Transition temperatures and molecular structures of poly(methyl methacrylate) thin films by principal component analysis: comparison of isotactic and syndiotactic poly(methyl methacrylate)

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Abstract

This study determines the glass transition temperatures of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) thin films and provides plausible molecular origins by principal component analysis (PCA). Principal components (PCs) are calculated for reflection–absorption FTIR spectra of isotactic and syndiotactic PMMA thin films in two spectral regions, 1000–1800 and 1100–1300 cm^{-1}. The glass transition temperature is assigned to the highest peak (or the lowest valley) in the PC score plot. The glass transition temperatures of isotactic and syndiotactic PMMA thin films thus determined are 60 and 110–120 °C, respectively, which are consistent with existing results obtained by other techniques. The PC loadings indicate that the carbonyl groups giving rise to bands in the range of 1700–1750 cm^{-1} affect the thermal properties and the flattened structure in the isotactic PMMA thin film but not in the syndiotactic PMMA thin film.
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1. Introduction

A number of methods have been developed to measure the glass transition temperatures of polymer thin films 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 has shown particular promise as a technique for measuring the glass transition temperature of polymers. The utility of FTIR stems from the specificity of the IR probe to different submolecular and segmental constituents of polymeric systems, which gives a unique capacity to elucidate the molecular origin of transition phenomena.

Principal component analysis (PCA) is a multivariate analysis technique that reduces the dimensionality of a data set [12–14]. Previously, PCA has been applied to liquid chromatographic data to select the number of compounds necessary to detect differences in stationary phases [15], and has been used to investigate the relationship between carboxylate selectivity and the concentration ratio of sodium bicarbonate to carbonate [16]. PCA has proved to be a very useful technique for extracting a pure component from several kinds of spectra, including near infrared (NIR),

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UV–vis, electron paramagnetic resonance (EPR), and FTIR [17–25]. PCA has been used to detect minute bands in the FTIR spectrum of a mixture [22,23]. Hasegawa et al. [25] applied PCA to the angle-resolved ATR FTIR spectra of water, and then evaluated the orientation of the water molecules using the plots of the loading vectors of the three significant PCs. Their analysis revealed the existence of an intermediate layer between the boundary water layer and bulk water. Iwata et al. [20] showed using PC loading vectors that the OH band of liquid water consists of two components. Recently, we successfully employed PCA to determine the glass transition temperature from the temperature-dependent FTIR spectra of poly(*tert*-butyl methacrylate) Langmuir–Blodgett Film [26].

In this paper, we determine the glass transition temperature of poly(methyl methacrylate) (PMMA) thin films by PCA. The results presented here show that the glass transition temperature of PMMA thin films can be identified in the low-dimensional PC space, and that this space preserves almost all of the structural information of the original data.

2. Experimental

2.1. Film preparation

Isotactic PMMA (tacticity > 80%, MW 300,000) from Aldrich Chemical Co. Ltd., and syndiotactic PMMA (tacticity: 85%; MW 50,000) from Scientific Polymer Products, Inc., were used. Au-coated silicon wafers from Lance Goddard Associate (USA) were used as the substrates for spin coating. All substrates were cleaned with fresh piranha solution (30% H_2O_2 mixed with concentrated H_2SO_4 in 1:5 ratio) prior to spin coating. Spin-coated films were prepared by spinning a PMMA solution (∼1 wt.%) dissolved in toluene onto a Au-coated silicon wafer at 1000 rpm for 30 s. The thicknesses of the isotactic and syndiotactic PMMA thin films determined from ellipsometry were 371 and 228 Å, respectively.

2.2. FTIR spectra

FTIR spectra were recorded at a spectral resolution of $4 \, cm^{-1}$ with a Bomem DA8 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector. Spectra were recorded at intervals of 10 °C over the range 30–140 °C for isotactic PMMA and 30–160 °C for syndiotactic PMMA. The Seagull Attachment (Harrick Scientific Corporation) with a heating block was used in this study. All reflection–absorption FTIR spectra were obtained using *p*-polarized radiation at an incidence angle of 82°. To ensure a high signal-to-noise ratio, 1024 scans were added. The sample and source compartments were evacuated to 0.8 Torr. Baseline correction was performed for FTIR spectra prior to the calculation for PCA.

3. Method for determining T_g using PCA

Spectral data can be expressed and visualized in a low-dimensional space with new orthogonal bases. It is much easier to predict chemical properties and determine chemical constituents from a few PC scores than from the raw spectral data. A change in the direction (from negative value to positive one or inverse) of a PC score at some temperature implies that some chemical property changes at that point. We assign T_g to the temperature at which the highest peak occurs in the absolute PC score plot, i.e., the point at which the most significant change occurs in terms of magnitude and direction. Formally, we propose to assign T_g to the temperature at which $|f_i(T_j)|$ is maximized subject to $[f_i(T_{j-1}) - f_i(T_j)][f_i(T_{j+1}) - f_i(T_j)] \geq 0$, where T_j is the *j*th temperature and $f_i(T)$ is the *i*th PC score at temperature *T*.

