Generalized Two-Dimensional Attenuated Total Reflection/Infrared and Near-Infrared Correlation Spectroscopy Studies of Real-Time Monitoring of the Initial Oligomerization of Bis(hydroxyethyl terephthalate)

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ABSTRACT: The initial oligomerization of bis(hydroxyethyl terephthalate), BHET, was monitored in situ at 220, 250, and 270 °C by attenuated total reflection (ATR)/infrared (IR) and near-infrared (NIR) transmission spectroscopy. The obtained sets of IR and NIR spectra, which include information about the progress of the reaction, were analyzed by means of generalized two-dimensional (2D) correlation spectroscopy. Both 2D IR and 2D NIR correlation spectra clearly identified bands at 1030, 880, and 861 $\mathrm{cm^{-1}}$ (IR region) and 5830 $\mathrm{cm^{-1}}$ (NIR region) arising from ethylene glycol (EG), which is expelled out of the system during the reaction. The synchronous hetero 2D NIR−IR correlation spectrum showed positive cross-peaks between the IR peaks at 1030, 880, and 861 $\mathrm{cm^{-1}}$ and the NIR band at 5830 $\mathrm{cm^{-1}}$ while no cross-peak appeared in the corresponding asynchronous spectrum, confirming that all these peaks arise from the same origin (EG). To carry out the 2D hetero correlation analysis, the experiment was modified so that both ATR/IR and NIR probes could be employed simultanously. The 2D NIR correlation analysis also suggested that a band at 5260 $\mathrm{cm^{-1}}$ is ascribed to water. It was found that NIR spectroscopy may be very useful to in situ monitor the amount of water in the reaction system.

1. Introduction

Real-time monitoring of chemical reactions is very important for investigating the chemistry from the points of basic science as well as industry. Various spectroscopic methods have recently been employed as analytical tools for on-line monitoring.[1−6]

Among them, vibrational spectroscopy such as mid-infrared (IR),[7−12] near-infrared (NIR),[5,6,13−17] and Raman spectroscopy[4,18−20] are particulary useful. By using vibrational spectroscopy, one can monitor in situ the progress of a reaction from intensity changes in absorption bands. Thanks to the developments in optical technology and spectral analysis methods over the past decade, the usefulness and versatility of vibrational spectroscopy in process analysis are rapidly growing.

We have been investigating real-time monitoring of the initial oligomerization of bis(hydroxyethyl terephthalate) (BHET) by attenuated total reflection (ATR)/IR and NIR spectroscopy.[21−24] Our studies have three purposes. One is to elucidate the kinetics of the condensation reaction itself (i.e., to examine the catalyst activity). Another is to collect information about reaction parameters such as the degree of oligomerization and the condensation of each component during the reaction. Yet another is to develop a novel method based on vibrational spectroscopy for monitoring the reaction in situ. For these purposes, we have analyzed the ATR/IR and NIR spectra of the initial oligomerization of BHET by use of chemometrics,[21,22] self-modeling curve resolution (SMCR),[23] and sample−sample (SS) and variable−variable (VV) two-dimenional (2D) correlation spectroscopy.[24] The ATR/IR and chemometrics study revealed that calibration curves can be developed on the basis of using partial least-squares (PLS) regression for the OH end groups and free ethylene glycol (EG).[21] These parameters were found to be very important in understanding the polymerization. The amounts of OH end groups and free EG were also predicted by NIR spectroscopy combined with PLS regression.[22] Although the amount of EG was small, it was possible to extract some spectral information about EG by use of loading plots of regression coefficients.[21]

The SMCR study on the ATR/IR spectra was successful in terms of the extraction of the spectra of the reactant (BHET) and product (PET, or its oligomer), yielding the two-component concentration profile of the reaction without any initial information about the spectrum of each component and its concentration.[23] Non-calibration-based approaches such as SMCR become important when no information can be obtained using conventional methods. Unfortunately, no clear evidence for EG was extracted by the SMCR study, perhaps because the concentration of free EG was small, and its bands are overlapped severely with those from other components. The generalized sample−sample (SS) 2D correlation study was able to predict the third component, and together with the wavenumber−wavenumber (WW) 2D it allowed us to extract a band near 1032 $\mathrm{cm^{-1}}$ that is assigned to the C−O stretching band of free EG.[24]

The purpose of the present study is to investigate further the real-time monitoring of the oligomerization reaction by use of 2D IR, 2D NIR, and hetero 2D IR−NIR correlation spectroscopy.

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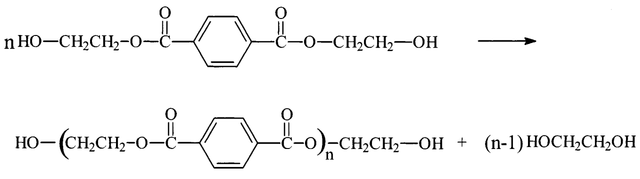
Scheme 1



Generalized 2D correlation spectroscopy is a powerful mathematical tool for enhancing apparent spectral resolution without assuming any line shape models for bands.[25−28] This method allows to monitor spectral variations as a function of reaction time. As a result, it becomes possible to identify bands not readily seen in the original spectra. The relative rates of the time-dependent spectral intensity changes of bands can also be investigated by 2D correlation spectroscopy.

Despite extensive applications of various chemometric analysis methods up to present, there are still unsolved issues to be addressed for the IR and NIR spectra of the oligomerization reaction. In the ATR/IR spectra, a more decisive analysis is necessary to clearly elucidate the information about free EG from a non-calibration-based system alone. For the NIR spectra set, a weak peak at 5264 cm^{-1}, which has a very important contribution in the principal component analysis (PCA) and PLS analysis, has not been assigned yet. Knowledge about the origin of this band is absolutely necessary since this largely affects the prediction models of OH end groups and free EG, and the lack of this knowledge may become a menace against a reliable and precise monitoring using NIR spectroscopy.

The present study provides two important findings. One is that NIR spectroscopy is powerful in probing water contaminated in the oligomerization. The other is that 2D IR, 2D NIR, and 2D IR−NIR correlation analyses yield solid assignments of EG bands in both IR and NIR regions. The present study may open the very efficient and useful way for monitoring in situ not only the product but also EG and water in the oligomerization reaction.

2. Experimental Section

Reagents and Oligomerization. The details of the starting material, bis(hydroxyethyl terephthalate) (BHET), and the catalyst, antimony trioxide (1.9 wt % ethylene glycol solution), and the method for oligomerization of BHET were reported in our previous paper.[21] The concentration of the catalyst was 500 ppm as Sb, and the reaction temperature was kept constant within ±0.5 °C throughout the reaction. The temperature range investigated was from 220 to 270 °C. The reaction mixture was kept under a blanket of nitrogen.

