation spectrum (Figure 2b). The existence of these bands is not readily

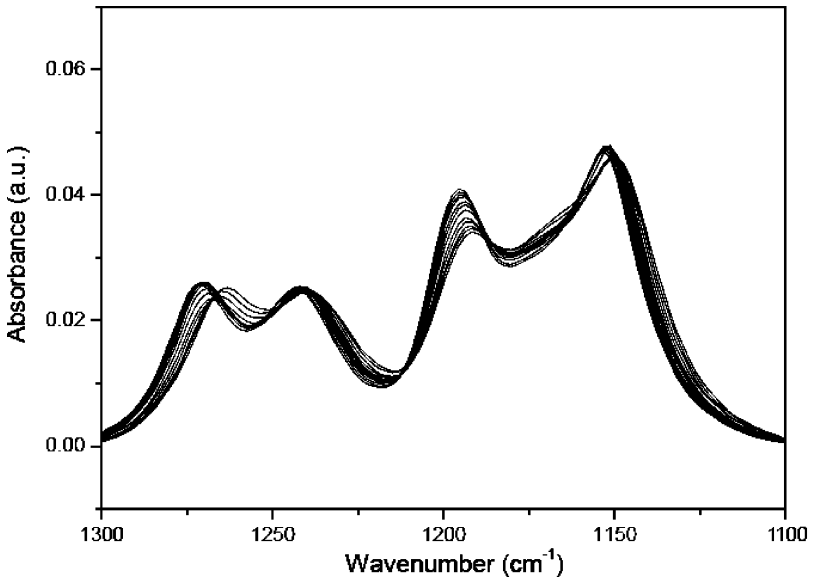

Figure 1. Reflection−absorption FTIR spectra of atactic PMMA thin film on the gold surface obtained during the heating from 30 to 140 °C at an interval of 10 °C in the region of 1100−1300 cm^{-1}.

