

Application of principal component analysis-based two-dimensional correlation spectroscopy to characterization of order–disorder transition of polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymer

Young Mee Jung ^{a,*}, Hye Jeong Kim ^b, Du Yeol Ryu ^c, Seung Bin Kim ^{d,*}, Jin Kon Kim ^{b,*}

^a Department of Chemistry, Kangwon National University, Chunchon 200-701, Republic of Korea

^b National Creative Research Initiative Center for Block Copolymer Self-Assembly, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

^c Department of Chemical Engineering, Yonsei University, Seoul 120-749, Republic of Korea

^d Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

Received 4 November 2005, received in revised form 7 December 2005; accepted 6 March 2006

Available online 24 April 2006

Abstract

Principal component analysis-based two-dimensional (PCA2D) correlation spectroscopy through eigenvalue manipulating transformation (EMT) of spectral data set was applied to temperature-dependent IR spectra of polystyrene-*block*-poly(*n*-pentyl methacrylate) (PS-PnPMA) for spectral selectivity enhancement. EMT technique which uniformly lowers the power of a set of eigenvalues associated with the original data highlights the subtle contributions from minor eigenvectors. Thus subtle differences in the thermal responses of PS-PnPMA, which are difficult to observe by conventional 2D correlation analysis, are accentuated much more strongly than the original data. A conclusion was reached on details of phase transition of PS-PnPMA which exhibited a closed-loop phase behavior bounded by a lower disorder-to-order transition (LDOT) and an upper order-to-disorder transition (UODT). We found that a disordered state at lower temperature is different from that at higher temperature.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Two-dimensional correlation spectroscopy; PCA2D correlation spectroscopy; Eigenvalue manipulating transformation; Closed-loop block copolymer; Phase transitions

1. Introduction

We have found, via small-angle X-ray scattering (SAXS), rheometry, and depolarized light scattering methods, that polystyrene-*block*-poly(*n*-pentyl methacrylate) [PS-PnPMA] exhibits a closed-loop phase behavior bounded by a lower disorder-to-order transition (LDOT) at lower temperature and an upper order-to-disorder transition (UODT) at higher temperature [1–5]. It is well documented that FTIR spectroscopy is sensitive to conformation and

local molecular environment of polymers [6,7]. We reported that the above two transition temperatures of PS-PnPMA could be measured spectroscopically [8]. The analysis of 2D IR correlation spectra revealed that the conformation of C–C–O group of PS-PnPMA is changed near the transitions and two disordered states occurring at lower and higher temperatures are different [8].

2D correlation spectroscopy is a now well-established technique for interpreting spectral data sets obtained during the observation of spectra with an external perturbation [9–11]. 2D correlation spectra simplify complex spectra consisting of many overlapped peaks, enhance spectral resolution by spreading peaks along the second dimension, establish unambiguous assignments through

* Corresponding authors. Tel.: +82 33 250 8495; fax: +82 33 253 7582.
E-mail address: ymjung@kangwon.ac.kr (Y.M. Jung).

the correlation of bands of selectively coupled by various interaction mechanisms, and determine the sequence of the spectral peak emergence. The details of this technique are described elsewhere [9–11].

To better understand the different characteristics of the two disordered states found in PS-PnPMA more clearly, we employed principal component analysis-based two-dimensional (PCA2D) correlation spectroscopy through eigenvalue manipulating transformation (EMT) of spectral data. We have already reported the potential of PCA2D correlation spectroscopy to improve the data quality for 2D correlation analysis, the great advantage of the noise suppression for generalized 2D correlation spectroscopy [12,13]. We have formulated the reconstructed data matrix \mathbf{A}^* , 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}

$$\mathbf{A}^* = \mathbf{W}\mathbf{V}^T, \quad (1)$$

where \mathbf{W} and \mathbf{V} are a score matrix and a loading matrix, respectively. The notation \mathbf{V}^T stands for the transpose of \mathbf{V} .

The PCA-reconstructed data matrix instead of the original data matrix has been successfully utilized for the calculation of improved 2D correlation spectra. The 2D correlation analysis of this reconstructed data matrix accentuated the most important features of synchronicity and asynchronicity without being hampered by noise. Furthermore, a radically new idea of *eigenvalue manipulating transformation* (EMT) for the generalized PCA2D correlation analysis was demonstrated [14–16]. A new data matrix for the PCA2D correlation analysis was reconstructed from the singular value decomposition (SVD) [17–19] followed by altering the eigenvalues associated with the data set.