We use mean-centered data because the variance of the absorbance at each wavenumber may be important. The first PC score is a weighted average of the absorbance levels at all wavenumbers and accounts for the majority of the total variance. Thus, we can determine T_g from the rest of PCs. Calculations and graphing were carried out using the software Pirouette (Infometrix, Inc.).

4. Results and discussion

4.1. Spectral features

Fig. 1 shows the reflection–absorption FTIR spectra of the isotactic and syndiotactic PMMA thin films measured at intervals of 10 °C. It is well documented that bands in the region of 1100–1300 cm^{-1} are sensitive to conformational changes [27,28]. Although the assignments of the bands in this region are not entirely clear, the bands have been assigned to the ν_a(C–C–O) mode coupled to the ν(C–O) mode [27,28]. The sensitivity of the bands in this region to conformational changes led us to undertake two separate analyses: in one analysis we considered the region of 1000–1800 cm^{-1}, which includes the C=O stretching mode in the region of 1700–1750 cm^{-1}, and in the other analysis we considered only the spectral features in the region of 1100–1300 cm^{-1}.

4.2. Glass transition temperature

The mobility of polymers changes substantially at the glass transition from a glassy to a rubbery state. Such changes in the physical properties with changing temperature are reflected in the PC scores. Fig. 2(a and b) show the score plots of the first three PCs (PC1–PC3) for the isotactic and syndiotactic PMMA thin films in the region of 1000–1800 cm^{-1}, respectively. These first three components account for 99.16 and 99.49% of the total variance in the isotactic and syndiotactic PMMA spectral data, respectively (Table 1). The number of PCs to be used in the determination
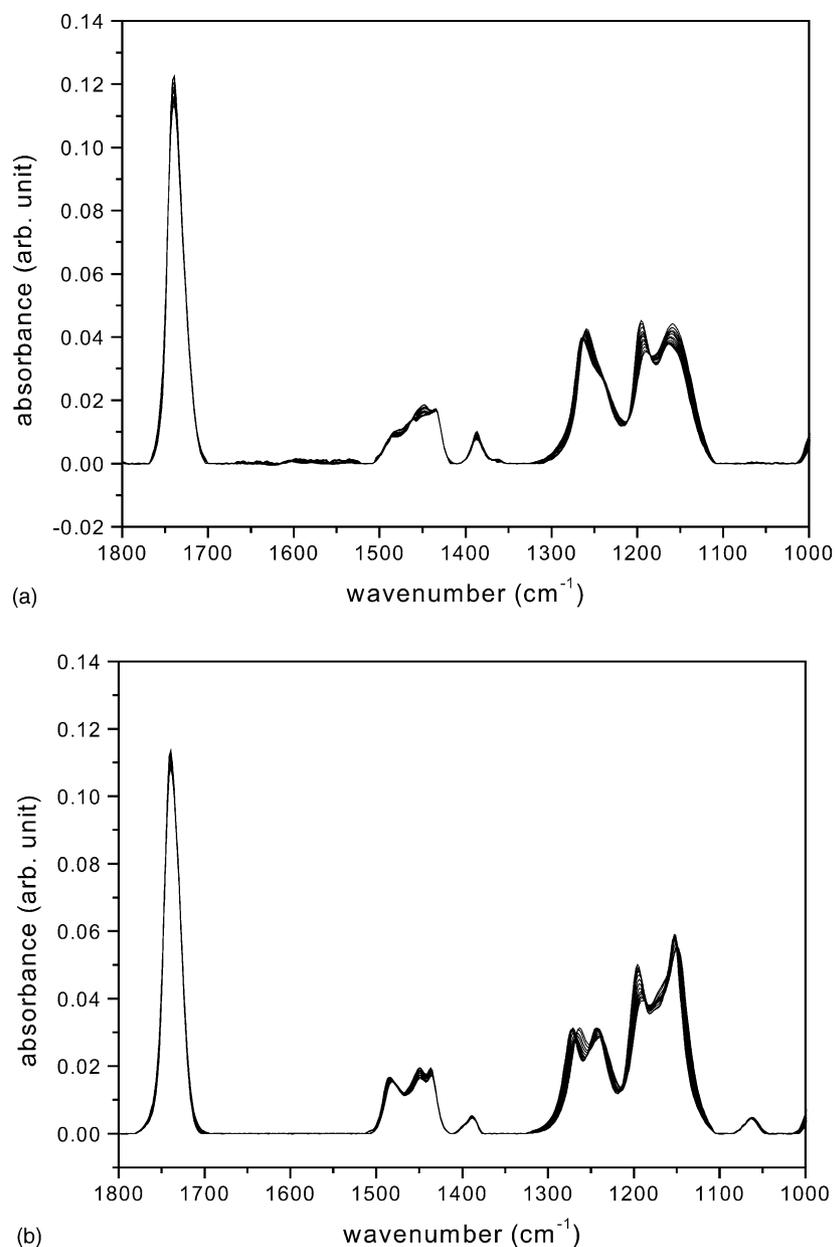
Fig. 1. Reflection–absorption FTIR spectra of (a) isotactic (30–140 °C) and (b) syndiotactic (30–160 °C) PMMA thin films.