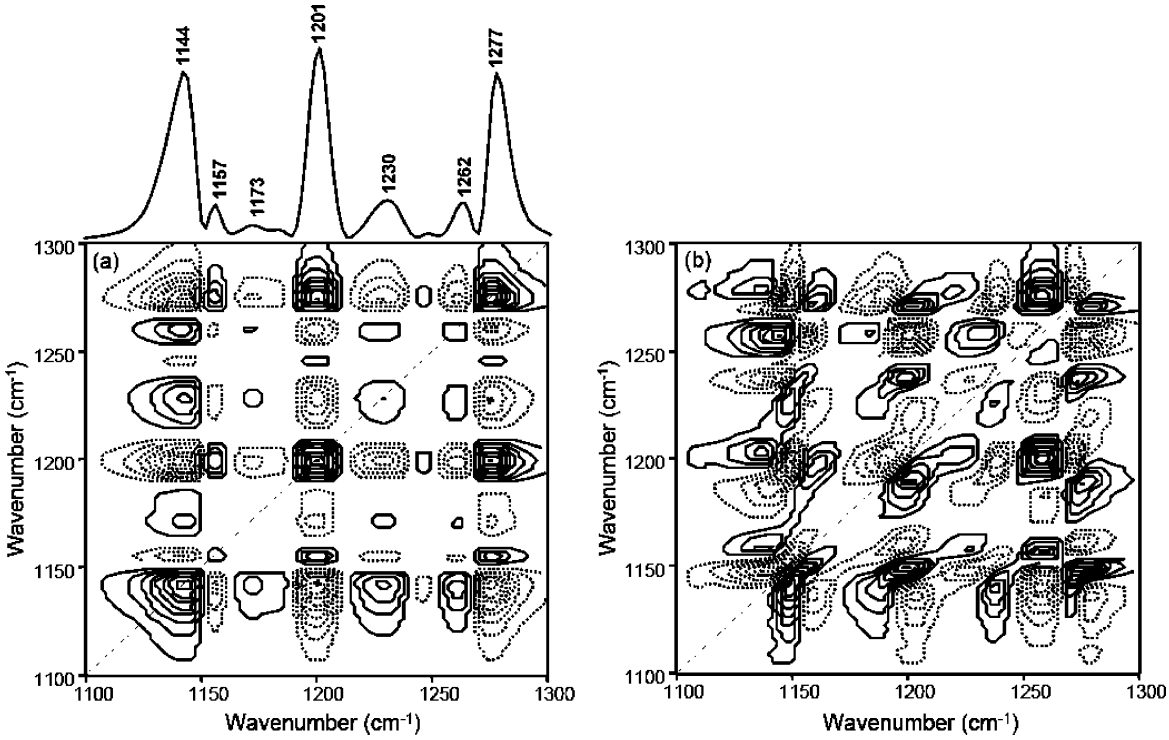

Figure 2. Synchronous (a) and asynchronous (b) 2D correlation spectra obtained using the PCA-reconstructed data from loading vectors and scores of PC1, PC2, and PC3. Solid and dashed lines represent positive and negative cross peaks, respectively.

detectable in the original 1D spectra. The sequence of intensity changes with increasing temperature is 1238 → 1158 → 1279 → 1150 → 1272 → 1227 → 1204 → 1140 → 1260 → 1250 → 1189 cm^{-1}. As indicated previously, it is difficult for each band to be assigned to a specific vibrational mode of a certain functional group. It is known that this spectral range is sensitive to the conformational changes of PMMA. When we examine the previous results, the sequence in intensity change of some bands matches well with some specific phenomena occurring in PMMA chains with increasing temperature. Herein, we only focus on the intensity change of a band at 1158 cm^{-1} occurring prior to those at 1279 and 1272 cm^{-1}. It is speculated that the conformational energy derived at temperatures below T_g refers to the change in conformation of the side group of PMMA, which is concerned with the intensity change of the band around 1154 cm^{-1} in the 1D spectrum.[12] Also, PMMA can undergo substantial molecular reorganization below T_g. The previous 2D gradient mapping study showed that this reorganization coincides with the abrupt changes of the first derivative at 1275 cm^{-1} in the 2D gradient map between 80 and 100 °C.[12] Thus, we believe that a change in the conformation of the PMMA side group precedes the molecular reorganization of PMMA chains.

To better understand the details of the thermal behavior of spin-coated film of PMMA, we performed an EMT operation by lowering the power of a set of eigenvalues associated with the original data. The new EMT-reconstructed data matrix **A**** was used instead of the usual PCA-reconstructed data matrix