The PCA-reconstructed data matrix \mathbf{A}^* is expressed by a singular value decomposition (SVD)

$$\mathbf{A}^* = \mathbf{U}\mathbf{S}\mathbf{V}^T \quad (2)$$

and

$$\mathbf{S} = \mathbf{L}^{1/2}, \quad (3)$$

where \mathbf{U} , \mathbf{S} , and \mathbf{V} are an orthonormal matrix, a diagonal matrix, and a loading matrix, respectively. Here $\mathbf{L} = \mathbf{W}^T\mathbf{W}$ is a diagonal matrix where each diagonal element corresponds to a principal component eigenvalue. The score matrix \mathbf{W} is expressed in the form $\mathbf{W} = \mathbf{U}\mathbf{S}$ and can be obtained directly from $\mathbf{W} = \mathbf{A}\mathbf{V}$.

The total number of PCs used to obtain the PCA-reconstructed data is kept relatively small to minimize the contribution of noise [12,13]. The initial truncation of the noise component becomes especially important in the current EMT operation, where the contributions from minor PCs are enhanced later.

The new transformed data matrix \mathbf{A}^{**} will be obtained by manipulating and replacing eigenvalues of \mathbf{A}^* as

$$\mathbf{A}^{**} = \mathbf{U}\mathbf{S}^{**}\mathbf{V}^T, \quad (4)$$

where \mathbf{S}^{**} is given by varying the corresponding eigenvalues in \mathbf{S} by raising or lowering them to the power of m

$$\mathbf{S}^{**} = \mathbf{S}^m. \quad (5)$$

This new EMT-reconstructed data matrix \mathbf{A}^{**} will be used instead of \mathbf{A}^* for the calculation of enhanced 2D correlation spectra.

By uniformly raising the power of a set of original eigenvalues, the influence of factors associated with major eigenvalues becomes more prominent, while 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. However, by uniformly lowering the power of a set of eigenvalues associated with the original data, the smaller eigenvalues become more prominent and the contributions of minor components become amplified. Thus, much more subtle difference of spectral behavior for each component is now highlighted.

In the present study, we have applied PCA2D correlation spectroscopy with EMT technique by lowering the power of a set of eigenvalues associated with the original data. Thus subtle differences in the thermal responses, which are difficult to observe by conventional 2D correlation analysis, are accentuated much more strongly than the original data. We then shed light on understanding the phase behavior of PS-PnPMA.

2. Experimental

PS-PnPMA was synthesized by the sequential, anionic polymerization of styrene and *n*-pentyl methacrylate in tetrahydrofuran (THF) at -78°C under purified argon using *sec*-BuLi as an initiator [1,2]. The number and weight average molecular weights (M_n and M_w) of PS-PnPMA were determined (49,000 and 49,900) by size exclusion chromatography coupled with a multi-angle laser light scattering detector. The volume fraction of the PS block was 0.5.

FTIR spectra were measured at a spectral resolution of 4 cm^{-1} 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 diffuse reflectance FTIR spectra were measured by co-adding 256 scans from 100 to 260°C at an interval of 5°C after the sample was equilibrated for 30 min at the measurement temperature.

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

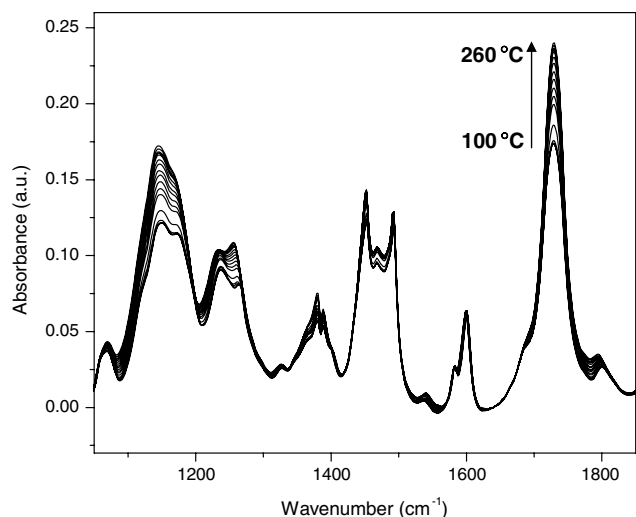


Fig. 1. FTIR spectra of PS-PnPMA during heating from 100 to 260 °C at an interval of 5 °C.