of T_g can be decided by considering the proportion of the total variance they explain. Here, we examine the first three PCs because they are sufficient to cover the total variance. PC1 shows the average change of the total variance with increasing temperature. As shown in Fig. 2, PC1 increases monotonically with increasing temperature for both types of thin film. Since the first PC of the spectral data gives little information beyond the average change of the total variance, determining the glass transition temperature is expected to manifest in the behavior of PC2 and PC3. The higher components PC4 and PC5 are unimportant because they capture negligible proportions of the total variance, as shown in Table 1.

In the score plots shown in Fig. 2, the temperatures corresponding to the highest absolute value in the PC plots (T_g) for the isotactic and syndiotactic PMMA thin films are 60 °C [in PC3, Fig. 2(a)] and between 110 and 120 °C [in PC2, Fig. 2(b)], respectively. These results are in agreement with the glass transition temperatures measured previously using other techniques [5,11]. Grohens et al. [5] determined

Table 1
Proportion of the total variance explained by each PC in the two regions

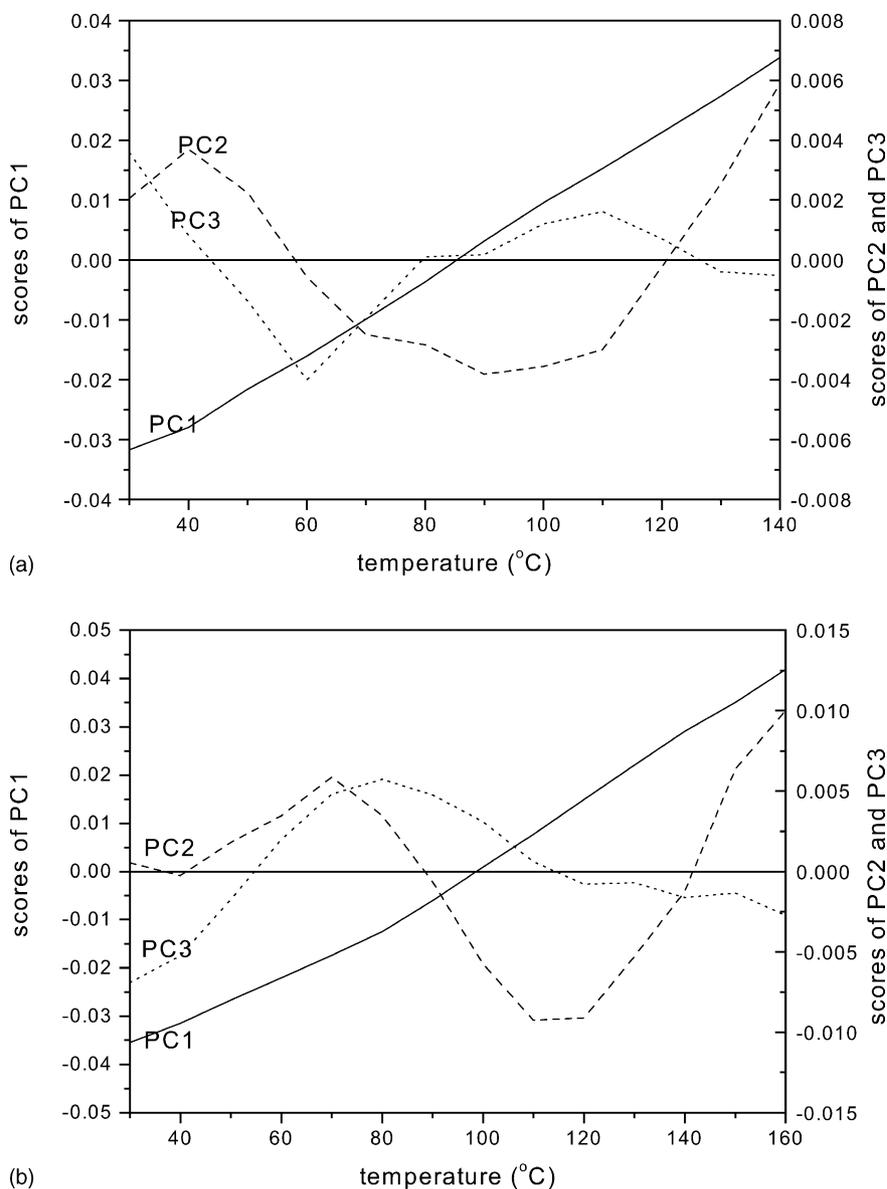| PC	1000–1800 (cm^{-1})		1100–1300 (cm^{-1})	
	Isotactic (%)	Syndiotactic (%)	Isotactic (%)	Syndiotactic (%)
PC1	96.22	92.28	98.40	93.83
PC2	2.14	4.89	0.95	3.53
PC3	0.80	2.32	0.36	2.35
PC4	0.18	0.14	0.05	0.14
PC5	0.15	0.05	0.05	0.03