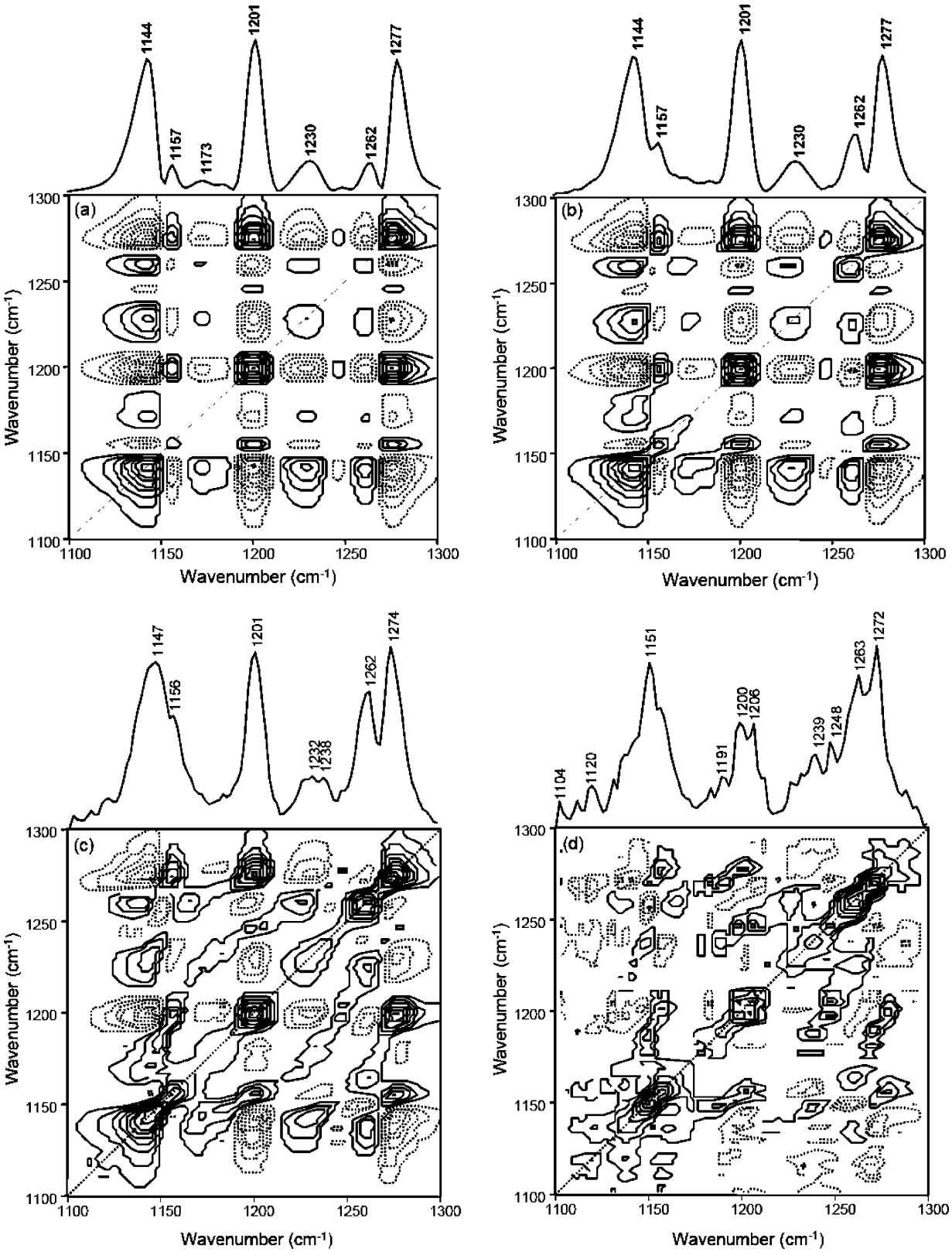

Figure 3. Synchronous PCA2D correlation spectra obtained from the EMT-reconstructed data by varying the value of the power parameter *m*, as $m = 1$ (a), $^1/_2$ (b), $^1/_4$ (c), and 0 (d). Solid and dashed lines represent positive and negative cross peaks, respectively.

A* for the 2D correlation analysis. Such EMT-reconstructed data matrix will emphasize the subtle contributions from minor eigenvectors much more strongly than the original data. Figure 3 shows the synchronous 2D correlation spectra from the newly transformed data matrix **A**** obtained by replacing the eigenvalues of **A***. The corresponding asynchronous 2D correlation spectra are shown in Figure 4. Additional enhanced features were observed in the synchronous 2D correlation spectra from **A****, as we have reported previously.[19,23−25,27] Clearly from Figure 3, changing the power of eigenvalues even from $m = 1$ to $m = {}^1/_2$ or $m = {}^1/_4$ has a very profound effect on the reconstructed spectra. It is noted that if the parameter *m* is 1, the EMT-reconstructed data matrix is the same as the noise-truncated PCA-reconstructed data matrix, i.e., **A**** = **A***. Any

