# Two-Dimensional Raman Correlation Spectroscopy Study of the Pathway for the Thermal Imidization of Poly(amic acid)

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The pathway producing imide ring closure during the thermal imidization of poly(amic acid) (PAA) was investigated in detail using a new analytical method, two-dimensional (2D) Raman correlation spectroscopy. The signs of the cross peaks in synchronous spectra provided evidence of the thermal imidization of PAA into PI as the heating temperature increased. The signs of the cross peaks in asynchronous spectra suggested that the imide-related modes changed prior to the amide or carboxylic mode, which indicates that cyclization occurred before the amide proton was abstracted.

**Key Words :** Thermal imidization, Poly(amic acid), Polyimides, Two-dimensional Raman

## Introduction

Aromatic polyimides (PIs) are widely used in various applications[1-4] due to their outstanding thermal and mechanical properties. PIs are generally synthesized from poly(amic acid) (PAA) precursors by either stepwise thermal or chemical imidization. The kinetics of thermal imidization from PAA to PI has been the subject of studies for some years, and has been extensively investigated using various spectroscopic methods, such as NMR, UV, IR, Raman, and fluorescence spectroscopy, by a number of research groups.[5-10] As a result, the activation energy and reaction order of the thermal imidization of PAA have been calculated,[11-13] and the effects of solvent, film thickness, and heating temperature on the thermal imidization have also been thoroughly studied.[14-16] Fewer studies have examined the detailed pathways of thermal imidization; in particular, the cyclization process during thermal imidization needs further investigation. Only a few papers have discussed plausible pathways for imide ring closure. For example, Kreuz *et al*. suggested that the proton attached to the nitrogen is lost either after or before cyclization.[17,18] They also suggested that the film type of PAA follows the former process, while deprotonation occurs first in basic solvents, such as N-methyl-2-pyrrolidone (NMP). Although their results are needed further confirmation, to our best knowledge, no studies have been performed. Since the physical and mechanical properties of PIs are closely related to the processing conditions,[19,20] a full understanding of the pathways of thermal imidization will provide useful information for producing PIs with enhanced properties.

Therefore, this study investigated the detailed pathway of imide ring closure during the thermal imidization of PAA using a powerful new analytical method, two-dimensional (2D) Raman correlation spectroscopy.

2D Raman correlation spectroscopy was initially developed by I. Noda in 1986 and has attracted much attention.[21-23] The basic concept of the 2D Raman correlation method is similar to that of 2D NMR, and a 2D Raman correlation spectrum is derived from a conventional one-dimensional (1D) Raman spectrum. In general, a 2D correlation contour map is obtained by spreading a 1D spectrum onto two axes, and then the correlation between bands is analyzed mathematically. 2D Raman correlation spectroscopy has been found to be especially advantageous for monitoring the dynamics of a system, which is not possible using 1D spectroscopy. This powerful technique has been applied to various fields, such as complex reactions, electrochemistry, photochemistry, and polymer blends.[23-25] The feasibility of analyzing polymers using the 2D Raman method is also well demonstrated in the literature.[26-28] For example, the kinetics of epoxy curing were studied, and very small changes in overlapping bands, which were not detectable by other methods, were clearly found.[28] A detailed description of the practical method and the complete numerical procedure to produce 2D correlation spectra from a set of spectral data are thoroughly introduced elsewhere.[28-31]

For this study, thin film type PIs were prepared from a PAA precursor *via* a stepwise heating process, and the 1D Raman spectrum was obtained at each heating step to collect dynamic spectra with respect to the heating temperature. These were then converted into a 2D Raman spectrum. The sequential order of cyclization in thermal imidization was determined by analyzing the correlations between bands in both synchronous and asynchronous spectra.

## Experimental Section

**Synthesis**. The general conventional synthetic scheme of polyimides (PI) *via* poly(amic acid) (PAA) is shown in Figure 1. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Aldrich and purified by vacuum sublimation before use. N-methyl-2-pyrrolidone (NMP, Duksan) was used after drying with calcium hydride

