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Real-Time Monitoring of the Initial Oligomerization of Bis(hydroxyethyl terephthalate) by Attenuated Total Reflection/Infrared Spectroscopy and Chemometrics

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ABSTRACT: The initial oligomerization of bis(hydroxyethyl terephthalate), BHET, was monitored in-situ by an attenuated total reflection (ATR)/infrared (IR) probe. The progress of the reaction can be probed by the intensity changes in IR bands, and calibration curves for the degree of oligomerization can be developed on the basis of these spectral changes. It was found that the calibration models can be improved significantly using partial least-squares (PLS) regression. The amount of hydroxyl end group, which is a function of the degree of the polymerization, was measured by use of ^{1}H NMR. This parameter was also used to construct the calibration models. The amount of ethylene glycol (EG) in the reaction solution was predicted by the same method. These parameters were found to be very important in understanding the polymerization reaction. From the degree of oligomerization and concentration of free EG, one may deduce the reaction rate constants. Conventional methods for monitoring the reaction involve manual samplings, so that it is both tedious and dangerous to collect enough data. The on-line method like the present one can solve these issues.

Introduction

Real-time monitoring of chemical reactions on-line is very important for understanding the chemistry of the reaction from the points of basic science as well as industry. In conventional methods, one would sample manually reaction solutions and then perform whatever analysis is necessary to obtain values that characterize the reaction. To understand the reaction fully, the concentration of each component must be known. Thus, after sampling the contents are analyzed, for example, by chromatographic or spectroscopic methods, and in most cases, the samples must be pretreated in order to perform such analysis. This is usually tedious, and in a case where a reaction is conducted under extreme conditions, the sampling procedure may become dangerous or at times even impossible. Thus, the reaction could only be evaluated by the final product.

In industry, formation of poly(ethylene terephthalate) (PET) by a condensation reaction is usually carried out under vacuum at high temperature. As the reaction proceeds, the viscosity increases and diffusion concerning ethylene glycol (EG) in the medium becomes important. To understand the kinetics of the condensation reaction itself (i.e., to examine the catalyst activity), it is useful to monitor the initial oligomerization reaction. Collecting information on parameters such as degree of oligomerization and concentration of each component during the reaction are essential. This can be accomplished by manual sampling, but the reaction itself is also carried out at high temperature and nonambient pressure. In these cases, it may not only be difficult to perform manual sampling but also be dangerous.

Recent advances in hardware and software of vibrational spectroscopy enable one to monitor in-situ various chemical reactions.[1−3] Such methods include mid-infrared (IR),[4−13] near-infrared (NIR),[14−18] and Raman spectroscopy.[19,20] All these methods may be applied to reactions such as polymerization. By using vibrational spectroscopy, one can monitor in-situ the progress of reaction from intensity changes in bands. For the present study, IR spectroscopy was used. The method applies an attenuated total reflection (ATR) probe immersed directly into the reaction solution. This probe is made so that they can endure high temperature and pressure.

As mentioned above, the initial oligomerization reaction of PET may be carried out in high vacuum, but in order to analyze IR spectra of the reaction system more closely, we began the study under ambient pressure. Real-time ATR/IR monitoring of PET polymerization have been reported,[21] but no information was provided concerning the initial portion of the reaction and, furthermore, no detailed spectrum analysis was made. We have attempted a more thorough analysis of the time-dependent spectral change using principal component analysis (PCA) and partial least squares (PLS).

Experimental Section

Reagents. The starting material, bis(hydroxyethyl terephthalate) (BHET), was obtained from Tokyo Kasei and used without further purification. Antimony trioxide, which was used as polymerization catalyst, was obtained from Kanto Chemical. It was dissolved in ethylene glycol to yield a 1.9 wt % (w/w) solution. This was used as a stock catalyst solution.