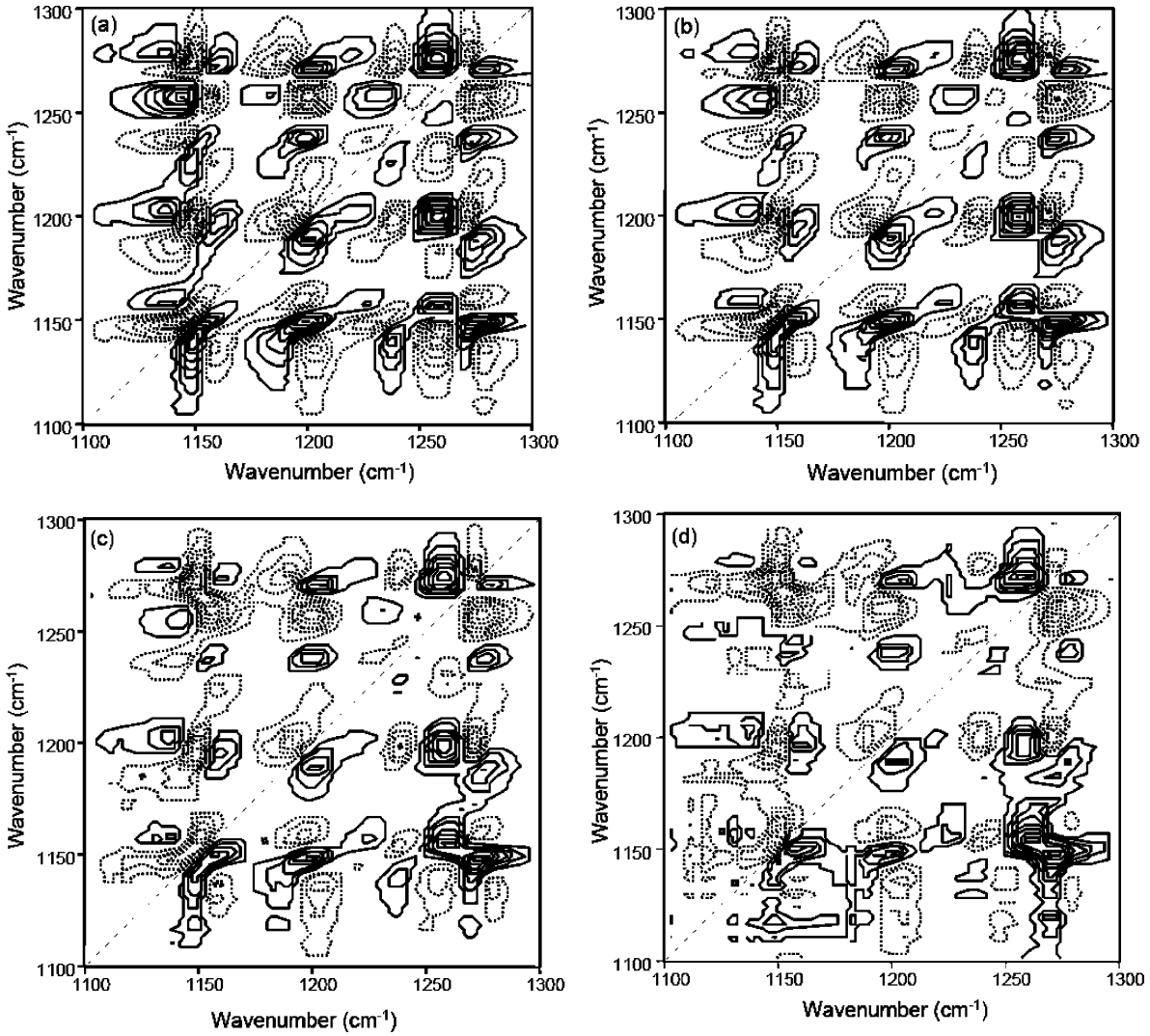

Figure 4. Asynchronous PCA2D correlation spectra obtained from the EMT-reconstructed data by varying the value of the power parameter m, as $m = 1$ (a), $^1/_2$ (b), $^1/_4$ (c), and 0 (d). Solid and dashed lines represent positive and negative cross peaks, respectively.

