Variable Temperature FTIR Study of Poly(ethylene-co-vinyl alcohol)-graft-poly(ε-caprolactone)

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A recently developed technique, i.e., two-dimensional infrared (2D IR) correlation spectroscopy, is used to study the thermal behavior of poly(ethylene-co-vinyl alcohol)-graft-poly(ε-caprolactone), a new synthesized highly grafted copolymer. The use of the 2D IR approach to analyze temperature-dependent spectra collected in situ during the temperature elevation process effectively enhanced the spectral resolution and revealed details on the hydrogen bonding and conformational change which are not easily detected in the traditional one-dimensional spectra. The sequence of the spectral changes of different OH and CH2 fundamental vibrations during heating the polymer was inferred from the signs of the asynchronous peaks. Evidence that the conformational changes of the methylene groups precede the loosening of hydrogen bonds is provided.

I. Introduction

The role played by the hydrogen bonds in the structure and properties of polymers has been the subject of numerous investigations.1−12 IR spectroscopy has proven to be an excellent tool to study the hydrogen bond in different kinds of polymers.2−12 Though the energies of hydrogen bonds are relatively weak (<50 kJ/mol) in comparison with covalent bonds (in the order of 400 kJ/mol), this type of molecular interaction is large enough to produce appreciable wavenumber and intensity changes in the vibrational spectra of the polymer under examination.

Valuable information regarding the temperature dependence of the hydrogen bond may be derived from IR studies at elevated temperature. Coleman and the co-workers studied the hydrogen bonding in Nylon 11 using infrared temperature studies.6 It was found that the strong dependence of the absorptivity coefficient with hydrogen bond strength led to the reduction in area of the hydrogen bonded N−H stretching mode with increasing temperature in the semicrystalline nylon 11.

However, the temperature changes not only influence the hydrogen bonding but also the structure of the hydrocarbon chains. Thus, it has been observed that the peak maximum wavenumber of the band associated with the antisymmetric stretching mode of the CH2 group in a polyesterurethane12 decreases linearly upon increasing temperature.

The theory of generalized two-dimensional 2D correlation spectroscopy was developed by Noda13 in 1993, as an extension of the original 2D correlation spectroscopy proposed by him. By use of 2D correlation spectroscopy, it is possible to enhance spectra resolution of individual component bands. In the 2D analysis, two kinds of correlation maps, synchronous and asynchronous ones are generated based upon a set of dynamic spectra calculated from dynamic fluctuations of spectroscopic signals.13d The generalized 2D method can handle signals fluctuating as an arbitrary function of time or any other physical variable such as temperature, pressure, or even concentration.14

Correlation peaks appearing in the synchronous and asynchronous maps represent in-phase and out-of-phase variation tendencies of corresponding band intensities, respectively. The generalized 2D correlation spectroscopy has been applied extensively to analyze IR spectra of polymer for two major reasons. One is that 2D spectroscopy enhances apparent spectral resolution, deconvoluting highly overlapped bands into an individual component band. Another reason is that it gives information about specific order of the spectral intensity changes taking place during the measurement from the analysis of the asynchronous spectra.

EVOH-g-PCL is a new synthesized highly grafted copolymer.15 Because of its low melting point and biodegradability, EVOH-g-PCL may become an attractive polymer in the future. It can lead to different end applications, for instance, hand-mouldable and degradable package. However, owing to the complex nature of the hydrogen bonding and the conformational structure of EVOH-g-PCL, many basic questions, for example, the temperature influence on the property of EVOH-g-PCL, still remain unsolved. Would it be possible, for instance, to determine the sequential order of structural changes in the hydrocarbon chain and the OH groups during a temperature elevation process?

In the present article, we will report the 2D correlation analysis based on 1D FTIR variable temperature spectroscopic data with reference to the dissociation of hydrogen bonding and conformational changes in EVOH-g-PCL.

II. Experimental Section

The sample of EVOH-g-PCL copolymer (Scheme 1) used in this work was synthesized by our group.15 The molecular
weight and polydispersity are 6.4×10^4 and 1.54, respectively, determined by GPC. The number average molecular weight of the PCL side chain is 840 g/mol which is calculated according to the H NMR result.