Oligomerization. For oligomerization of BHET, a 1 L round-bottom flask with five necks was used. A condenser was attached to one of the necks to collect any distillates released during the reaction. BHET was incorporated into the vessel and heated to the desired temperature. The catalyst stock solution was added to the molten BHET. The concentration of catalyst was between 150 and 750 ppm, and the reaction

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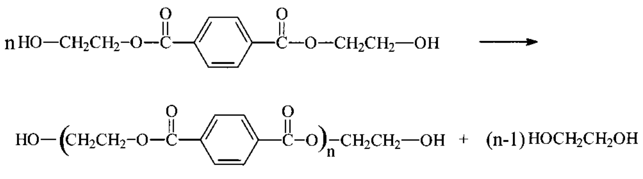
Scheme 1



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.

ATR/IR Spectrometer. For the spectroscopic 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.

Compositional Analysis. The reaction is shown in Scheme 1. As the reaction proceeds, ethylene glycol (EG) is released. Some EG is expelled out of the system, while some will remain in the reaction solution. The degree of oligomerization correlates with the decrease in the OH end groups. The amounts of OH end groups and EG remaining in the solution were measured by ^{1}H NMR as described elsewhere.[22] The reaction usually took about 3−4 h before it reached equilibrium. Samples (approximately 1 mL) were withdrawn from the mixture during the reaction for the NMR analysis. IR spectra were measured in-situ at constant time intervals. Spectral data collected by the IR instrument were converted into Unscrambler ver.6.11 (Camo, Norway) software program to perform the data processing. The 1800−650 cm^{-1} region of IR spectral data was employed for multivariate analysis. For each reaction, the baseline of the set of spectra was adjusted to zero at 2700 cm^{-1}. PLS regression analysis was applied to the data to develop multivariate calibration and prediction models. The optimum number for the PLS regression was selected automatically by the Unscrambler software program.

Results and Discussion

Figure 1 displays time-dependent ATR/IR spectral changes of the reaction mixture in the 1800−650 cm^{-1} region. Although the total amount of ester links does not change during the reaction, intensity changes can be observed for several IR bands. Bands at 1723, 1240, and 1092 cm^{-1} show a marked intensity increase during the course of reaction while those 1370, 980, and 895 cm^{-1} show a small intensity decrease. Bands at 1407, 1016, and 873 cm^{-1} change little with time. The bands that show the intensity increase can be attributed to the ester links formed during the reaction. These peaks correspond to those for PET oligomers. The bands that show the small intensity decrease are of ethylene glycol origin. The intensity decrease results from the decrease in EG being expelled out of the system. The bands that do not give significant intensity variation have their origin in the benzene rings of the terephthalate functionality.

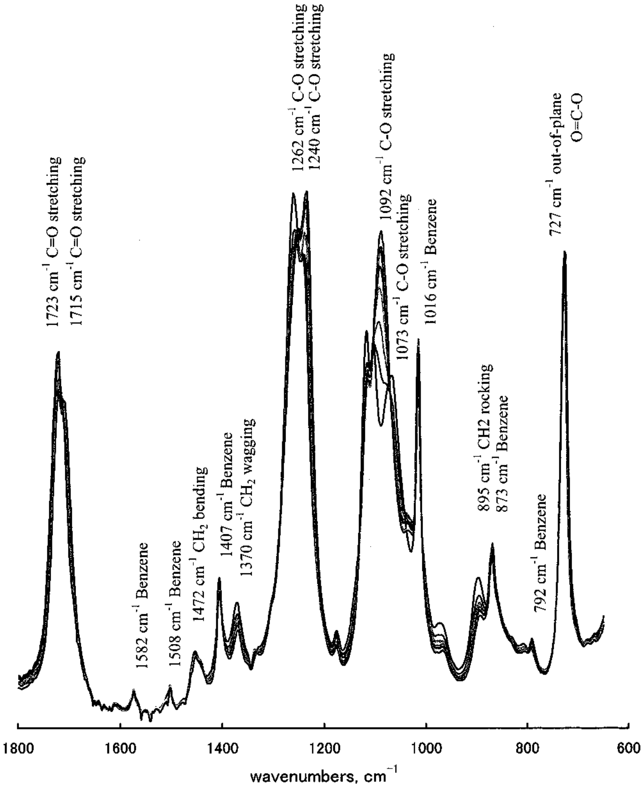


Figure 1. IR spectra of the reaction in the 1800−650 cm^{-1} region.