Spectroscopic Measurements. The details of the spectroscopic measurements were described in our previous papers,[21,22] so that here they are mentioned only breifly.

(1) ATR/IR Spectroscopic Measurement. For this measurement, an Applied Systems React-IR 1000 equipped with a diamond ATR prism was employed. The ATR probe was immersed into the solution in the vessel, and IR spectra were measured at a spectral resolution of 4 cm^{-1} by accumulating 128 scans.

The reaction investigated is shown in Scheme 1. As the reaction proceeds, ethylene glycol (EG) is released. Some EG is expelled out of the system, while some remains in the reaction solution. IR spectra were measured in situ with a constant time interval (5 min).

(2) NIR Spectroscopic Measurements. NIR spectra were measured with an Analect Diamond 20 FT-NIR spectrometer equipped with an InGaAs detector. A transmission probe with a 2 mm path length that can withstand temperatures up to 300 was connected to the spectrometer by optical fibers. The transmission probe was immersed into the solution in the reaction vessel, and NIR spectra were measured at a spectral

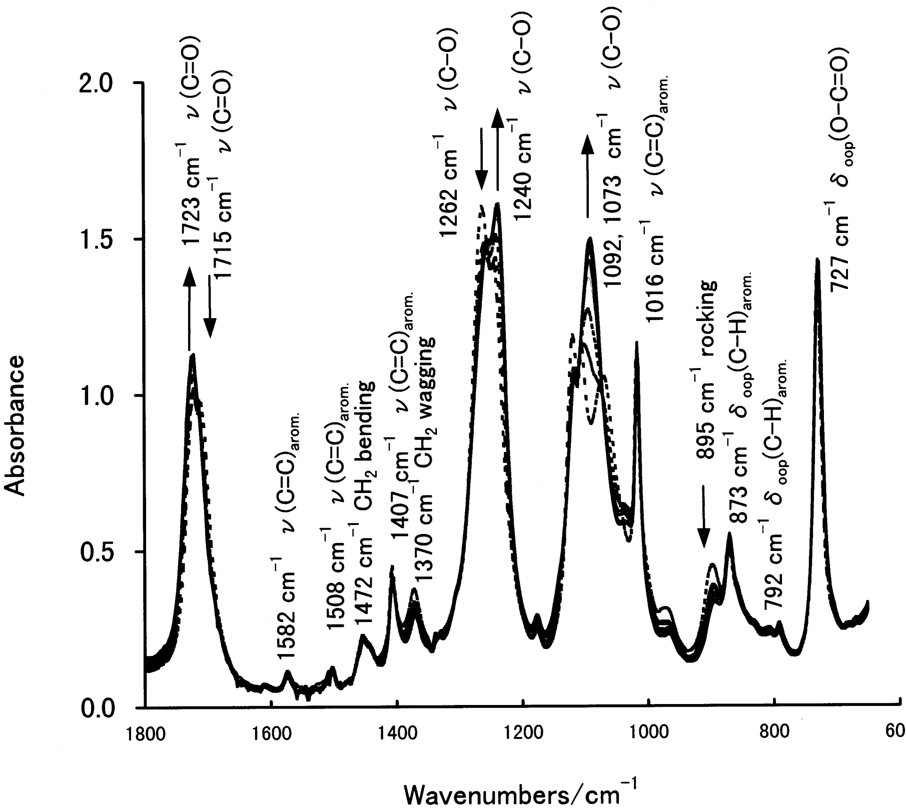


Figure 1. ATR/IR spectra measured in situ during the oligomerization reaction shown in Scheme 1 at 250 °C. Arrows show the directions of intensity changes during the course of the reaction.

resolution of 4 cm^{-1} by accumulating 128 scans. The NIR spectra were also measured at a constant time interval (5 min).

Data Treatments. Spectral data collected by the IR and NIR instruments were converted into a generalized 2D correlation software developed in our laboratory (KG2D). The 1800−650 cm^{-1} region and the 8000−4500 cm^{-1} region were employed for the 2D correlation analysis of IR and NIR spectra, respectively. The obtained spectra were smoothed with a 11-point Savitsky−Golay function to reduce the noise.

3. Results and Discussion

ATR/IR Spectra. Figure 1 displays time-dependent ATR/IR spectral changes of the reaction mixture at 250 °C shown in Scheme 1. We previously discussed the band assignments of the IR spectra based on SMCR,[23] SS and VV 2D correlation spectroscopy,[24] and chemometrics.[21] The assignments have been given for most bands in Figure 1.[21] However, the assignments for free EG are still unclear.

The amounts of OH end group and free EG were predicted by the PLS regression in our previous study,[21] and reaction profiles for these two values at 220, 250, and 270 °C are shown in Figure 1 of ref 21. The OH end groups decrease with time for all the temperatures, which is an indication for the oligomer formation. For free EG, more complicated profiles were seen at the beginning of the reaction.[21] For the reaction at 270 °C, after an instant increase of the EG concentration, there was a gradual decrease toward an equilibrium value at the end of the reaction. On the other hand, a monotonic increase in the EG concentration was observed for the reaction at 220 °C. For the reaction at 250 °C, after an initial buildup of EG for 20 min, its steady decrease was seen.

The first 10 spectra (first 45 min of the reaction) collected at 270 and 220 °C were used for the 2D correlation analysis.

2D Correlation Spectra in the 1000−800 cm^{-1} Region. Figures 2 and 3 show the synchronous and asynchronous 2D correlation maps in the 1000−800 cm^{-1} region calculated from the time-dependent ATR/IR spectra measured at 270 and 220 °C, respectively. In Figure 2, autopeaks are observed at 903 and 870 cm^{-1} in the synchronous spectrum. The two peaks share a negative cross-peak. The former peak is attributed to BHET, and the intensity of the corresponding band at 903 cm^{-1} decreases upon oligomerization. The latter peak at 870 cm^{-1}, which is characteristic of an aromatic vibration, shows a slight increase with time. In the asynchronous spectrum, the two peaks also share a cross-peak. Since EG is being released from the solution as the reaction proceeds, the concentrations of the species remaining in the solution should increase. This should be the case for the aromatic ring structure, and the intensity change of the corresponding peak may be out-of-phase with the peak at 903 cm^{-1}.