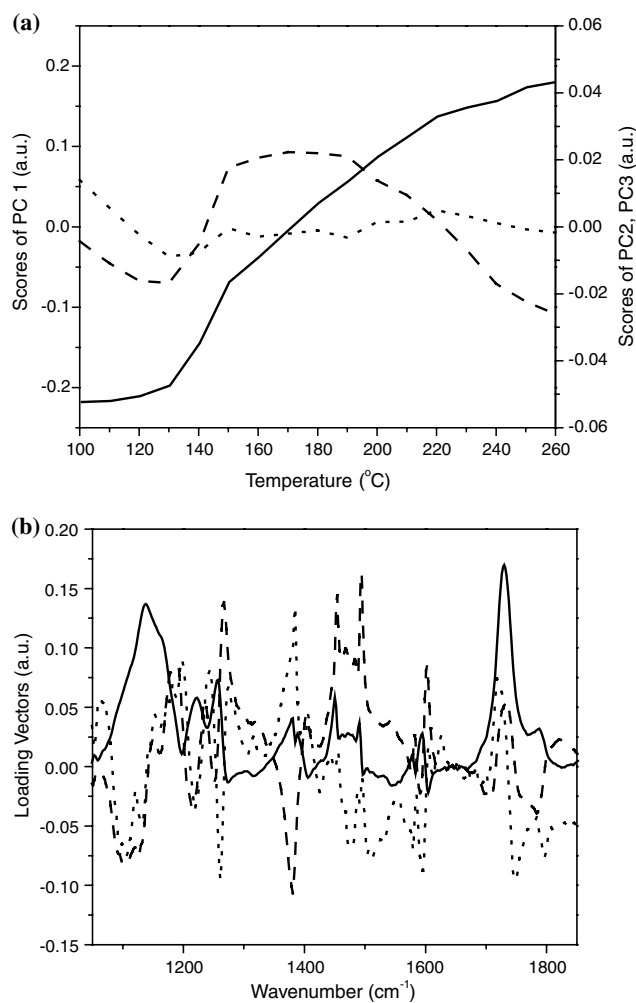


Fig. 2. (a) Score plots of PC1 (solid line), PC2 (dashed line), and PC3 (dotted line) versus temperature obtained from FTIR spectra of PS-PnPMA. (b) Plots of loading vectors of PC1, PC2, and PC3 versus wavenumber.

of data according to the standard deviation were not carried out. PCA was performed in the Pirouette software (Infometrix Inc.).

Synchronous and asynchronous PCA2D correlation spectra were obtained by using the same software as described previously [11–16]. To minimize the interfering noise effect in the EMT operation, only the dominant three principal components are used, and the rest are truncated, in this study.

3. Results and discussion

Fig. 1 shows the temperature-dependent IR spectra of PS-PnPMA measured during heating from 100 to 260 °C at an interval of 5 °C. The original spectral data set in Fig. 1 was decomposed into the scores and loading vectors by standard PCA. The plots of scores and loading vectors of PCs are shown in Figs. 2a and b, respectively. PCA