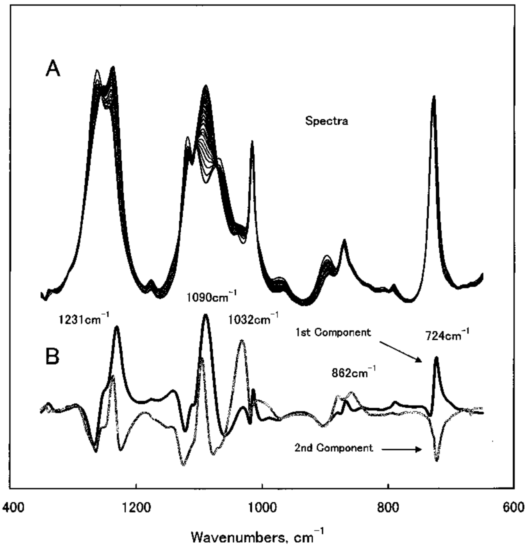


Figure 2. Principal component analysis of reaction spectra: (A) original spectra, (B) first principal component (bold line) and second principal component (light line).

To monitor the reaction, one may use a peak that corresponds to a PET peak. The suitable peak would be the one at 1092 cm^{-1}. The intensity of this peak changes significantly during the reaction and should reflect the increase in the degree of oligomerization. To explore the spectral changes systematically, a PCA was performed for all the spectra shown in Figure 1. Figure 2A,B compares original spectra in the 1350−650 cm^{-1} region with loadings plots for the first two principal components. Note that first principal component show upward peaks at 1231 and 1090 cm^{-1}. These two peaks correspond to the PET bands increasing with the progress of the reaction. In the loadings plot for the second principal component upward peaks appear at 1032, 878, and 860 cm^{-1}. In the original spectra in Figure 1, there are no distinctive absorption bands at these wavenumbers that are distinguishable from other peaks nearby. What has emerged here may be due to free EG, since an IR spectrum of EG shows peaks at 1081, 1030, 875, and 857 cm^{-1} as shown in Figure 1.

The amounts of OH end groups and free EG determined by ^{1}H NMR have been used to develop calibration models for the quantification of these species using PLS regression. A loadings plot of regression coefficients and the original spectra are shown in Figure 3 for the OH

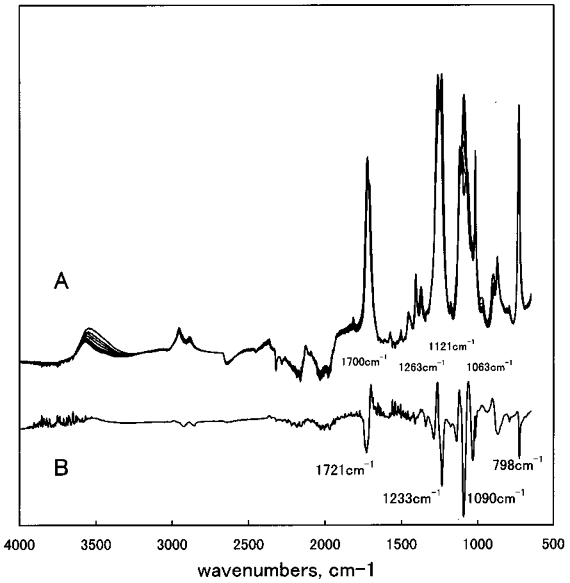


Figure 3. Results of PLS regression for predicting the concentration of the OH end group: (A) original spectra, (B) regression coefficients.

