Two-dimensional infrared correlation spectroscopy as a probe of sequential events in the diffusion process of water in poly($\varepsilon$-caprolactone)

Yun Peng, Peiyi Wu, and Yuliang Yang
Department of Macromolecular Science Key Lab of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, 200433, Peoples Republic of China

(Received 1 April 2003; accepted 24 July 2003)

In this study, the diffusion process of water molecules in poly($\varepsilon$-caprolactone) (PCL) has been investigated using in-situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In our system, the original broad water OH bands in 1D IR spectra can be effectively differentiated into four bands, located at 3641, 3593, 3410, and 3203 cm$^{-1}$, respectively, using 2D correlation analysis. The bands at 3641 cm$^{-1}$ (antisymmetric) and 3593 cm$^{-1}$ (symmetric) are assigned to the OH stretching vibration of water partially hydrogen bonded with hydrophilic carbonyl group (%C=O) of PCL, while the other band pair at 3410 cm$^{-1}$ (antisymmetric) and 3203 cm$^{-1}$ (symmetric) could be attributed to the stretching vibration of water fully hydrogen bonded with another water molecule. According to the result of the asynchronous correlation, it was concluded that the water molecules at first diffuse into free volume (microvoids) or are molecularly dispersed into the PCL matrix and then form hydrogen bond with the C=O group of the polymer during the process of water diffusion. In addition, the diffusion coefficient was estimated using nonlinear curve fitting of OH band areas in the range of 3800–3000 cm$^{-1}$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1610441]

I. INTRODUCTION

The diffusion of small molecules through polymer membranes is an important phenomenon in many different areas of science and engineering. It is one of the important physical properties of polymers and related to many material fields. For example, the diffusivity in polymer films and membranes is important in connection with the use of polymers as barrier coatings (for protection of an underlying substrate) in packaging applications and for separation science applications. Because of its widespread presence (both vapor and liquid) in the ambient environment in which polymers are used, water is probably the most important diffusant.

However, many aspects of the molecular mechanism of diffusion in polymers are still not well understood. This is due in part to the reality that the hydrodynamic effects in polymer are quite complex. For epoxy resin polymer, two mechanistic approaches have emerged that generally characterize the nature of water in epoxy. One is the free-volume approach, which presumes that water diffuses into epoxy resin and resides in the free volume of the material. The other approach is the interaction concept, that suggests water molecules couple strongly with certain hydrophilic functional groups such as hydroxyl or amine in polymer. For other polymers, Sammon found that there are four different states of OH stretching vibration of water diffusion into polymer, and there are some differences in the different polymer materials for the four states of OH stretching vibration.

In other words, for different materials the situations are different when water diffuses into the polymer matrix.

Much work has been published in this area already using vibration spectroscopy. As a technique sensitive to the interaction between water and polymer, ATR-FTIR technique has been applied to measure the diffusion of water behavior in the polymer surface. The ATR-FTIR analysis methods are convenient, rapid, accurate, and simplify sample handling. The penetration depth of the IR beam into the polymer film sample varies generally in the 0.5–10 μm range, and can be set by adjusting the incidence angle.

The basic concept of the generalized 2D correlation spectroscopy was first introduced by Noda in 1993. Using a generally applicable mathematical formalism, the generalized 2D correlation spectroscopy allows one to construct 2D correlation spectra from any transient or time-resolved variations of spectra having an arbitrary waveform. This generalized 2D correlation spectroscopy was found to be applicable to intensity fluctuations not only in time but also of any other physical or chemical variable, such as temperature, pressure, electric field strength, or concentration. Thus, it offers the possibility to study the dependence of vibrational spectra on any external perturbation in much greater detail than has previously been possible. Owing to the enhancement of the spectral resolution by spreading the peaks over the second dimension, it is possible to identify the spectral features not readily observable in the original data set. Additionally, 2D correlation spectra include information about the relative rate of the spectral intensity changes taking place in the course of the perturbation for different molecular functionalities. Another important feature of 2D IR studies is the possibility...
to correlate different absorptions to support the band assignments.\textsuperscript{20}

In our investigated system,\textsuperscript{21} poly(e-caprolactone) (PCL), an attractive synthetic biomaterial polymer that has been used in many fields, is a material easy to absorb water due to containing the hydrophilic C=O group. The purpose of this study is to investigate the dynamics of water diffusion into PCL film by use of 2D ATR-FTIR spectroscopy. Through 2D correlation analysis, the original wide water OH bands in 1D IR spectra can be effectively differentiated as four bands. In addition, the behavior of water diffusion into polymer was discussed and the effective diffusion coefficient also was measured by a nonlinear curve-fitting method.

II. EXPERIMENT

A. Materials and samples preparation

The PCL (purchased from Solvay Co. in Britain) and solvent (tetrahydrofuran, purchased from Feida Industry and Trade Co. in Shanghai, China) were used without further purification.

