Use of Microscopic FT-IR/DSC Combined System for the Study of Glass Transition Temperatures of Polymers

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(Received August 26, 1994)

KEY WORDS Glass Transition / Differential Scanning Calorimetry /
Microscopic FT-IR / DSC System / Polymers /

Polymers exhibit significantly different physical and mechanical properties near glass transition (T_g) temperature.^{1,2} Since glass transition is related to change in the molecular motion of polymers, the infrared (IR) spectrum in the transition regions probably provides certain information on vibrational motion in relation to polymer transition. Hannon *et al.* suggest that IR spectroscopy is a sensitive and unique means for determining transition behavior in polymers, but sample preparation and the sample cell designed for T_g determination seem to be complicated.³ Lin *et al.* recently used newly-developed microscopic Fourier transform infrared (FT-IR) spectroscopy equipped with differential scanning calorimetry (DSC) to study simultaneously the thermal behavior and structural changes of samples such as drug polymorphs, porcine stratum corneum, silicone elastomer, and encapsulated squil oil.^{4–8} This newly-designed system is a simple, quick, and powerful apparatus, in which the sample is only sealed within a KBr disc and set on a DSC microscopic cell. Since chain motion is the major mechanism in the transition state, T_g of a sample may be easily predicted by this microscopic FT-IR/DSC system. The purpose of this

report is to show experimentally the usefulness of the newly-developed microscopic FT-IR/DSC combined system by exploring the glass transition temperature of polymers in a short period of time, instead of other known techniques.

EXPERIMENTAL

Materials

Polystyrene (PS, M_w , 130000), poly(vinyl chloride) (PVC, M_w , 70000) and poly(ethylene terephthalate) (PET, M_w , 17500) were kindly supplied from Formosa Chem. & Fibre Co. (Taipei, ROC), Taiwan Plastic Ltd. (Taipei, ROC) and Forest Textile Ltd. (Hsin Chu, Taiwan, ROC), respectively. Eudragit L-100 (copolymer of methacrylic acid and methylmethacrylate, M_w , 135000) and poly(lactic acid) (PLA, M_w , 2500) were obtained from Röhm Pharma (Darmstadt, Germany) and Kokusan Chem. Works, (Tokyo, Japan).

Differential Scanning Calorimetry

The thermal behavior of samples was examined in open aluminium pans using a differential scanning calorimetry (DSC-910, TA Instruments. Inc., USA) at a scanning

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rate of 5 or 10°C min⁻¹ under N₂ gas stream. The samples of PLA and Eudragit L-100 were heated to 150 and 180°C, respectively and held at constant temperature for 5 min, and then rapidly cooled with ice to obtain quenched samples. The quenched samples and other native samples were measured by a DSC analyser. T_g were taken from an inflexion point on the DSC curves.⁹

Microscopic FT-IR/DSC Combined System

Polymers were used without further treatment. The samples were sealed between KBr discs (6 mm) by hydraulic pressing. The KBr disc was placed in the DSC microscopy cell (FP 84, Mettler, Switzerland) and set in the FT-IR microscopic spectrometer (Micro FT-IR-200, Jasco, Japan) equipped with an MCT detector. The position and focus of the sample were adjusted by microscope. The temperature of the DSC microscopy cell was controlled with a central processor (FT80HT, Mettler, Switzerland). During each experiment, the sample disc was equilibrated to the starting temperature for 3 min and then heated. The heating rate of the DSC microscopy cell was set at 5 or 10°C min⁻¹. A 3-dimensional plot and changes in intensity of the specified peaks were studied by Data Processing Program.⁴⁻⁸ T_g was taken from a change in slope or midpoint of the descending graphs of peak absorption vs. temperature.³

RESULTS AND DISCUSSION

In this study, two types of profiles on the plot of peak absorption vs. temperature were obtained. The first typical profile is a slow descending curve with temperature; the other profile is a descending curve with dramatic change.