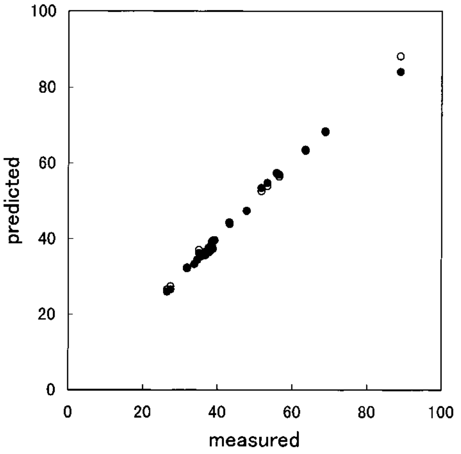


Figure 4. Measured vs predicted plot for the concentration of OH end group: (○) prediction; (●) validation.

end group. Peaks at 1700, 1263, 1121, and 1063 cm^{-1} have positive values whereas those at 1721, 1233, 1090, and 798 cm^{-1} have large negative values. The former peaks are due to BHET, and most of the latter arise from PET oligomer. This is in a good agreement with the assignment described above. The calibration curve measured vs predicted for the OH end group concentration is shown in Figure 4. The vertical axis value of 100 is the amount of OH end group at the beginning of the reaction, which is the amount of this end group for BHET. The number of factor used is 3. The correlation coefficients for prediction and validation were 0.998 and 0.996, respectively.

Figure 5A,B depicts the original spectra and loadings plot of regression coefficients for the model predicting free EG. A large positive value appears around 1026 cm^{-1} in the regression coefficient. This clearly shows that the PLS model for free EG uses a peak of the EG origin. This peak has a counterpart in the second principal component in the PCA analysis (Figure 2B). These results reveal that the PLS model successfully extracts information about free EG from the original spectra. The corresponding calibration curve is shown in Figure 6. The number of factors used is eight, which is much larger than that for the OH end groups. The correlation coefficients for prediction and validation were 0.983 and 0.926, respectively.

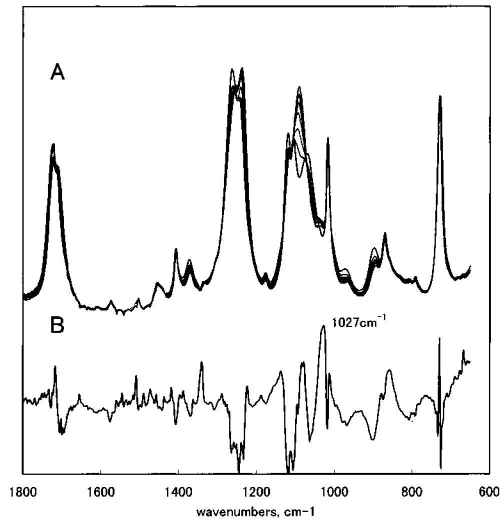


Figure 5. Results of PLS regression for predicting the concentration of free EG: (A) original spectra, (B) regression coefficients.

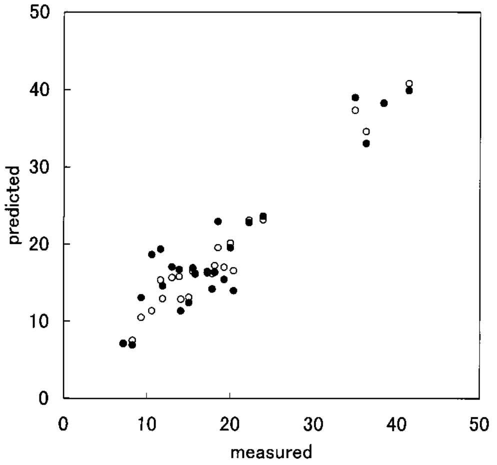


Figure 6. Measured vs predicted plot for the concentration of free EG: (○) prediction, (●) validation.