detectable asynchronicity was already presented in our original 2D correlation spectrum from **A***. Figure 3 clearly shows that by accentuating the minor PCs, the intensity changes of bands at 1262 and 1157 cm^{-1} with temperature are indeed quite significant. The simple PCA2D correlation spectra showed prominent intensity of the band at 1277 cm^{-1}, but the PCA2D correlation spectra with the EMT operation successfully extracted the substantial contribution of the band at 1262 cm^{-1} next to 1277 cm^{-1}. The two bands at 1262 and 1277 cm^{-1} show characteristics for trans and gauche conformation of PMMA spin-coated film. Since the conformational energy of the whole chain segment could be calculated by the van't Hoff equation using the intensities of negative and positive bands of the doublet (1277/1262) cm^{-1} in the difference spectra,[28] probing the two bands at 1262 and 1277 would be important. It is also known that the band at 1157 cm^{-1} coupled to one at 1144 cm^{-1} as a doublet reflects conformational change of the side chains. The PCA2D result modified by EMT extracted the substantial contribution of the band of 1157 cm^{-1}, which was not an outstanding feature in simple PCA2D. Thus, we believe that this method readily captures small but important intensity changes of bands. Subtle differences in the thermal responses, which are difficult to be observed by conventional 2D correlation analysis, are accentuated much more strongly.

We now introduce an idea of the 2D gradient mapping technique that utilizes the EMT of the spectral data set. Figure 5 shows the 2D gradient map that plots the values of the first derivatives of the absorbance of the EMT-reconstructed spectral data (at $m = {}^1/_2$) with respect to temperature over the space of temperature versus wavenumber on a single map. In this 2D gradient map, we can really detect various wavenumber-specific transition temperatures. By comparing with the corresponding asynchronous spectrum shown in Figure 4b, we can also observe in amazing clarity and resolution that the individual bands resolved by the 2D correlation analysis can also be seen by the gradient mapping. Furthermore, the location of the steepest gradient, which may correspond to a transition temperature, can also be seen very clearly by the gradient map. Accordingly, two transition temperatures at around 65 and 95 °C are determined in the gradient map because most of the bands experience severe intensity changes at the transition temperature. The temperature showing the most change of band intensities is 95 °C which is very similar to the glass transition temperature determined by our previous 2D gradient mapping method.[12] The extent of the intensity change at 65 °C is smaller than that at 95 °C, and the temperature may be concerned with movement of side chains below T_g.

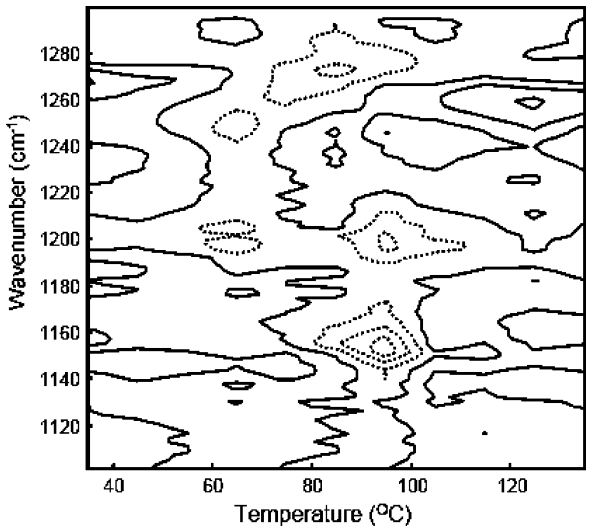

Figure 5. Gradient 2D map that plots the values of the first derivatives of the absorbance of EMT-reconstructed spectral data (at $m = {}^1/_2$) with respect to temperature over the space of temperature vs wavenumber on a single map.

Conclusion

In this study, we have proposed a new 2D mapping technique that utilizes the EMT operation of the spectral data set. The successful application of this new gradient 2D mapping technique to real experimental spectral data was demonstrated. The transition temperatures and the details of thermal behavior of spin-coated film of PMMA were revealed by applying this gradient 2D mapping technique. The steepest gradient is observed at 95 °C for all bands. And another maximum is observed at 65 °C, though this was smaller than that observed at 95 °C. The transition temperature at 95 °C observed in the gradient 2D map is the glass transition temperature of spin-coated film of PMMA. A transition temperature at 65 °C observed in the gradient 2D map is concerned with the movement of side chains below T_g. The gradient 2D map visualized the entirety of complex spectral events occurring during a transition phenomenon much more clearly than the ordinary 2D mapping technique.