Polymer thin film was prepared by casting from the solvent THF (tetrahydrofuran). To begin with, PCL was completely dissolved in the solvent at about 80 °C for 1 h, and then was stirred for 12 h at room temperature to make the solution homogeneous. The concentration of the solution is 2\% (m/v). The solution was then cast onto a 75 × 25 mm microscope slide. Immediately after casting, the slide was kept in the vacuum oven at room temperature for about 12 h to remove residual solvent. Finally, the film was peeled off for use.

B. ATR diffusion experiments

An FTIR spectrometer (a Nicolet Nexus Smart ARK equipped with a DTGS detector) with a horizontal ATR cell (Fig. 1) and a zinc selenide trapezoidal IRE ATR crystal was used to obtain all infrared spectra for the diffusion experiments. Before each experiment, the crystals were cleaned by washing with acetone and were dried under the infrared lamp (10 min). Spectra were collected for the film at increasing times after water contact. All time-resolved ATR-FTIR measurements were carried at 26 °C. The IRE crystal covered by the sample film with a filter paper on it was mounted in an ATR cell; distilled water was injected into the filter paper while starting the data acquisition using a macro program.

![Fig. 1. Schematic description of the ATR-FTIR experimental arrangement.](image)

![Fig. 2. ATR-FTIR spectra of sorbed water in PCL as a function of time.](image)

The spectra were collected at a resolution of 4 cm\textsuperscript{-1} with 16 scans. The time interval between two successive spectra is about 3 min. The original measured wave number range was 4000–650 cm\textsuperscript{-1}. All the original spectra were baseline corrected using OMNIC 5.1 software. The program for the nonlinear curve fitting is ORIGIN 6.1 software.

C. 2D correlation analysis

For the generalized 2D correlation analysis, five spectra at intervals of 6 min in certain wave number range were selected and the 2D software used was a macro program named 2D POCHA produced by Adachi (Kwansei Gakuin University). 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. Five spectra at equal time intervals in certain wave number range were chosen to 2D correlation analysis.

III. RESULTS AND DISCUSSIONS

A. IR spectra of the investigated system

Time-evolved spectra for water diffusion into the polymer film are shown in Fig. 2. Two bands are present in the range of 3800–3000 cm\textsuperscript{-1} and 1600–1650 cm\textsuperscript{-1}, representing the stretching and deformation vibration of OH group in water, respectively. Compared to the OH stretching vibration, the intensity changes of OH deformation band is not sensitive to our system, which limits its use for measuring water diffusion processes in the polymer film. Hence, the \(\nu\) (OH) stretching band (3800–3000 cm\textsuperscript{-1}) was used for subsequent analysis in our study.

B. Two-dimensional analysis

Figure 3 shows contour map representation of (A) synchronous and (B) asynchronous 2D correlation spectra in the region of 3800–3000 cm\textsuperscript{-1}. Throughout this paper, shaded and unshaded cross peaks in the contour maps denote negative and positive correlation peaks, respectively. Note that only one strong auto peak is clearly observed at 3384 cm\textsuperscript{-1}.
in the synchronous spectrum, which is assigned to the OH stretching band of water. Bands originating from other elements are obscured by this strong band. Thus, from the synchronous spectrum we cannot obtain solid information about the diffusion behavior of water in polymer.

Absorption bands characteristic of water can be clearly separated in the corresponding asynchronous spectrum shown in Fig. 3(A). The asynchronous spectrum is antisymmetric with respect to the diagonal line. In the 2D spectra, an asynchronous cross peak develops only if the intensities of two spectral features change out of phase (i.e., delayed or accelerated) with each other. Three cross peaks (3641/3410 cm$^{-1}$, 3410/3203 cm$^{-1}$, 3593/3410 cm$^{-1}$) dominate the asynchronous map in the upper left triangle of Fig. 3(B). The existence of these asynchronous bands reveals that during the diffusion the broad water stretching vibration at 3800–3000 cm$^{-1}$ is split into four separate bands located at 3641, 3593, 3410, and 3203 cm$^{-1}$, respectively, which overlap in the 1D-IR spectra. The sign of the cross peaks in the asynchronous spectrum gives more useful information about relative temporal relationships for different bands. According to the rule proposed by Noda, the three peaks (3641/3410 cm$^{-1}$, 3410/3203 cm$^{-1}$, and 3593/3410 cm$^{-1}$) indicate that the intensity of the band at 3410 cm$^{-1}$ varies prior to intensities of the bands at 3641, 3593, and 3203 cm$^{-1}$, and the intensity of the band at 3203 cm$^{-1}$ varies earlier than the intensities of the bands at 3641 and 3593 cm$^{-1}$.