Figure 1 shows three-dimensional plots of FT-IR spectra of the PS sample in the region from 1400 to 1700 cm⁻¹ when temperature increases from 28 to 200°C. DSC curve and IR absorbances at 1601, 1493, and 1454 cm⁻¹ of

Figure 1. Three-dimensional plots of IR spectra of polystyrene, DSC thermogram and absorbance of the specified bands as a function of temperature.

the PS sample are also plotted as a function of temperature in Figure 1. Apparently, the peak intensities of the bands at 1601, 1493, and 1454 cm⁻¹ gradually decreased with increasing temperature and then disappeared. T_g of PS is about 89°C obtained from the inflexion point of DSC thermogram, which was near 85°C of the literature value, as shown in Table I.¹⁰ When the T_g point was taken from the midpoint of the descending graph of peak absorption vs. temperature, T_g for 1601, 1493, and 1454 cm⁻¹ absorption bands were 98, 92, and 89°C, respectively. T_g of the 1454 cm⁻¹ band was close to T_g in the DSC curve, suggesting the 1454 cm⁻¹ band to be a sensitive band corresponding to conformational change in PS. This is consistent with the report in which different absorption peaks showed different T_g .¹¹ This might be attributed to the fact that these transitions are associated with change in

the dipole moment.^{2,12} At the glass transition temperature, the freedom of polymer molecules might increase to allow some intramolecular rotations and/or molecular motion of main chain or side chain,² resulting in change in the intensity of the IR band. The IR absorption spectra for the PET and PLA samples also exhibited slow decending profiles, which is in good agreement with the observations of PS. It should be noted that T_g of the PLA by DSC was obtained from the quenched sample, but the microscopic FT-IR/DSC system might directly obtain T_g without further quenching process.

Figure 2 shows 3-dimensional IR plots, DSC thermogram and absorbance of the 1728, 1265, 1192, and 1161 cm^{-1} bands as a function of

Figure 2. Three-dimensional plots of IR spectra of Eudragit L-100, DSC thermogram and absorbance of specified bands as a function of temperature.

Table I. Glass transition temperatures of polymers determined by DSC and the microscopic FT-IR/DSC system^a

Samples	DSC		Microscopic FT-IR/DSC system	Value of literature
	Direct determination	Indirect determination		
Polystyrene	89°C	—	1601 cm^{-1} : 98°C 1493 cm^{-1} : 92°C 1454 cm^{-1} : 89°C	85°C
Poly(ethylene terephthalate)	77°C	—	1720 cm^{-1} : 78°C 1408 cm^{-1} : 77°C 1242 cm^{-1} : 79°C 1095 cm^{-1} : 80°C	68°C
Polylactic acid	—	47°C (150°C)	1755 cm^{-1} : 56°C 1450 cm^{-1} : 71°C 1188 cm^{-1} : 65°C 1095 cm^{-1} : 68°C	44°C
Eudragit L-100 ^b	—	157°C (200°C)	1728 cm^{-1} : 148°C 1245 cm^{-1} : 150°C 1192 cm^{-1} : 150°C 1161 cm^{-1} : 150°C	160°C
Poly(vinyl chloride)	88°C	—	1435 cm^{-1} : 95°C 1331 cm^{-1} : 97°C 1250 cm^{-1} : 94°C 972 cm^{-1} : 97°C	81°C

^a Value in parentheses: isothermal temperature for 5 min. ^b Copolymer of methacrylic acid and methyl methacrylate.

temperature for the Eudragit L. It clearly indicates that all the IR spectra of the Eudragit L in the 3-dimensional plot change suddenly at 140–160°C, and then disappear as temperature increases. This abrupt change in the profile of absorbance vs. temperature was more apparent beyond 140°C. The dramatic change in IR absorbance might be due to glass transition of the Eudragit L. The T_g point of the quenched Eudragit L sample on the DSC curve was 157°C, while T_g obtained from the midpoint of the descending curve for above four specified peaks was within 148–150°C (Table I). The two different methods might explain these different T_g . However, these values are approximately equal. PVC also showed similar results. An abrupt change in temperature was within 80–100°C in the plot of the absorbance vs. temperature. This abrupt change at 94–97°C for four specified peaks (1435, 1331, 1250, and 972 cm^{-1}) was approximately the T_g of the PVC sample determined by DSC.^{10,11}

In conclusion, the newly-developed microscopic FT-IR/DSC system seems to be a simple, quick and powerful means for analyzing glass

transition temperatures of polymers.

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