The corresponding synchronous and asynchronous spectra at 220 °C in Figure 3 show autocorrelation peaks at 903 and 861 cm^{-1}. The autopeak at 870 cm^{-1} has disappeared, but in the asynchronous spectrum, this peak shares a cross-peak with the peak at 861 cm^{-1} and also weakly with the 880 cm^{-1} peak. The two peaks at 861 and 880 cm^{-1} , which cannot be clearly seen in the 2D spectra at 270 °C, are likely to arise from EG. According to our previous study,[21] there is no marked concentration change of EG for the reaction at 270 °C, but a large increase in the EG concentration is seen for the reaction at 220 °C. Thus, EG relevant peaks may appear in the 2D maps at 220 °C. To confirm the band assignments, a spectrum of neat EG was measured at 200 °C and is shown in Figure 4. Note that there are two peaks at 878 and 860 cm^{-1} assigned to the CH$_2$ twisting modes of EG. This confirms that the peaks extracted by the 2D correlation analysis arise from the free EG being produced during the oligomerization.

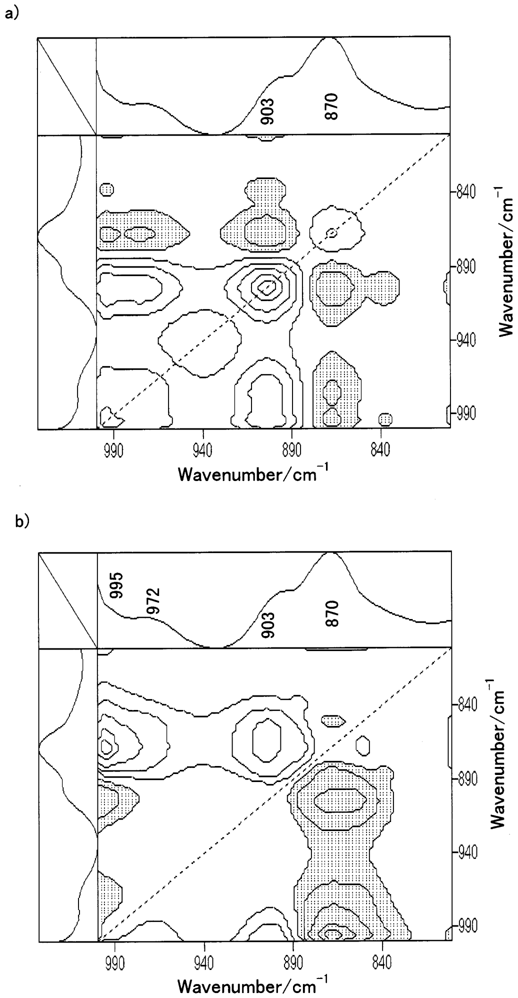


Figure 2. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1000−800 cm^{-1} region generated from the time-dependent spectral variations of the oligomerization reaction at 270 °C.

2D Correlation Spectra in the 1400−1000 cm^{-1} Region. The synchronous and asynchronous 2D correlation spectra in the 1400−1000 cm^{-1} region at 270 and 220 °C are shown in Figures 5 and 6, respectively. The interpretation of the synchronous map at 270 °C is straightforward. The peaks at 1233 and 1090 cm^{-1}, which share a positive cross-peak, are due to the C−O vibrations of the oligomer. The weaker peaks at 1262 and 1061 cm^{-1} arising from BHET decrease as the reaction proceeds. These two peaks have negative cross-peaks with the band at 1090 cm^{-1}.

The synchronous map at 220 °C is rather complicated. The number of autopeaks increases. In addition to the two peaks at 1233 and 1090 cm^{-1}, which appear in the correlation map at 270 °C, new peaks emerge at 1262, 1115, and 1065 cm^{-1}. These new peaks have negative correlation with the first two peaks and thus are attributed to the bands of BHET. Another new peak at 1032 cm^{-1} has positive cross-peaks with peaks at 1233 and 1090 cm^{-1}. In the previous study[21] and from Figure

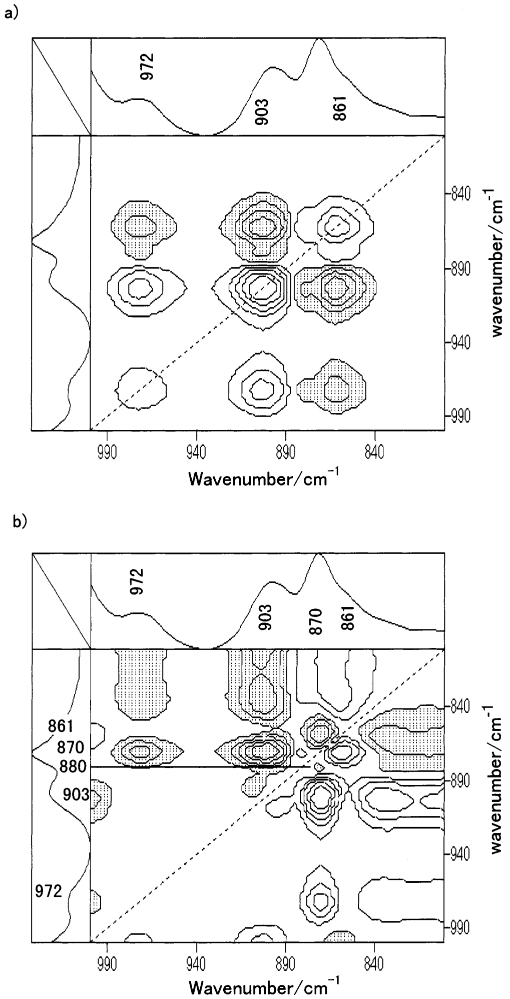


Figure 3. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1000−800 cm^{-1} region of the oligomerization reaction at 220 °C.

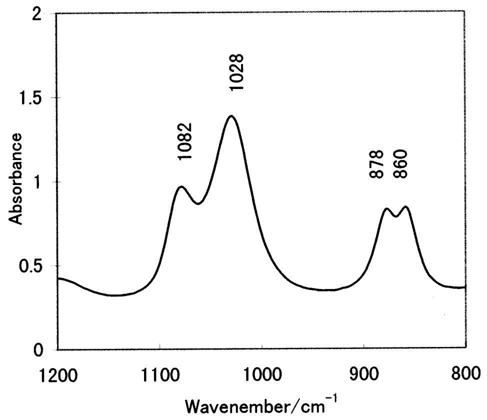


Figure 4. IR spectrum of EG at 200 °C in the 1200−800 cm^{-1} region.