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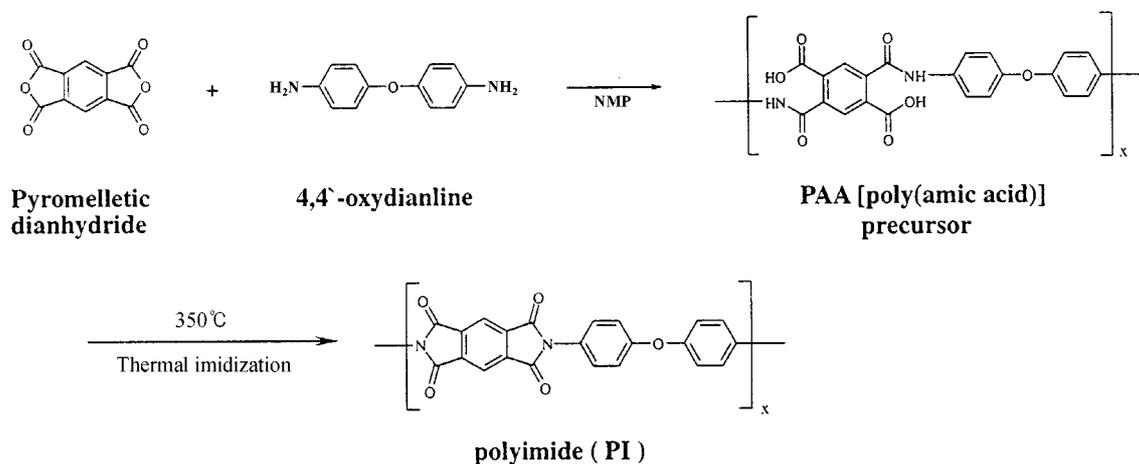
**Figure 1**. The general synthetic scheme of polyimide (PI) *via* poly(amic acid) (PAA).

and subsequent vacuum fractional distillation. The detailed synthetic procedure is as follows: 0.01 M of PMDA was added to 0.01 M of ODA dissolved in 50 mL of NMP. The mixture was then stirred for 18 h under nitrogen at room temperature. The solution gradually became viscous and a clear PAA solution was obtained.

A thin film was made by spreading one drop of the PAA precursor solution in NMP (10 wt.%) onto a clean glass slide and drying the solvent at room temperature in a vacuum oven for 24 h. The absence of solvent in the film before thermal treatment was confirmed by the FT-IR spectra. Thermal imidization of the cast film involved a stepwise heating for 2 h at 80 °C, for 1 h at 160 °C, and then for 30 min each at 250, 300, and 350 °C. The thermal treatments were carried out in a furnace (Thermolyne 62700) under a nitrogen atmosphere. After completing each thermal treatment, the film was allowed to cool to room temperature. The thin film was removed from the glass slide by dipping it in distilled water. Then, the film was dried in a vacuum oven at 50 °C for 24 h to remove residual water.

**Measurement**. One-dimensional Raman spectra of the polymer films were obtained by using Fourier-transform (FT) Raman (Bruker RFS-100S) spectrometry. All 1D FT-Raman spectra were collected with a resolution of 2 cm$^{-1}$ and 400 scans.

**Analysis**. Two-dimensional Raman correlation analysis was carried out using the software kindly supplied by Prof. Yukihiro Ozaki at Kwansei Gakuin University in Japan. The software program was written using Matlab 5.3 following the algorithm developed by I. Noda.

## Results

Figure 2 shows the 1D FT-Raman spectra of PAA as a function of heating temperature. The spectral assignments of the peaks for PAA and PI are summarized in Table 1. The characteristic bands of PAA (Fig. 2(a)) are as follows: 881 cm$^{-1}$, amide I; 1247 cm$^{-1}$, amide III; 1330 cm$^{-1}$, symmetric stretching of carboxylic acid; 1565 cm$^{-1}$, amide II; 1606 cm$^{-1}$, ring vibration of carboxylic acid; 1662 cm$^{-1}$, amide I; 1724

cm$^{-1}$, C=O of carboxylic acid. The characteristic bands for polyimide obtained after heating PAA at 350 °C (Fig. 2(f)) are imide I (1788 cm$^{-1}$), imide II (1394 cm$^{-1}$), and imide III (1124 cm$^{-1}$). The imidization of PAA was easily identified by the disappearance of the amide-related bands and the appearance of the corresponding imide bands as the heating temperature increased. In more detail, the respective bands for carboxylic acid and amide II at 1330 and 1565 cm$^{-1}$ gradually diminished as the temperature increased, and finally disappeared at 250 °C. Conversely, the typical imide peaks at 1394 and 1788 cm$^{-1}$ began to appear at 80 °C and were enhanced as the temperature increased to 250 °C. The other typical bands for amic acid and the imide behaved in the same manner as those of PAA and PI, respectively. Although the progress of the thermal imidization of PAA into PI is well represented in Figure 2, the detailed pathway could not be understood only from Figure 2.