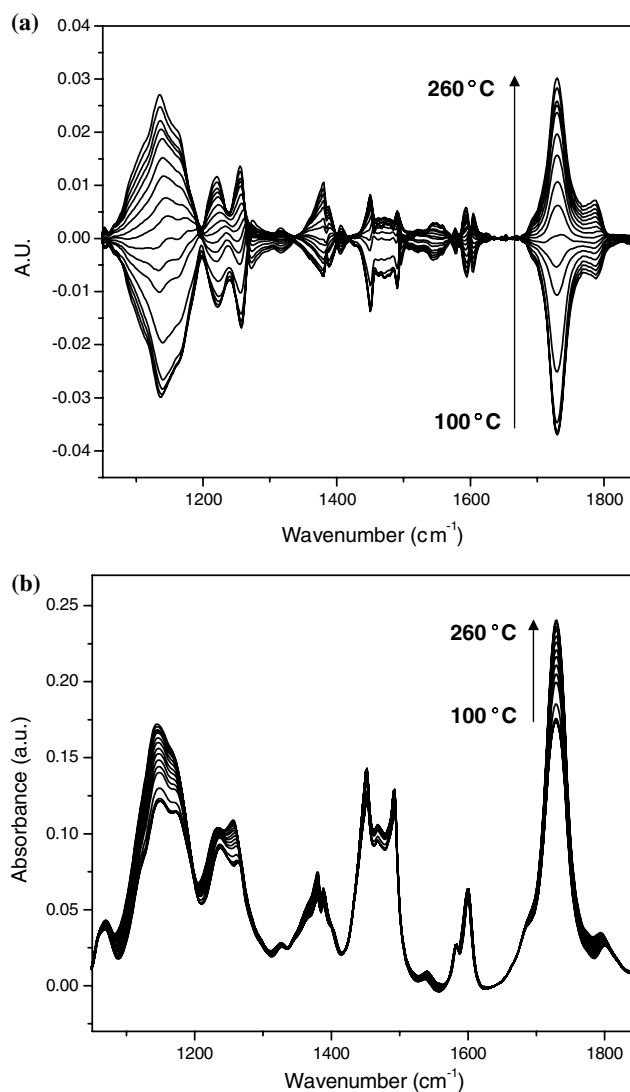


Fig. 3. (a) Mean-centered and (b) base-centered (i.e., average added back) spectra of the reconstructed data from loading vectors and scores of PC1, PC2, and PC3.

factor 1 (PC1), factor 2 (PC2), and factor 3 (PC3) account for 98.4%, 1.3%, and 0.2%, respectively, of the total variance of spectral intensities along the time axis. The recon-

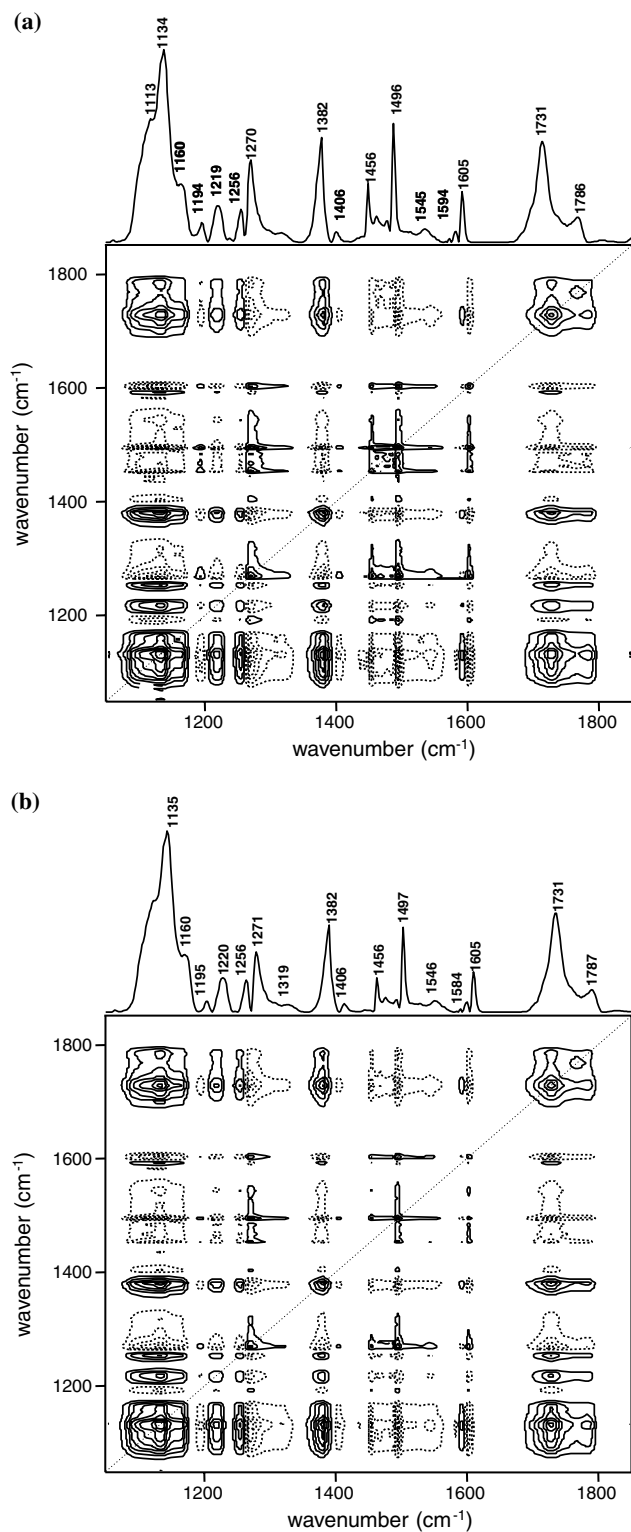


Fig. 4. Synchronous 2D correlation spectra obtained from the raw spectra in Fig. 1 for disordered states in lower (a) and higher (b) temperatures. Solid and dashed lines represent positive and negative cross peaks, respectively.