The thin copolymer film on a KBr window for the IR measurement is prepared by tetrahydrofuran (2% (m/v)) solution casting. The film is then put into a small sealed temperature cell to prevent the influence of water vapor in air on the OH vibrations from polymer hydroxyl groups. FTIR spectra were collected between 30 and 69 °C with a temperature increment of 3 °C (accuracy: 0.1 °C) using a Nicolet FTIR spectrometer equipped with a DTGS detector at a resolution of 4 cm⁻¹ with 32 scans. The bands were integrated using Omnic 5.1 without baseline correction. All of the spectra were not normalized.

For the generalized 2D correlation analysis, spectra at an interval of 3 °C in certain wavenumber range were selected, and the 2D software used was a macro program named 2D Pocha composed by Daisuke Adachi (Kwansei Gakuin University, Japan). Compared with the 2D correlation spectrum that is shown in the center of the map, the time-averaged 1D reference spectrum is at the side and top of the map. In the 2D correlation maps, unshaded regions are defined as the positive correlation intensities, whereas shaded regions are defined as negative ones.

III. Results and Discussion

Figure 1 shows the FTIR spectrum of EVOH-g-PCL at room temperature. The tentative assignments of bands observed are made according to the relevant study of Holland-Moritz and Kirpatrik (Table 1). The prominent IR bands are hydrogen-bonded O–H stretching modes (3534 and 3436 cm⁻¹), antisymmetric (2944 cm⁻¹), and symmetric (2868 cm⁻¹) CH₂ stretching modes, respectively, carbonyl stretching band (1730 cm⁻¹) and the C–O stretching bands and CH₂ wagging bands (1350–1100 cm⁻¹).

The temperature-dependent infrared spectra of EVOH-g-PCL, recorded as a function of increasing temperature are displayed in Figure 2. The heating process was carried out from room temperature to temperatures above the polymer melting point. During the course of measurement, the copolymer was converted from the crystalline to amorphous phase. The OH bands in the spectral range 3700–3100 cm⁻¹ are very sensitive to the temperature elevation. Figure 3
shows the temperature dependence of the integrated band area of the hydroxyl group. It can be seen that, with the increase of temperature, the absorption of hydroxyl group decreases. This is mainly due to the fact that the hydrogen bond was weakened upon increasing temperature and not the dehydration of the copolymer. The temperature dependence of the CH$_2$ (2800–3020 cm$^{-1}$) absorption intensity is shown in Figure 4. In contrast to the gradual decrease of the OH bands, the integrated area of the C–H band remains almost constant till 45 °C. There is an abrupt increase from the temperature from 48 to 54 °C, which indicates that the graft copolymer is melting during this temperature range. After 57 °C, the integrated band area of C–H becomes almost constant again, which means that the copolymer has melted thoroughly.

Figure 5 depicts the asynchronous 2D correlation spectra of EVOH-g-PCL in the range of 2800–3600 cm$^{-1}$. Throughout this paper, the unshaded and shaded areas in the contour maps denote positive and negative correlation peaks, respectively. In the 2D spectra, an asynchronous cross-peak develops only if the intensities of two spectral features change out of phase with each other. In the spectral region of OH stretching vibration, a positive cross-peak (3556/3436 cm$^{-1}$) can be observed in the upper left triangle of Figure 5. The separation of the both components (120 cm$^{-1}$) is too large to be due to the existence of the O–H groups in two different phases (ordered and disordered). Thus, it seems reasonable to assume that we observe two structures of hydrogen bonding of OH groups rather than one type of OH-hydrogen bonding in two different phases. In the first structure, the associated OH group is adjacent to another OH group and forms (relatively) strong hydrogen bonding (3436 cm$^{-1}$), whereas in the second one, the OH group is (relatively) weakly hydrogen-bonded (3556 cm$^{-1}$) with a carbonyl (C=O) group or an ether (C–O) group. The sign of the cross-peaks in an asynchronous spectrum provides additional information about the specific order of the intensity changes in different bands. The positive sign of the cross-peak (3556/3436 cm$^{-1}$) indicates that the weakening of the relatively weak hydrogen bonding (3556 cm$^{-1}$) occurs earlier than that of the relatively strong hydrogen bonding (3436 cm$^{-1}$). On the other hand, the negative sign of the cross-peaks (3398/2969, 3398/2846, 3398/2923, and 3398/2877 cm$^{-1}$) between the CH$_2$ stretching bands (2980–2820 cm$^{-1}$) and the OH stretching bands (3700–3100 cm$^{-1}$) reveals that, during the temperature elevation process, the conformational changes in the hydrocarbon chains proceed faster than the loosening of the OH hydrogen bonds.