The pathways of cyclization during thermal imidization suggested by Kreuz *et al.*[17,18] are depicted in Figure 3. In
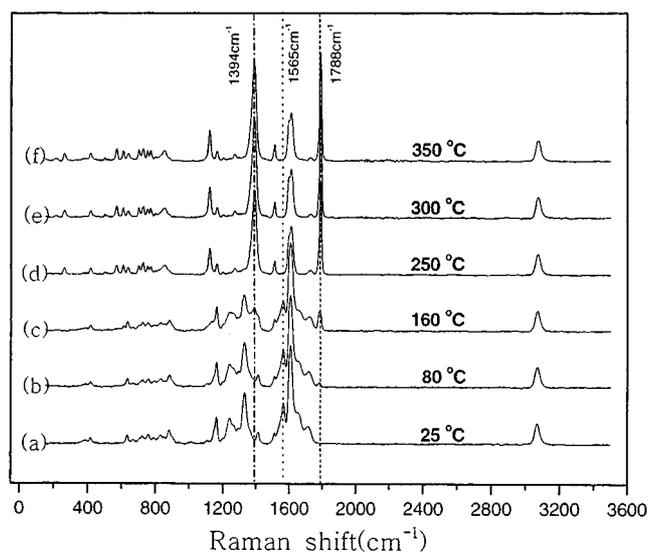
**Figure 2**. The one-dimensional (1D) FT-Raman spectra of PAA as a function of heating temperature. (a) 25 °C, (b) 80 °C, (c) 160 °C, (d) 250 °C, (e) 300 °C, (f) 350 °C.

**Table 1**. The band assignments of the peaks of FT-Raman spectra for PAA and PI

| Assignment (cm$^{-1}$) | PAA [poly(amic acid)] | PI [polyimide] |
|:---:|:---:|:---:|
| 881 | O-C=O or O=C-N (amide I) | |
| 1124 | | Imide III |
| 1247 | Amide III ( NH bend + CN stretch) | |
| 1330 | Symmetric carboxylate stretch | |
| 1394 | | Imide II (C-N-C stretch) |
| 1565 | Amide II ( NH bend + CN stretch) | |
| 1606 | Ring vibration of carboxylic acid | |
| 1614 | | Aromatic ring |
| 1662 | Amide I (carbonyl stretch) | |
| 1685 | Asymmetric carboxylate stretch | |
| 1724 | C=O stretch of free carboxylic acid | |
| 1728 | | Imide I (C-C(O)-C asymmetric stretch) |
| 1788 | | Imide I (C-C(O)-C symmetric stretch) |
| 3070 | Aromatic CH bend | Aromatic CH bend |

pathway 1, the cyclization occurs first *via* nucleophilic attack of the nitrogen on to a carbonyl, and then the proton attached to the nitrogen atom is abstracted with simultaneous protonation of the alkoxide. Subsequent dehydration of the intermediate results in the complete imide ring structure. Conversely, deprotonation of the amide hydrogen occurs first in pathway 2, and is followed by cyclization and dehydration, in order. Moreover, Kreuz *et al.* suggested that the presence of solvent molecules in PAA solution assists the loss of the carboxylic proton (pathway 1), while the ring closure may proceed *via* the attack of the neutral amide on the undissociated acid of PAA in the film state.

In order to investigate the most plausible pathway for PI formation from PAA in the film state, the powerful 2D Raman correlation method was used to produce 2D Raman contour maps. In general, synchronous and asynchronous correlation spectra are generated from the 2D analysis. Terminology such as auto peak and cross peak originated from 2D NMR. The synchronous correlation spectrum in the region from 1800 to 1550 cm$^{-1}$ is displayed in Figure 4(a). The diagonal peaks referred to as auto peaks are present on the diagonal positions at 1606 and 1788 cm$^{-1}$. A synchronous spectrum is generally symmetric with respect to the diagonal line corresponding to coordinates $v_1 = v_2$. According to the

2D correlation rules,[24,29] strong auto peaks are supposed to appear when any peaks in the region of interest change in intensity to a great extent under a given perturbation. Few or no auto peaks correspond to no susceptibility of the applied perturbation for that spectral region. Therefore, the presence of auto peaks at 1606 and 1788 cm$^{-1}$ in Figure 4(a) indicates that spectral changes were induced by the temperature increase. The peaks at 1606 and 1788 cm$^{-1}$ were assigned to amide and imide vibrational modes, respectively, providing evidence for the thermal imidization of PAA into PI, which is also already observed in 1D Raman spectra.