Figure 7 plots the OH end group values predicted from the PLS regression and the corresponding experimental values from ^{1}H NMR for several experiments under different temperatures. The corresponding plot for the free EG contents is shown in Figure 8. The vertical axes in Figures 7 and 8 are the mole percent of OH end groups and free EG against terephthalate ring, respectively. The predicted values from the ATR/IR measurements, and experimental values from ^{1}H NMR are in a good agreement with each other for both the OH end groups and free EG. Since all the reactions reach equilibrium, the concentration of each component at the equilibrium is dependent on the reaction temperature. This can be seen for the both cases.

For free EG, a more complicated profile is seen at the beginning of the reaction. For the reactions at higher temperatures, an overshoot in the EG concentration is observed. This implies that, in the initial part of the reaction, the rate of evaporation of free EG cannot catch up with the fast evolution of free EG. It may be very difficult to obtain this information with other techniques; the sampling procedure must not perturb the system. For a high precision of the analysis, numerous

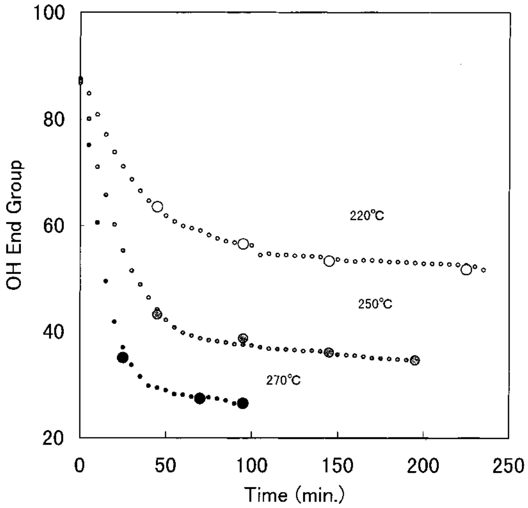


Figure 7. Monitoring of OH end group by ATR/IR spectroscopy for the three experiments at 220, 250, and 270 °C: small circles, ATR/IR; large circles, NMR measurement.

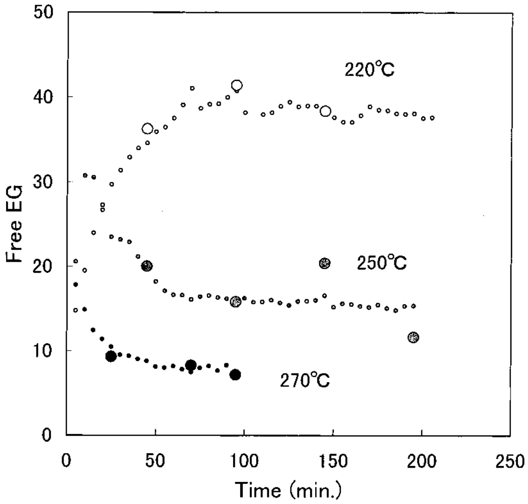


Figure 8. Monitoring of free EG by ATR/IR spectroscopy for the same experiments as those in Figure 7: small circles, ATR/IR; large circles, NMR measurement.

data points are often necessary. Manual sampling and conventional analytical procedures may not be suitable for the task.

Conclusion

By use of ATR/IR spectroscopy in combination with chemometrics, we were able to successfully monitor in-situ the initial oligomerization reaction of PET through the decrease in the end OH group concentration. Excellent agreement was obtained between the present results and those by ^{1}H NMR data, which is the conventional analytical method. The concentration of evolved EG in the course of the reaction was also monitored by the present method. A rather complicated concentration profile was observed for EG concentration in the reaction solution at the beginning of the reaction. This would be extremely difficult to monitor by an analytical technique with manual sampling.

To analyze the time-dependent IR spectra in more depth, a two-dimensional correlation analysis and self-modeling curve resolution study are being carried out in our group, and they will be reported elsewhere. The reaction will be monitored by NIR and compared with the ATR/IR results.

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