Fig. 2. Score plots of PC1 (principal component factor 1), PC2 (principal component factor 2), and PC3 (principal component factor 3) for reflection–absorption FTIR spectra of (a) isotactic and (b) syndiotactic PMMA thin films in the region of 1000–1800 cm^{-1}.

the glass transition temperature of isotactic and syndiotactic PMMA thin films using kinetic ellipsometric scans, which measure the change in ellipsometric angle (Δ) with temperature (T). In this method the glass transition temperature is identified as a discontinuity in (dΔ/dT), the slope of the plot of Δ versus T. In addition, FTIR spectroscopy has been used to probe conformational changes in PMMA chains at gold and aluminum surfaces [11]. The results of that work indicated an increase in conformational energy at the surface relative to the bulk. Additionally, it was reported that the basic trend of the temperature dependence of bands related to the conformation of PMMA thin films was the same as that for bulk PMMA, and the glass transition temperature was determined from the discontinuity in the slope of the plot of the logarithm of absorbance versus (1/T).

The second highest peak of PC2 for isotactic PMMA chains appears at 90 °C [Fig. 2(a)]. This secondary change may be due to the behavior of the PMMA chains adsorbed directly on the surface. Grohens et al. [11] found that the glass transition of isotactic PMMA occurs at 60 °C for the bulk and at 90 °C for PMMA adsorbed on an aluminum surface. They suggested that the increase of 30 °C in the value of T_g on adsorption was attributed to the isotactic PMMA chains spreading out on the surface with a large contact area, combined with interactions between the polymer ester groups and the aluminum substrate. Such interactions between ester groups and the surface are very unlikely in the system studied here, because a gold substrate was used. Thus, it is expected that the peak in PC2 at 90 °C results from the flattened structure of isotactic PMMA chains spread out on the gold surface. (This point is discussed later in more detail.) For the

syndiotactic PMMA thin film, the second highest peaks in PC2 and PC3 occur between 70 and 80 °C. These features may be related to the onset of the reorganization process of the syndiotactic PMMA thin film in which the fraction of *gauche* conformers decreases with increasing temperature [29]. The glass transition temperatures determined using PCA are summarized in Table 2.

Fig. 3(a and b) show the score plots of PC1–PC3 for the reflection–absorption FTIR spectra of isotactic and syndiotactic PMMA thin films in the region of 1100–1300 cm^{-1}, respectively. The first three PCs cover 99.71% of the total variance in the spectra of both films (Table 1). The value of T_g for isotactic PMMA in the range 1100–1300 cm^{-1} is at 60 °C, which is consistent with the result obtained from data over the range 1000–1800 cm^{-1}. PC2 displays a minimum at

Table 2
Glass transition temperatures determined by PCA in the two spectral regions

Thin film	1000–1800 (cm^{-1})	1100–1300 (cm^{-1})
Isotactic (°C)	60 (90)	60 (60)
Syndiotactic (°C)	110–120 (70–80)	110–120 (70–80)

Temperature of the second highest peaks are in parentheses.