4, this band is attributed to the C−O stretching mode of free EG. The slice spectra at 1032 cm^{-1} extracted from the synchronous and asynchronous 2D correlation spectra in Figure 6 are shown in Figure 7. A slice spectrum is a spectral pattern in the second axis at a certain wavenumber in the first axis. In the present case, the correlation between 1032 cm^{-1} and the rest of the wavenumbers is emphasized using this presentation method. The synchronous slice spectrum shows that positive cross-peaks appear at (1032, 880) and (1032, 861) cm^{-1}. The pattern of this synchronous slice spectrum resembles the spectrum of EG (Figure 4), and thus it can be concluded that the 1032 cm^{-1} peak belongs to EG. The asynchronous slice spectrum shows the development of a cross-peak at (1032, 870) cm^{-1}. The 870 cm^{-1} band is due to the aromatic ring vibration.

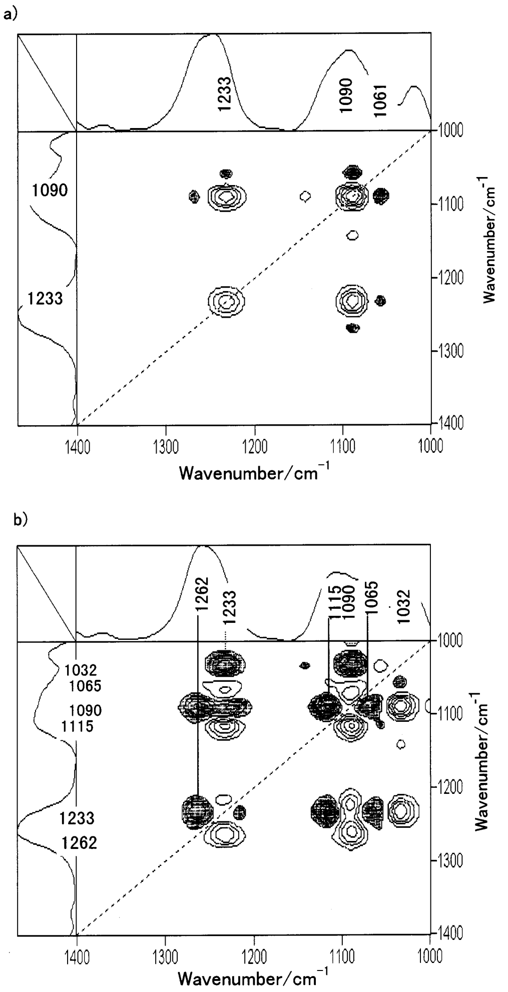


Figure 5. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1400−1000 cm^{-1} region of the oligomerization reaction at 270 °C.

The patterns of the asynchronous correlation maps at 270 and 220 °C look very similar to each other. The 1032 cm^{-1} band has cross-peaks with those at 1233 and 1090 cm^{-1}, which are assigned to the oligomer C−O stretching modes, but does not show cross-peaks with the BHET bands (1262, 1115, and 1065 cm^{-1}). This means that the intensity increase of the free EG band at 1032 cm^{-1} and the decrease of BHET band proceed in-phase. This implies that the intensity decrease of the BHET bands are at least partly due to the concentration decrease of BHET upon the formation of free EG. This is probably the reason that the bands from BHET and oligomers have cross-peaks in the asynchronous maps or, in other words, change out-of-phase.

2D Correlation Spectra in the 1800−1600 cm^{-1} Region. The synchronous and asynchronous 2D correlation maps of the carbonyl stretching region for the reactions at 220 and 270 °C are shown in Figures 8 and 9, respectively. Despite the differences in the appearance of the autopeaks (the 1730 cm^{-1} peak of the oligomers and the 1700 cm^{-1} peak of BHET) between the two synchronous maps, the asynchronous spectra are again very similar.

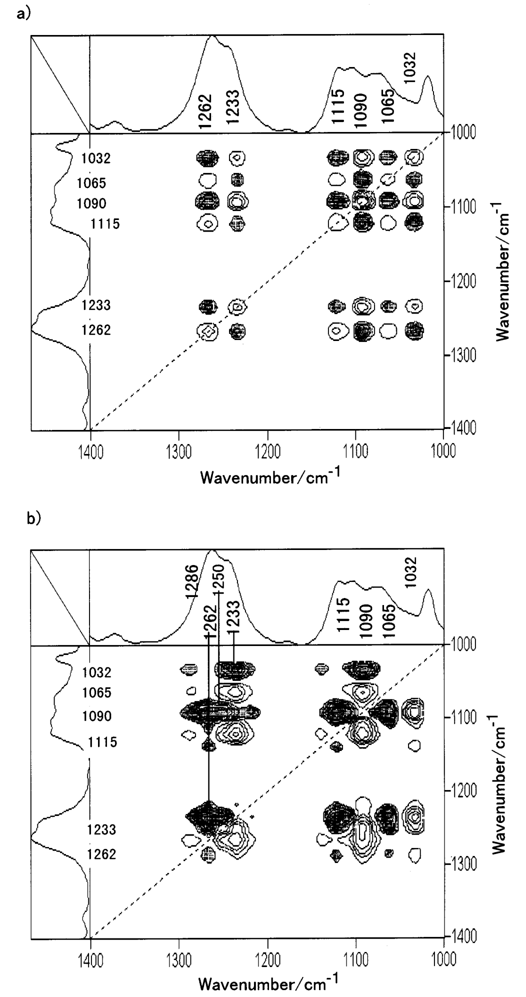


Figure 6. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1400–1000 cm^{-1} region of the oligomerization reaction at 220 °C.

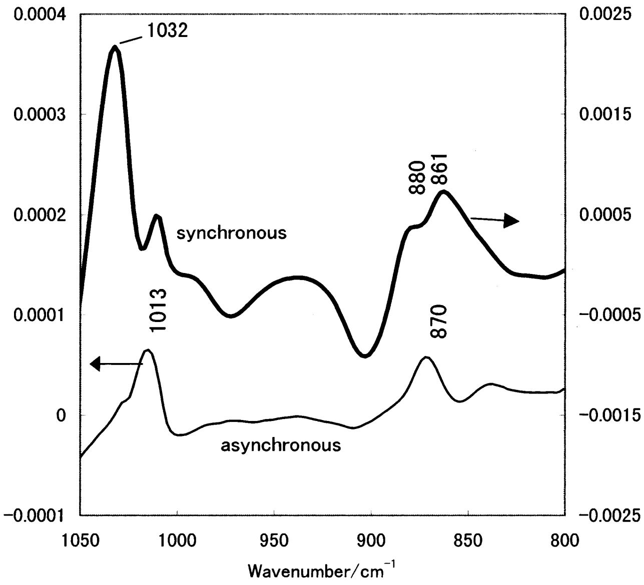


Figure 7. Slice of the synchronous and asynchronous 2D IR correlation spectra at 1032 cm^{-1} of the oligomerization reaction at 220 °C.