structed data matrix \mathbf{A}^* obtained by Eq. (1) from the three principal components was used instead of the original raw spectral data matrix \mathbf{A} for the subsequent 2D correlation analysis. Fig. 3a depicts mean-centered spectra of the reconstructed data represented in the matrix \mathbf{A}^* from loading vectors and scores of PC1, PC2, and PC3. Fig. 3b shows the PCA-reconstructed spectra with average spectrum added back to make a meaningful comparison to Fig. 1. We found clearly that the reconstructed spectra (Fig. 3b) are virtually indistinguishable from the original spectra (Fig. 1), suggesting that most of the pertinent information is retained in the PCA-reconstructed data.

Since synchronous 2D correlation spectra constructed from these raw spectra are already reported [8], the interpretation of conventional synchronous 2D correlation spectra is not further discussed. In this study, we focus on the potential of PCA2D correlation spectroscopy with EMT for specific spectral enhancement. For comparison, conventional synchronous 2D correlation spectra for two disordered states are shown in Fig. 4. Fig. 5 shows the spectrum of the new reconstructed data obtained by replacing eigenvalues with $m = 1/2$. Synchronous 2D correlation spectra generated from the EMT-reconstructed spectral data matrix \mathbf{A}^{**} obtained by replacing the original eigenvalues with $m = 1/2$ for disordered state at lower temperature, ordered state, and disordered state at higher temperature are shown in Fig. 6a–c, respectively. By lowering the power of a set of eigenvalues associated with the original data, the contribution of the minor but potentially interesting factors such as hidden property of phase transition is greatly accentuated compared with conventional 2D correlation spectra. As shown in Fig. 6, the EMT effect for spectral selectivity enhancement is very much apparent. The synchronous spectrum of the ordered state is completely different from those in the two disordered states. These results are in a good agreement with our previous

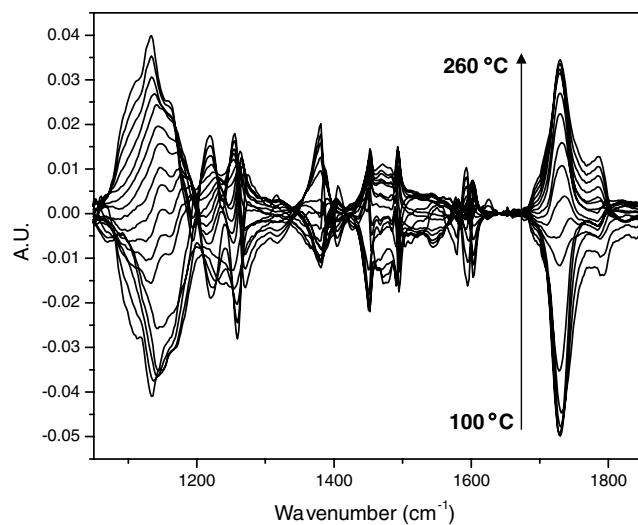


Fig. 5. Spectrum of the new reconstructed data obtained by replacing eigenvalues with $m = 1/2$.