60 °C (T_g) in the analysis of the region 1100–1300 cm^{-1}, whereas it shows a different pattern in the PCA results from the region 1000 to 1800 cm^{-1}. This dependence on the spectral region used in the calculation arises because the spectral region of 1100–1300 cm^{-1} includes mainly information on physical properties or conformational changes of the PMMA polymers.
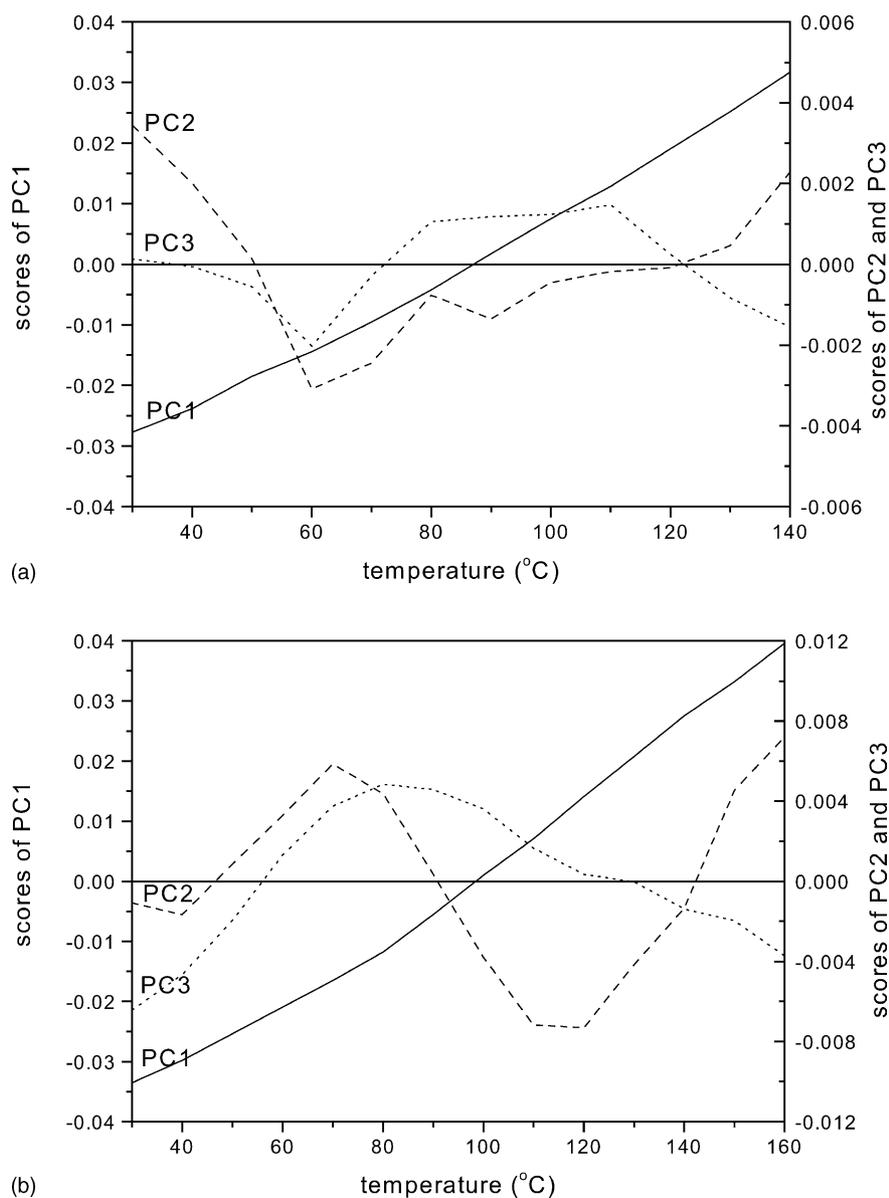

Fig. 3. Score plots of PC1 (principal component factor 1), PC2 (principal component factor 2), and PC3 (principal component factor 3) for reflection–absorption FTIR spectra of (a) isotactic and (b) syndiotactic PMMA thin films in the region of 1100–1300 cm^{-1}.

For the syndiotactic PMMA thin film [Fig. 3(b)], the analysis of the spectral data over 1100–1300 and 1000–1800 cm^{-1} yields PCs with very similar patterns, indicating that the PCA result of the syndiotactic PMMA thin film is not affected by different spectral regions. The carbonyl groups in the region 1700–1750 cm^{-1} do not affect the thermal property change in syndiotactic PMMA but they do affect this change in isotactic PMMA. The carbonyl groups giving rise to spectral features in the region 1700–1750 cm^{-1} for the syndiotactic PMMA thin film may undergo local reorientation due to the localized strong interaction as the temperature increases [28], and then may not affect the thermal property change. This difference between the behavior of isotactic and syndiotactic PMMA thin films can be attributed to differences in the tacticity and the adsorbed structure of the PMMA chains on the surface. Comparing the sensitivity of the two regions, 1000–1800 and 1100–1300 cm^{-1}, the spectral region of 1100–1300 cm^{-1} contributes dominantly to the determina-

tion of T_g in transition phenomenon as shown in Figs. 2 and 3.