The infrared spectrum of pure water has an intense and broadband envelope at about 3300 cm$^{-1}$ (shown in Fig. 4) that is due to the OH stretching modes. According to Sammon, decomposition of the spectral band envelope into Gaussian bands can give four adequately resolved bands located at 3192, 3386, 3510, 3606 cm$^{-1}$, respectively. The bands appear at 3192 and 3386 cm$^{-1}$ due to the $\nu_s$ and $\nu_a$ modes of strongly hydrogen-bonded water molecules; the additional two bands are assigned to the vibrations of partially hydrogen-bonded water molecule. Partially hydrogen-bonded water molecule has one of its OH groups participating in hydrogen bonding to another water molecule, whereas the second OH group is considered as free or weakly hydrogen bonded and appears at the higher wave number than two additional deconvoluted band positions given above.

Compared to the pure liquid water, the $\nu$(OH) band envelope in the ATR-IR spectra of the water in PCL moves to higher wave number, which indicates that the water hydrogen bond is weakened due to the interaction of water with PCL. In our case, the OH stretching IR band of water appears at 3410 and 3203 cm$^{-1}$ due to the $\nu_s$ and $\nu_a$ modes of water molecules that are in strongly hydrogen-bonded environments. The two additional bands in the infrared spectrum are due to the vibrations of a weakly hydrogen-bonded water molecule with the C==O group in PCL. In addition, accord-
ing to the asynchronous map in Fig. 3, the bands due to the strong hydrogen-bonded $v_s + v_f$ OH of water (bulk water) vary ahead of the weakly hydrogen bonded $v_s$ OH of water (bound water), which means that the intensity changes of the PCL networks could be caused in the following way: during the process of water uptake in the PCL, the water molecules at first diffuse into free volume or are molecularly dispersed into the polymer matrix and then hydrogen bond with the $C=O$ group of the polymer as bound water.

C. Estimation of diffusion coefficient

For Fickian diffusion in polymers, Eq. (1)\(^4\) is given to estimate the effective diffusion coefficient of water from ATR-FTIR spectra

$$A_t = 1 - \frac{8 \gamma}{\pi [1 - \exp(-2 \gamma L)]} \times \sum_{n=0}^{\infty} \left[ \frac{\exp(g)[f \exp(-2 \gamma L) + (-1)^n(2 \gamma)]}{(2n+1)(4 \gamma^2 + f^2)} \right],$$ \(1\)

where

$$g = -\frac{D(2n+1)^2 \pi^2 t}{4L^2},$$ \(2\)

$$f = \frac{(2n+1) \pi}{2L}.$$ \(3\)

In Eq. (1), $A_t$ is the band absorbance of ATR-FTIR spectra at time $t$, $A_\infty$ is the band absorbance at equilibrium, $\gamma$ is the penetration depth of the evanescent wave, $L$ is the thickness of the polymer film (invariable), and $D$ is the diffusion coefficient. The diffusion coefficient can be calculated by a nonlinear curve fitting\(^12\) to Eq. (1) from integral of OH stretching variation band area versus time. In the nonlinear curve-fitting program,\(^12\) $A$ means zero correction parameter, $M_f$ means the band area of ATR-FTIR spectra at time $t$ (it corresponds to $A_t$), and $M_\infty$ means the equilibrium band area (it corresponds to $A_\infty$). The fitting curve and analysis results are shown in Fig. 5 and Table I, respectively. This method is very convenient to estimate the diffusion coefficient.

IV. CONCLUSIONS

In this study, a time-resolved 2D ATR-FTIR correlation spectroscopy was used to study water diffusion processes in PCL film. The asynchronous correlation spectra have provided more detailed information that cannot be observed in 1D-IR spectra. Using a 2D correlation analysis, the original wide water OH bands in 1D-IR spectra can be effectively differentiated as four bands and their band positions and relative variation rates are determined. According to the corresponding asynchronous correlation spectra, water molecules (bulk water) at first disperse into the polymer and then form hydrogen bond (bound water) with carbonyl group of polymer during the diffusion process into the polymer film.

ACKNOWLEDGMENTS

The study reported in this paper was supported by the National Science Foundation of China (NSFC) (No. 20274010, No. 50103003), the “Qimingxing” Project (No. 01QE14011) of Shanghai Municipal Science and Technology Commission, the “Shuguang” Project (No. 01SG05) of the Shanghai Municipal Education Commission, and the Special Funds for Major State Basic Research Projects (G1999064800).

### Table I. The fitting results from ATR-FTIR spectra.

<table>
<thead>
<tr>
<th>$A$ (s)</th>
<th>$M_f$</th>
<th>$L$ (cm)</th>
<th>$D(10^{-10} \text{ cm}^2 \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6.10231</td>
<td>500.24255</td>
<td>0.0016</td>
<td>9.1187</td>
</tr>
</tbody>
</table>

19. Y. Wang, K. Murayama, Y. Myojo, R. Tsenkova, N. Hayashi, and...