NIR Spectra. The time-dependent NIR spectral changes of the reaction mixture are shown in Figure 10. Band assignments for this spectral region were reported in our previous paper.[22] The assignments of major bands are the following: 7060 cm^{-1}, O–H stretching (first overtone); 6501 cm^{-1}, O–H stretching (first overtone, hydrogen bonded); 6011 cm^{-1}, aromatic C–H stretching (first overtone); 5798 cm^{-1}, aliphatic C–H stretching (first overtone); 5118 cm^{-1}, ester C=O stretching (second overtone); 4910 cm^{-1}, combination of O–H stretching and bending; 4677 cm^{-1}, combination of aromatic C–H vibrations. It is noted that the bands at 7060 and 4910 cm^{-1} decrease with time due to the decrease in amount of hydroxyl groups, whereas the peak at 6011 cm^{-1} increases. In our previous study,[22] the peak at 5260 cm^{-1} which had some influence on the PLS models for OH end groups and free EG was not identified in the NIR spectra of the oligomerization reaction. 2D correlation spectroscopy is employed here in order to gain a better understanding of the origin of this peak. The concentration profiles of the OH end group and free EG of the oligomerization reaction obtained from the NIR spectra were almost identical with those in the study by ATR/IR[22] but will not be shown here. For simplicity, the NIR spectra collected at 270 and 230 °C will be used to analyze the reaction. The first eight spectra of Figure 10 will be used for the 2D correlation analysis.

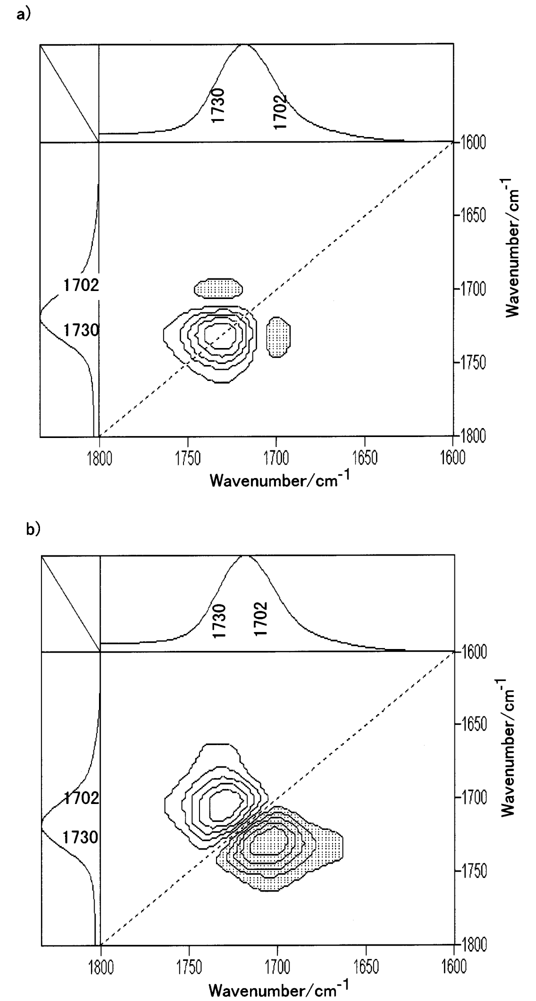


Figure 8. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1800–1600 cm^{-1} region of the oligomerization reaction at 270 °C.

The synchronous and asynchronous 2D maps generated from the time-dependent spectral variations in the 7500–4500 cm^{-1} region at 270 °C are shown in parts a and b of Figure 11, respectively. The synchronous map

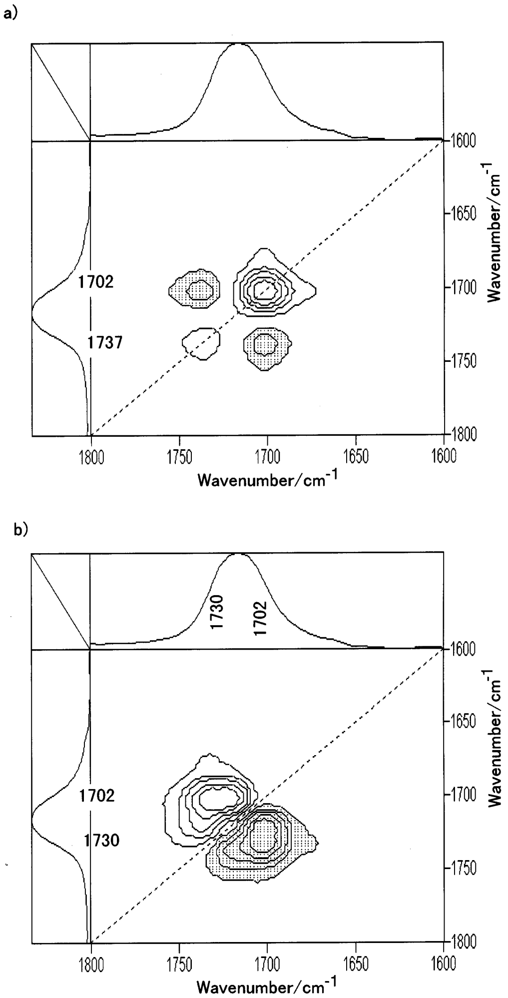


Figure 9. (a) Synchronous and (b) asynchronous 2D IR correlation maps in the 1800–1600 cm^{-1} region of the oligomerization reaction at 220 °C.