4.3. Characteristics of carbonyl groups in loadings

Loadings plots may give a better understanding of the molecular origin of the glass transition. The loadings used here are the normalized eigen vectors of the covariance matrix of spectral data. PC loadings in the region 1000–1800 cm^{-1} for isotactic and syndiotactic PMMA thin films are shown in Fig. 4(a and b), respectively. A large value of the loading indicates that the band at that wavenumber has a greater effect on the PC score than other spectral regions. Loadings plots are useful for extracting hidden components from FTIR spectra and for identifying the band position of these hidden components [22,23,25]. In the region 1700–1750 cm^{-1} assigned to the C=O stretching mode, the loadings of PC1 are considerably higher for the isotactic PMMA [Fig. 4(a)] than for the syndiotactic PMMA
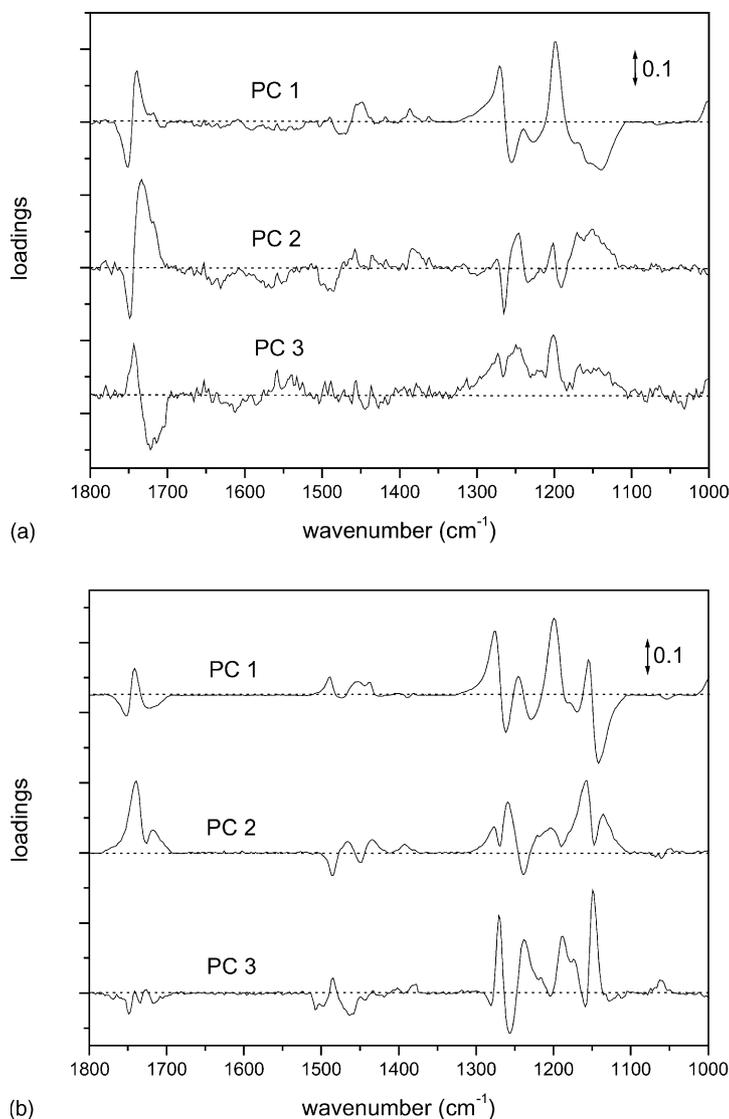