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References and Notes

(1) Reiter, G. *Macromolecules* **1994**, *27*, 3046.
(2) See, Y.; Cha, J.; Chang, T.; Ree, M. *Langmuir* **2000**, *16*, 2351.
(3) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
(4) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219.
(5) Grohens, Y.; Brogly, M.; Labbe, C.; David, M.; Schultz, J. *Langmuir* **1998**, *14*, 2929.
(6) Demaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524.
(7) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett*. **1996**, *77*, 2002.
(8) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. B* **1997**, *56*, 5705.
(9) Prucker, O.; Christian, S.; Bock, H.; Ruhe, J.; Frank, C.; Knoll, W. *Macromol. Chem. Phys.* **1998**, *199*, 1435.
(10) Grohens, Y.; Brogly, M.; Labbe, C.; Schultz, J. *Eur. Polym. J*. **1997**, *33*, 691.
(11) Grohens, Y.; Brogly, M.; Labbe, C.; Schultz, J. *Polymer* **1997**, *38*, 5913.
(12) Shin, H. S.; Jung, Y. M.; Oh, T. Y.; Chang, T.; Kim, S. B.; Lee, D. H.; Noda, I. *Langmuir* **2002**, *18*, 5953.
(13) Jung, Y. M.; Shin, H. S.; Czarnik-Matusewicz, B.; Noda, I.; Kim, S. B. *Appl. Spectrosc.* **2002**, *56*, 1568.
(14) Kim, H. J.; Kim, S. B.; Kim, J. K.; Jung, Y. M.; Ryu, D. Y; Lavery, K. A.; Russell, T. P. *Macromolecules* **2006**, *39*, 408.
(15) Jung, Y. M.; Noda. I. *Appl. Spectrosc. Rev.* **2006**, *41*, 515.
(16) Noda, I.; Ozaki, Y. *Two-Dimensional Correlation Spectroscopy: Applications in Vibrational Spectroscopy*; John Wiley & Sons, Inc.: New York, 2004.
(17) Noda, I. *Appl. Spectrosc*. **1993**, *47*, 1329.
(18) Kim, H. J.; Kim, S. B.; Kim, J. K.; Jung, Y. M. *J. Phys. Chem. B* **2006**, *110*, 23123.
(19) Jung, Y. M.; Kim, H. J.; Ryu, D. Y.; Kim, S. B.; Kim, J. K. *J. Mol. Struct.* **2006**, *779*, 96.
(20) Šašic, S.; Katsumoto, Y.; Sato, H.; Ozaki, Y. *Anal. Chem.* **2003**, *75*, 4010.
(21) Watanabe, A.; Morita, S.; Ozaki, Y. *Biomacromolecules* **2006**, *7*, 3164.
(22) Jung, Y. M. *Vib. Spectrosc.* **2004**, *36*, 279.
(23) Jung, Y. M.; Kim, S. B.; Noda, I. *Appl. Spectrosc.* **2003**, *57*, 850.
(24) Jung, Y. M.; Kim, S. B.; Noda, I. *Appl. Spectrosc.* **2003**, *57*, 557.
(25) Jung, Y. M.; Kim, S. B.; Noda, I. *Appl. Spectrosc.* **2003**, *57*, 564.
(26) Jung, Y. M.; Shin, S. H.; Kim, S. B.; Noda, I. *Appl. Spectrosc.* **2002**, *56*, 1562.
(27) Jung, Y. M.; Sato, H.; Noda, I. *Anal. Sci.* **2007**, *23*, 881.
(28) O'Reilly, J. M.; Mosher, R. A. *Macromolecules* **1981**, *14*, 602.