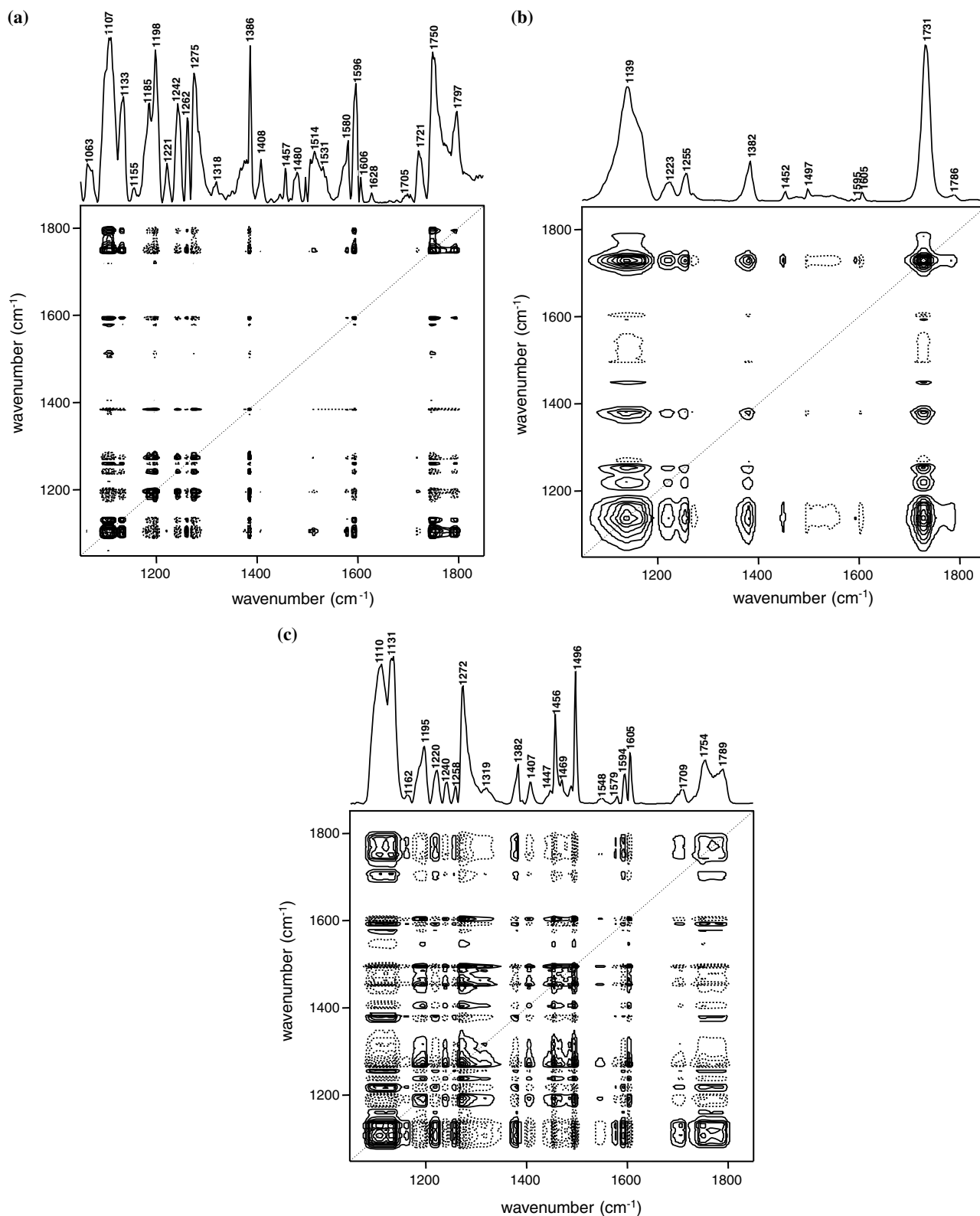


Fig. 6. Synchronous PCA2D correlation spectra obtained from the EMT reconstructed data with $m = 1/2$ for disordered state in lower temperature (a), ordered state (b), and disordered state in higher temperature (c), respectively. Solid and dashed lines represent positive and negative cross peaks, respectively.

2D correlation analysis [8]. When the EMT effect is included, the synchronous spectra for two disordered states are also clearly different. The intensity of peaks located at the

diagonal positions in the synchronous 2D spectrum represents the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external

perturbation is applied to the system. The power spectrum, extracted along the diagonal line of the synchronous 2D correlation spectrum, given in the top of Fig. 6a and c, reveals that the intensity changes with temperature for bands at 1185, 1198, 1386, 1596, 1721, and 1750 cm^{-1} at lower temperatures are larger than those at higher temperatures. On the other hand, the intensity change with temperature for bands at 1496 and 1456 cm^{-1} , assigned to phenyl ring stretching of PS, at lower temperatures is smaller than that at higher temperatures. Intensities of bands from C–C–O stretching, C–H deformation, and C=O stretching of PnPMA and those from phenyl ring of PS change greatly at lower and higher temperatures, respectively. The distinct differences in two disordered states in the cross correlations of the bands from phenyl group in PS with that from C–C–O group in PnPMA are clearly observed. These results again confirm that the conformation of PS-PnPMA in the two disordered states is different, and that the weak directional interaction between phenyl group of PS and the side chain of PnPMA in the two disordered states is different. This kind of difference was not clearly observed in conventional 2D correlation spectra, as shown in Fig. 4. Therefore, the EMT technique with even $m = 1/2$ could distinguish the very subtle differences of spectra which are not detected by conventional 2D correlation spectra.