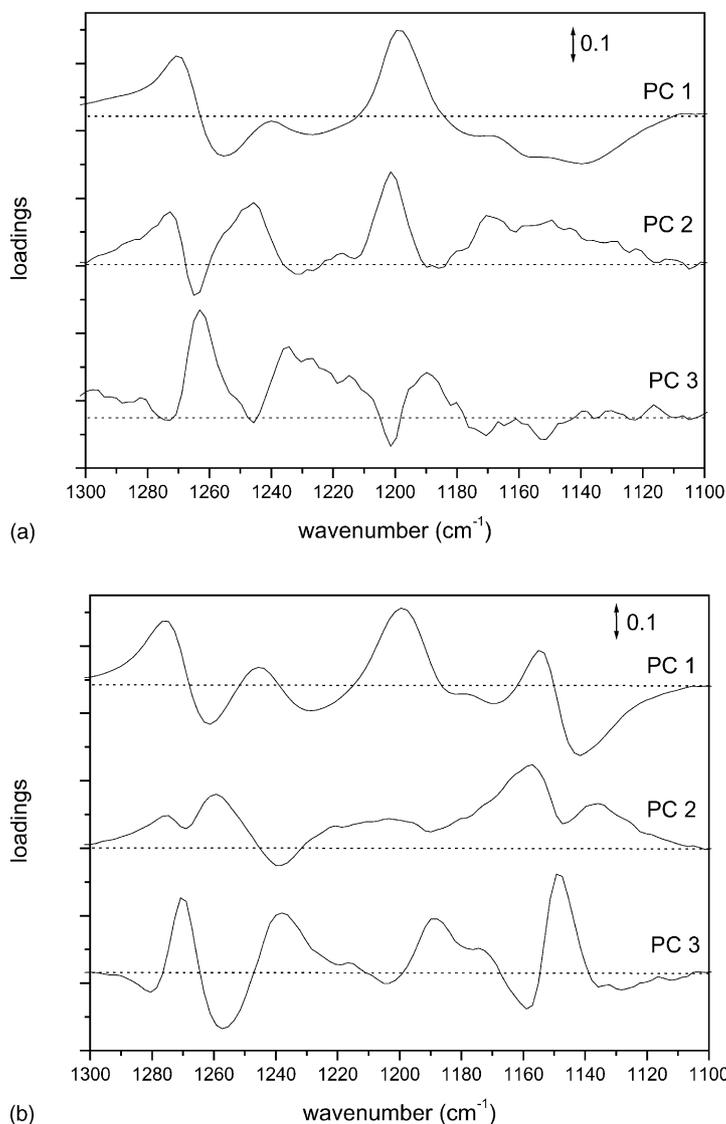Fig. 4. PC loadings for (a) isotactic and (b) syndiotactic PMMA thin films in the region of 1000–1800 cm^{-1}.

Fig. 5. PC loadings for (a) isotactic and (b) syndiotactic PMMA thin films in the region of 1100–1300 cm^{-1}.

[Fig. 4(b)]. This indicates that as the temperature increases the carbonyl groups reorient to a greater extent in the isotactic PMMA than in the syndiotactic PMMA.

Fig. 5 shows the PC loadings in the spectral region of 1100–1300 cm^{-1}. The patterns of the PC scores for isotactic PMMA in the region 1100–1300 cm^{-1} are different from those obtained for the broader region 1000 to 1800 cm^{-1} [see Figs. 2(a) and 3(a)]. This change in the PCs, which is particularly evident in PC2, is reflected in the loadings. The patterns of the loadings of PC2 and PC3 from the region of 1100 to 1300 cm^{-1} for isotactic PMMA [Fig. 5(a)] are different from those obtained from the region of 1000 to 1800 cm^{-1} [Fig. 4(a)]. The loadings of PC2 in the region of 1700–1750 cm^{-1} in Fig. 4(a) are higher than those of PC1 and PC3. The loading patterns in PC2 indicate that the carbonyl group affects the physical properties (or hidden structure) of the isotactic PMMA thin film. That is, the characteristic of the carbonyl group in the isotactic PMMA

thin film is indicative of the flattened structure as mentioned above.

For the syndiotactic PMMA thin film, the loadings for the region 1100–1300 cm^{-1} [Fig. 5(b)] are the same as those obtained for the region 1000–1800 cm^{-1} [Fig. 4(b)]. This indicates that the PCA results for the syndiotactic PMMA thin film are not affected by the spectral range selected for the calculation, and that the carbonyl groups do not affect the determination of the glass transition temperature.

5. Conclusion

An approach for determining the glass transition temperatures of PMMA thin films from PC scores of reflection–absorption FTIR spectra was proposed. In this method, T_g is taken to be the temperature at which the PC plot has the highest absolute value. The proposed technique

was applied to FTIR spectra from isotactic and syndiotactic PMMA thin films at a range of temperatures. PCA was performed on spectral data spanning two regions: 1000–1800 and 1100–1300 cm^{-1}. The glass transition temperatures determined by PCA for isotactic and syndiotactic PMMA thin films were 60 and 110–120 °C, respectively, which are consistent with the values reported by Grohens et al. [5,11] Additionally, temperatures of the second highest peaks were observed for the isotactic and syndiotactic PMMA thin films. In the isotactic PMMA thin film the second highest peak was observed at 90 °C, which may be due to the flattened structure of isotactic PMMA chains adsorbed directly on the substrate surface. For the syndiotactic PMMA thin film, the second highest peak was observed between 70 and 80 °C; this change may be related to the onset of the reorganization process. The score plot for syndiotactic-PMMA did not show temperature of the second highest peak at higher temperature than T_g, resulting from the adsorbed structure at the surface such as isotactic-PMMA. This can be due to differences in tacticity and adsorbed structure between isotactic-PMMA and syndiotactic-PMMA.