Figure 6 shows the FTIR spectra of the carbonyl (C=O) absorbance band for the EVOH-g-PCL in the region from 1690 to 1770 cm$^{-1}$. In this figure, it can be seen that the peak position of the graft copolymer remains constant for the temperature from 30 to 45 °C. Although the absorption peak moves to a higher wavenumber for the temperatures 48 and 51 °C, which means that the graft copolymer is melting with increasing temperature. The absorption peak remains at the same wavenumber again between 54 and 69 °C. Also it can be seen that, with the increase of temperature, the shape of the band became more symmetric and is characteristically broader than that in the room temperature, reflecting an increase in conformational freedom.

IR spectra of EVOH-g-PCL in the 1325–1125 cm$^{-1}$ region measured in the temperature range from 30 to 69 °C are overlaid in Figure 7. The bands in this spectral range are coupled modes variously associated with C–C–H and
O–C–H bending and C–C and C–O stretching vibration. At 30 °C, there are at least three bands (1192, 1244, and 1295 cm\(^{-1}\)) in the spectral 1120–1320 cm\(^{-1}\) region. The thermal behavior of these bands are quite different, according to Zhao et al.; the 1295 cm\(^{-1}\), related to the C–C and C–O stretching vibrations of crystalline PCL, is a typical crystalline band and is totally absent in the amorphous PCL. In the present study, upon the temperature increase in a stepwise fashion from 30 to 69 °C, the absorption at 1295 cm\(^{-1}\) is absent from 51 °C, whereas the 1244 cm\(^{-1}\) band loses intensities with a small peak shift of 9 cm\(^{-1}\). The 1192 cm\(^{-1}\) band disappears gradually and a new absorption at 1161 cm\(^{-1}\) appears. The 1161 cm\(^{-1}\) band is associated with the amorphous state, whereas the 1192 cm\(^{-1}\) band can be associated with ordered conformations of the PCL chain. The temperature dependence of the integrated band area of 1295 cm\(^{-1}\) (1285–1315 cm\(^{-1}\)) is shown in Figure 8. The integrated band area is decreasing slowly from the temperature of 30–45 °C and then an abrupt decrease to almost zero at 54 °C. After the temperature of 54 °C, the integrated band area is zero, which is mainly due to the fact that the graft copolymer melts completely. This is consistent with what Zhao has concluded in his paper. Figure 9 shows the influence of the temperature on the integrated band area of 1244 cm\(^{-1}\) (1220–1265 cm\(^{-1}\)); the integrated band area of C–O changes only a little bit from 30 to 45 °C, has an abrupt decreasing process from 48 to 54 °C, and remains almost constant once again from 54 °C. It can be seen that the area of the ordered band decreases to about half of its original value over a range 30–54 °C.
Figure 10 depicts the asynchronous correlation spectra of EVOH-g-PCL in the range of 1120–1220 cm$^{-1}$. The existence of a negative cross-peak (1161/1192 cm$^{-1}$) in the upper left triangle means that the decrease of the intensity of the 1192 cm$^{-1}$ band and the increase of the 1161 cm$^{-1}$ band occur at different rates. It may suggest the existence of an intermediate species between the amorphous one (1161 cm$^{-1}$) and the ordered one (1192 cm$^{-1}$).

**Conclusion**

The results presented in this study have demonstrated that 1D and 2D IR spectra could be used to study the hydrogen bonding and conformational change in EVOH-g-PCL. The application of generalized 2D correlation spectroscopy could also be used to detect subtle spectral variations in the IR regions. It is found that with the increase of temperature the absorption of hydroxyl group decreases, whereas the integrated band area of the CH$_2$ stretching vibration is almost constant for the temperature from 30 to 45 $^\circ$C, then an abrupt increase between the temperature 48 and 54 $^\circ$C, and at last constant again. Upon the temperature increase in a stepwise fashion from 30 to 69 $^\circ$C, the band at 1295 cm$^{-1}$, related to the C–C and C–O stretching vibrations of crystalline PCL, disappears after the temperature 51 $^\circ$C. In 2D IR, it is found that with the increase of temperature the conformational changes in the hydrocarbon chains take place first and the hydrogen bonds are weakened later on.

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**References and Notes**