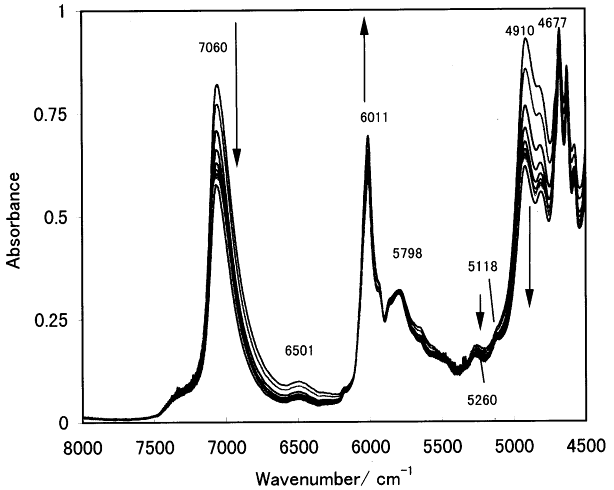


Figure 10. NIR spectra measured in situ during the oligomerization reaction in the 8000–4500 cm^{-1} region. Arrows show the directions of intensity changes during the course of the reaction.

shows a broad autocorrelation peak at 4890 cm^{-1} whose corresponding band decreases with time. The corresponding band is due to the combination of the OH stretching and bending modes.[22] In the asynchronous map, the 4890 cm^{-1} peak consists of two peaks at 4927 and 4743 cm^{-1} which correlate out-of-phase to each other. Another autocorrelation peak at 7060 cm^{-1} actually consists of three peaks 7100, 7020, and 6855 cm^{-1}. The reason for having these peaks is probably that the O–H vibrations from both free EG and BHET overlap in this region. The 5260 cm^{-1} band has a cross-peak with bands around 4890 cm^{-1} and at 7020 cm^{-1}.

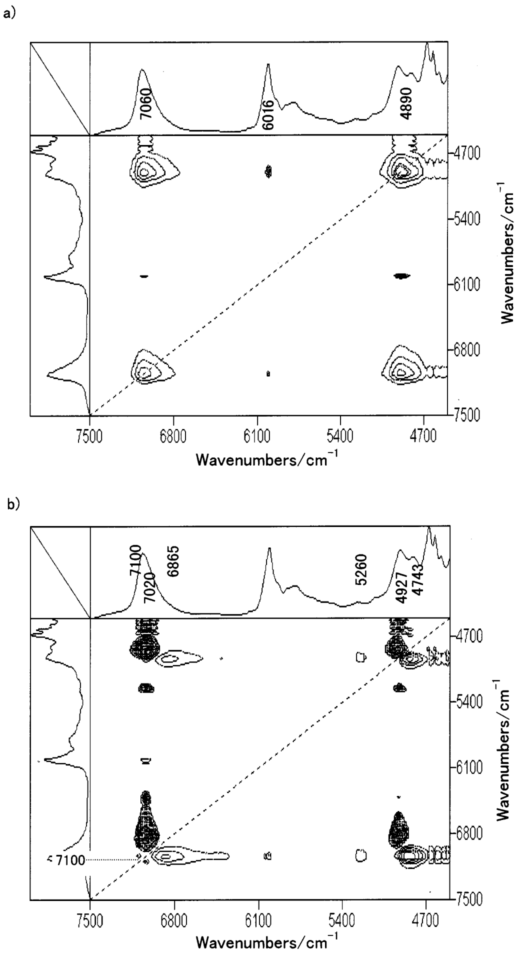


Figure 11. (a) Synchronous and (b) asynchronous 2D NIR correlation maps in the 7500–4500 cm^{-1} region generated from the time-dependent spectra variations of the oligomerization reaction at 270 °C.

Figure 12a,b depicts the corresponding 2D maps at 230 °C. A strong autopeak is observed at 5260 cm^{-1} in the synchronous map. This peak has not only a positive cross-peak with the band at 4860 cm^{-1} due to the combination of O–H stretching and bending modes but also a cross-peak with a band at 6865 cm^{-1}. In the asynchronous spectrum, this peak shows cross-peaks with bands centered at 7060 and 4800 cm^{-1}. The peak at 5260 cm^{-1} decreases out-of-phase with the O–H bands and decreases in-phase with the 6865 cm^{-1} band. The area of the band at 5260 cm^{-1} in the original spectra is plotted vs the reaction time in Figure 13. The plots show monotonic decreases and do not bear a significant resemblance to the concentration profiles of EG.[22] Thus, it does not seem that the band at 5260 cm^{-1} arises from the compounds that are directly involved in the oligomerization reaction itself. The intensity of the peak strongly depends on the temperature of the reaction; the lower the reaction temperature, the stronger the peak. Since the O–H combination band of water appears near 5200 cm^{-1},[29] it is likely that this peak is concerned with the amount of water in the reaction medium. To confirm this, NIR spectra of BHET with

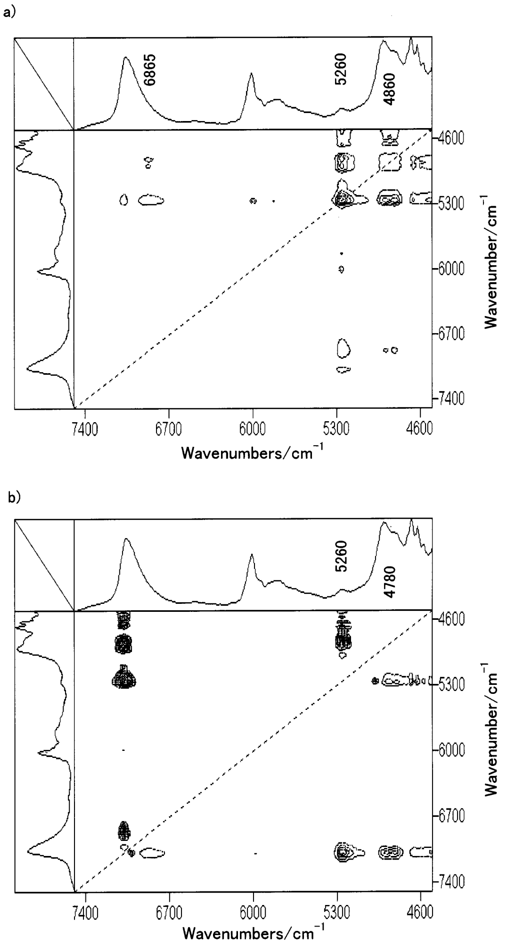


Figure 12. (a) Synchronous and (b) asynchronous 2D NIR correlation maps in the 7500−4500 cm^{-1} region of the oligomerization reaction at 230 °C.

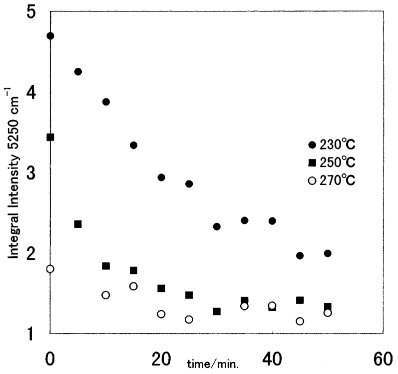


Figure 13. Plots of the peak area intensity of the NIR absorption at 5260 cm^{-1} vs time at 230, 250, and 270 °C.