The PC patterns of the isotactic PMMA thin film obtained from the region 1000 to 1800 cm^{-1} differ from those obtained considering only the region 1100–1300 cm^{-1}. The behavior of PC2 for isotactic PMMA in the spectral region of 1000–1800 cm^{-1} indicates that as the temperature is increased there is a change in a physical property that is affected by the carbonyl group. For syndiotactic PMMA, application of PCA to spectral data from the region 1000 to 1800 and 1100 to 1300 cm^{-1} gave similar PC scores. Comparison of the PC loadings obtained over the region 1000–1800 and 1100–1300 cm^{-1} for the isotactic and syndiotactic thin films showed that the carbonyl groups affect the thermal properties and the flattened structure in the isotactic PMMA thin film, whereas these groups do not affect the behavior of the syndiotactic PMMA thin film.

Acknowledgments

References

[1] G. Reiter, Macromolecules 27 (1994) 3046.
[2] Y. See, J. Cha, T. Chang, M. Ree, Langmuir 16 (2000) 2351.
[3] J.L. Keddie, R.A.L. Jones, R.A. Cory, Europhys. Lett. 27 (1994) 59.
[4] J.L. Keddie, R.A.L. Jones, R.A. Cory, Faraday Discuss. 98 (1994) 219.
[5] Y. Grohens, L. Hamon, P. Carriere, Y. Holl, J. Schultz, Mat. Res. Soc. Symp. 629 (2000) FF1.7.1.
[6] G.B. Demaggio, W.E. Frieze, D. Gidley, M. Zhu, H.A. Hristov, A.F. Yee, Phys. Rev. Lett. 78 (1997) 1524.
[7] J.A. Forrest, K. Dalnoki-Veress, J.R. Stevens, J.R. Dutcher, Phys. Rev. Lett. 77 (1996) 2002.
[8] J.A. Forrest, K. Dalnoki-Veress, J.R. Stevens, J.R. Dutcher, Phys. Rev. B 56 (1997) 5705.
[9] O. Prucker, S. Christian, H. Bock, J. Ruhe, C. Frank, W. Knoll, Macromol. Chem. Phys. 199 (1998) 1435.
[10] Y. Grohens, M. Brogly, C. Labbe, J. Schultz, Eur. Polym. J. 33 (1997) 691.
[11] Y. Grohens, M. Brogly, C. Labbe, J. Schultz, Polymer 38 (1997) 5913.
[12] E.R. Malinowski, Factor Analysis in Chemistry, Wiley-Interscience, New York, 1991.
[13] H. Martens, T. Nas, Multivariate Calibration, John Wiley & Sons, New York, 1991.
[14] S.D. Brown, S.T. Sum, F. Despagne, B.K. Lavine, Anal. Chem. 68 (1996) 21R.
[15] R.J.M. Vervoort, M.W.J. Derksen, F.A. Maris, J. Chromatogr. A 678 (1994) 1.
[16] U. Haldna, J. Pentchuk, M. Righezza, J.R. Chretien, J. Chromatogr. A 670 (1994) 51.
[17] Y.-P. Sun, D.F. Sears, J. Saltiel, Anal. Chem. 59 (1987) 2515.
[18] J. Saltiel, D.F. Sears, Y.-O. Choi, Y.-P. Sun, D.W. Eaker, J. Phys. Chem. 98 (1994) 35.
[19] O. Steinbock, B. Neumann, B. Cage, J. Saltiel, S.C. Muller, N.S. Dalal, Anal. Chem. 69 (1997) 3708.
[20] T. Iwata, J. Koshoubu, C. Jin, Y. Okubo, Appl. Spectrosc. 51 (1997) 1269.
[21] C.W. Brown, S.-C. Lo, Anal. Chem. 70 (1998) 2983.
[22] T. Hasegawa, Anal. Chem. 71 (1999) 3085.
[23] T. Hasegawa, Trends Anal. Chem. 20 (2001) 53.
[24] Y. Wu, K. Murayama, Y. Ozaki, J. Phys. Chem. B 105 (2001) 6251.
[25] T. Hasegawa, J. Nishijo, T. Imae, Q. Huo, R.M. Leblanc, J. Phys. Chem. B 105 (2001) 12056.
[26] Y.M. Jung, H.S. Shin, B. Czarnik-Matusewicz, I. Noda, S.B. Kim, Appl. Spectrosc. 56 (2002) 1568.
[27] S. Havriliak, N. Roman, Polymer 7 (1966) 387.
[28] Y. Grohens, R.E. Prud'homme, J. Schultz, Macromolecules 31 (1998) 2545.
[29] H.S. Shin, Y.M. Jung, T.Y. Oh, S.B. Kim, D.H. Lee, I. Noda, Langmuir 18 (2002) 5953.