4. Conclusion

We have demonstrated in this study that the phase behavior of PS-PnPMA is more clearly understood by using PCA2D correlation spectroscopy through EMT technique. The PCA2D correlation spectra for the EMT-reconstructed spectral data matrix \mathbf{A}^{**} , obtained by replacing the original eigenvalues with the power parameter $m = 1/2$, positively identified and confirmed that two disordered states in lower and higher temperatures are completely different, which is not clearly demonstrated in conventional 2D correlation spectra. The PCA2D correlation analysis through the EMT technique becomes a complementary technique to conventional 2D correlation analysis to identify the hidden features in the original spectra.

Acknowledgements

This work was supported by the National Creative Research Initiative Program supported by KOSEF. Y.M. Jung acknowledges the support from the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-204-C00031).

References

- [1] D.Y. Ryu, U. Jeong, J.K. Kim, T.P. Russell, *Nat. Mater.* 1 (2002) 114.
- [2] D.Y. Ryu, U. Jeong, D.H. Lee, J. Kim, H.S. Youn, J.K. Kim, *Macromolecules* 36 (2003) 2894.
- [3] D.Y. Ryu, M.S. Park, S.H. Chae, J. Jang, J.K. Kim, T.P. Russell, *Macromolecules* 35 (2002) 8676.
- [4] D.Y. Ryu, D.J. Lee, J.K. Kim, K.A. Lavery, T.P. Russell, Y.S. Han, B.S. Sung, C.H. Lee, P. Thiyagarajan, *Phys. Rev. Lett.* 90 (2003) 235501.
- [5] D.Y. Ryu, D.H. Lee, U. Jeong, S.H. Yun, S. Park, K. Kwon, B. Shon, T. Chang, J.K. Kim, T.P. Russell, *Macromolecules* 37 (2004) 3717.
- [6] H.S. Shin, Y.M. Jung, T. Chang, Y. Ozaki, S.B. Kim, *Langmuir* 18 (2002) 5523.
- [7] Y.M. Jung, H.S. Shin, B. Czarnik-Matuszewicz, I. Noda, S.B. Kim, *Appl. Spectrosc.* 56 (2002) 1568.
- [8] H.J. Kim, J.K. Kim, S.B. Kim, Y.M. Jung, D.Y. Ryu, *Macromolecules* 39 (2006) 408.
- [9] I. Noda, *Appl. Spectrosc.* 47 (1993) 1329.
- [10] I. Noda, A.E. Dowrey, C. Marcott, G.M. Story, Y. Ozaki, *Appl. Spectrosc.* 54 (2000) 236A.
- [11] I. Noda, Y. Ozaki, *Two-Dimensional Correlation Spectroscopy: Applications in Vibrational Spectroscopy*, John Wiley, New York, 2004.
- [12] Y.M. Jung, S.H. Shin, S.B. Kim, I. Noda, *Appl. Spectrosc.* 56 (2002) 1562.
- [13] Y.M. Jung, *Vib. Spectrosc.* 36 (2002) 279.
- [14] Y.M. Jung, S.B. Kim, I. Noda, *Appl. Spectrosc.* 57 (2003) 557.
- [15] Y.M. Jung, S.B. Kim, I. Noda, *Appl. Spectrosc.* 57 (2003) 564.
- [16] Y.M. Jung, S.B. Kim, I. Noda, *Appl. Spectrosc.* 57 (2003) 850.
- [17] E.R. Malinowski, *Factor Analysis in Chemistry*, second ed., Wiley, New York, 1991.
- [18] H. Martens, T. Næs, *Multivariate Calibration*, John Wiley, New York, 1991.
- [19] B.G.M. Vandeginste, D.L. Massart, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, *Handbook of Chemometrics and Qualimetrics: Part B*, Elsevier Science B.V., Amsterdam, The Netherlands, 1998.