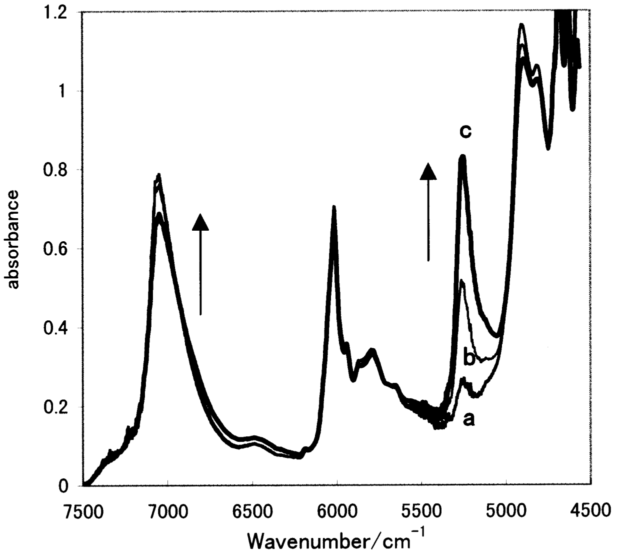


Figure 14. NIR spectra BHET measured in situ at 200 °C: (a) BHET only; (b) addition of 10 mL of water; (c) addition of 16 mL of water.

water were measured as follows. In a 1 L round-bottomed flask with a condenser, 500 g of BHET was heated to 200 °C. Water was then added into the reaction melt, into which a NIR transmission probe was inserted. Mixing was performed throughout the procedure. The method for the NIR measurement was the same as that for the NIR monitoring of the oligomerization.[22] The obtained spectra are shown in Figure 14. As the amount of water is increased, the intensity of the peak at 5250 cm^{-1} also increases. The region around 6800 cm^{-1} also shows a slight increase. From these observations, the peaks at 5260 and 6865 cm^{-1} discussed in Figure 12 are assigned to the OH stretching and bending combination and the first overtone of the OH stretching modes of water, respectively. The addition of 10 mL of water corresponds to approximately 2 wt % concentration. Using the peak area of the 5260 cm^{-1} band, the initial concentration of water for the reaction at 230 °C is calculated to be around 0.4 wt %. The concentration would be only a rough estimate, since a rigorous boiling of water and reflux occur in the course of water addition, and the exact amount of water in the solution has not been measured. However, it should suffice to get an estimate of the content of water. The effect of moisture on the reaction has not been explored in the present study, but it is expected that moisture can disturb the reaction by inducing hydrolysis and interaction with the catalysts. To monitor the amount of water in the reaction medium may become very important in such cases. This study demonstrates that NIR spectroscopy is very useful to probe in situ the water content in a reaction.

Some comments on other peaks in the asynchronous 2D map in Figure 11 are addressed here. A cross-peak is developed between peaks at 4927 and 4800 cm^{-1}, which indicate that the two peaks are not from the same chemical origin. This region was considered to be due to the O−H combination modes. To inspect this region more closely, second derivatives of the first eight spectra are plotted in Figure 15. A peak at 4927 cm^{-1} decreases with time, and thus it is attributed to a band of O−H vibration origin. In contrast, no intensity change is observed for the peak at 4806 cm^{-1}.

Peaks at 7100 and 7020 cm^{-1} also share an asynchronous cross-peak. The former is due to the first overtone of the O−H stretching mode whereas the latter is believed to be a combination peak of C−H vibrations.

The peak near 6016 cm^{-1} does not provide much information. To investigate this region further, the synchronous 2D correlation spectra in the 6500−5500 cm^{-1} region at 270 and 230 °C are shown in parts a and b of Figure 16, respectively. Note that a strong autopeak emerges at 6005 cm^{-1}. This peak is due to the first overtone of the aromatic C−H stretching vibration that increases with time.[22] The relative increase in the concentration of the terephthalate aromatic ring with time is the cause of this intensity change. Peaks in the

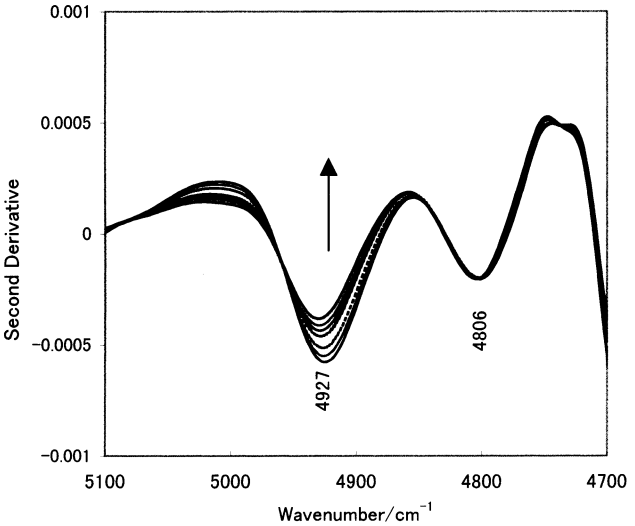


Figure 15. Second derivative NIR spectra in the 5100−4700 cm^{-1} region for the oligomerization reaction at 270 °C.

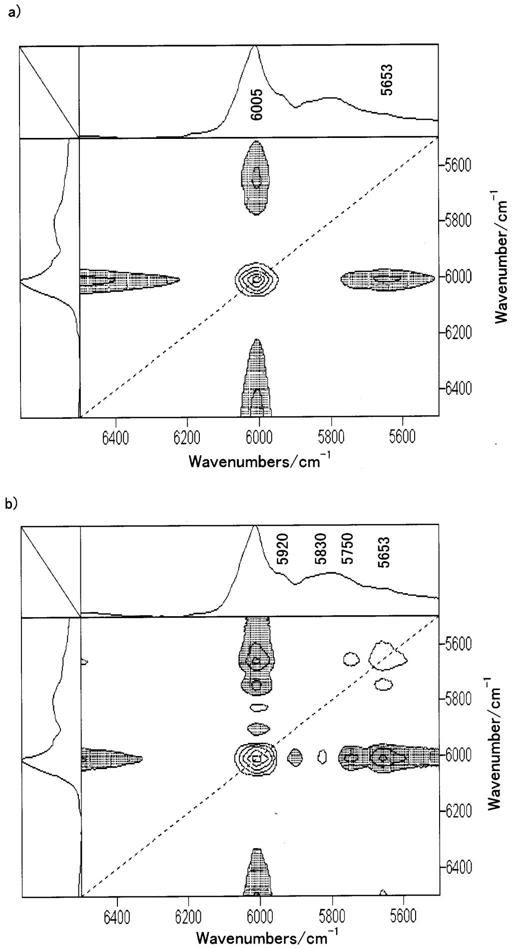


Figure 16. Synchronous 2D NIR correlation maps in the 6500−5500 cm^{-1} region of the oligomerization reaction at (a) 270 and (b) 230 °C.

5900−5500 cm^{-1} region have negative cross-peaks with the aromatic C−H band. These bands originate from the aliphatic C−H stretching vibrations. As can be seen in Scheme 1, the relative contributions of the aromatic C−H bonds to the NIR spectra increase while those of the aliphatic C−H bonds decrease with the oligomerization, if one ignores the contribution from EG that is expelled from the reaction system.

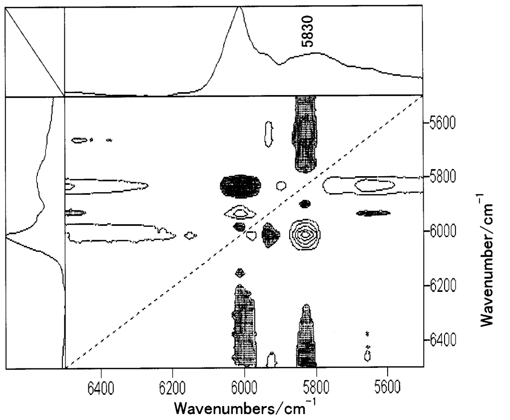


Figure 17. Asynchronous 2D NIR correlation map in the 6500−5500 cm^{-1} region of the oligomerization reaction at 230 °C.

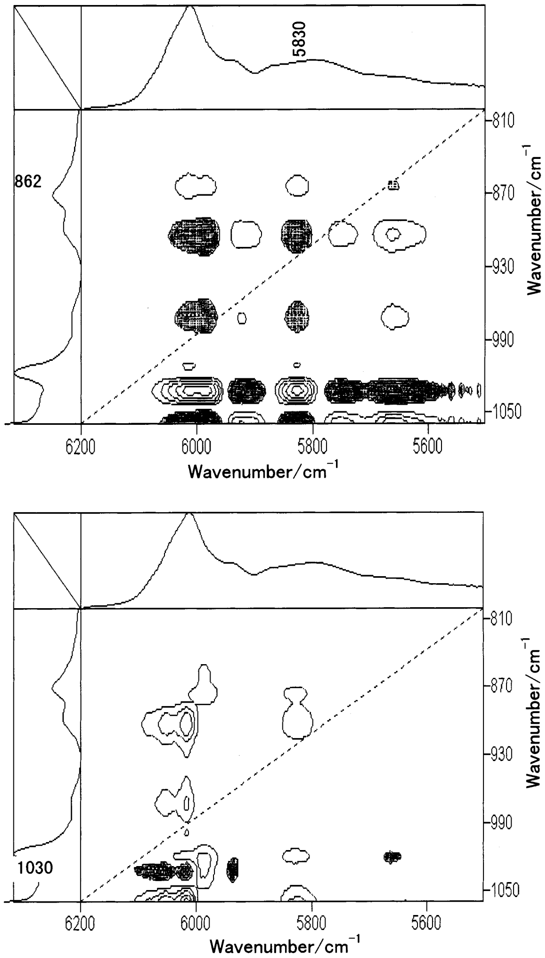


Figure 18. Synchronous and asynchronous 2D NIR−IR correlation maps of the oligomerization reaction at 235 °C.

At 230 °C, the synchronous map looks somewhat complex. An increasing peak is identified at 5830 cm^{-1}. The corresponding asynchronous map at 230 °C is shown in Figure 17. The two peaks at 6005 and 5830 cm^{-1} share a cross-peak. This shows that the peak at 5830 cm^{-1} increases out-of-phase with the aromatic C−H band at 6005 cm^{-1}. Therefore, it is very likely that this peak corresponds to the aliphatic C−H vibration of free EG, since the amount of free EG increases with time at 230 °C.

The detection of free EG has been investigated in the IR experiments,[21] so that it should be worthwhile to compare the present result with those obtained from the IR spectra. For this purpose, 2D NIR−IR correlation spectroscopy is employed. In the hetero correlation analysis, taking data of NIR and IR spectra under the same reaction conditions is imperative. Moreover, using data obtained from separate experiments is questionable because the size and shape of the probes are somewhat different. The change in the probe structure causes slight differences in the liquid−vapor equilibrium for the separate reactions.[22] To overcome this problem, the reaction vessel was modified so that both ATR/IR and NIR probes could be employed at the same time. The reaction was carried out at 235 °C. All the data were collected by the same methods as in the previous experiments.[21,22] The first 10 spectra (50 min) were used for the 2D correlation analysis. The synchronous and asynchronous 2D hetero NIR−IR correlation maps are shown in parts a and b of Figure 18, respectively. The region used was 6200−5500 cm^{-1} for NIR and 1060−800 cm^{-1} for IR. The 1060−800 cm^{-1} region contains key peaks that are associated with free EG. In the synchronous spectrum, the peak at 5830 cm^{-1} in the NIR region has positive cross-peaks with a band centered at 862 cm^{-1} and a peak at 1030 cm^{-1}. In the asynchronous map, the 5830 cm^{-1} band does not share any cross-peak with either of the two peaks. This strongly suggests that the peak at 5830 cm^{-1} belongs to free EG, and this is in accord with the finding from the NIR spectral analysis of the 6500−5500 cm^{-1} region. This is a good example that shows the potential of 2D hetero correlation spectroscopy in extracting the origin of a particular band which is overlapped with many other bands and in making its band assignments.

4. Conclusion

The IR and NIR spectra obtained for the in-situ monitoring of the initial oligomerization of bis(hydroxyethyl terephthalate), BHET, have been investigated by using generalized 2D correlation spectroscopy. Careful inspection of the 2D IR spectra has revealed that the small intensity changes in the 1000−800 cm^{-1} region are due to evolving free EG. The 2D NIR study elucidated that the peak at 5260 cm^{-1} is due to the small amounts of water involved in the reaction. 2D correlation spectroscopy has also successfully extracted the peak at 5830 cm^{-1} of free EG origin in the aliphatic CH_2 stretching band region despite the severe overlap with other bands. The 2D NIR−IR hetero correlation analysis has provided a strong supporting evidence for the assignment of the peak at 5830 cm^{-1}. These conclusions obtained in the present study could not be reached by the previous studies based on PCA and PLS analysis. Since water is a potential threat for oligomerization reactions such as hydrolysis, the fact that NIR spectroscopy can be utilized to monitor water in situ may become vital.

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