Cross peaks are peaks located at the off-diagonal positions of a synchronous 2D spectrum and represent simultaneous or coincidental changes in spectral intensities observed at two different spectral variables, $v_1$ and $v_2$. Their signs are either positive or negative, and are shown as open or solid circles on a 2D contour map, respectively. Referring to the 2D correlation rules,[24,29] a positive sign indicates that the intensities of the corresponding bands in the one-dimensional spectra are either increasing or decreasing together, while a negative sign indicates that one is increasing and the other is decreasing. In Figure 4(a), positive cross peaks positioned at 1565 and 1606 cm$^{-1}$ (or 1606, 1565 cm$^{-1}$) are both assigned as amide bands, showing that the amide bands vary together

Pathway 1
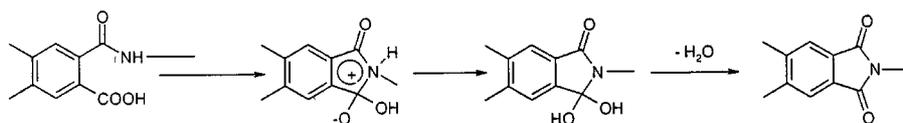


Pathway 2
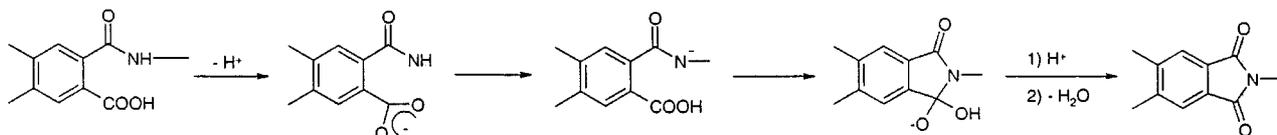


**Figure 3**. The suggested pathways of cyclization during the thermal limidization of PAA.
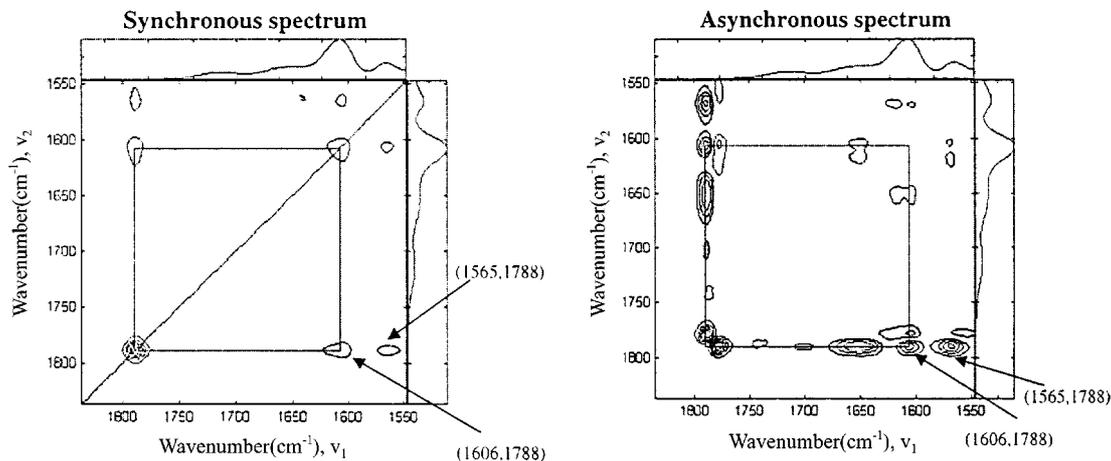
**Figure 4**. The 2D Raman correlation spectra in the region of 1800-1550 cm$^{-1}$, (a) synchronous and (b) asynchronous.

in the same direction. Negative cross peaks are observed at 1606, 1788 cm$^{-1}$; 1565, 1788 cm$^{-1}$, representing the anti-correlation between the amide and imide modes. In other words, the amide mode diminished, while the imide mode was enhanced as temperature increased or *vice versa*. Consequently, the thermal imidization of PAA into PI was easily confirmed with this 2D correlation map, and this result is in good agreement with that obtained from the 1D method.

Figure 4(b) shows the asynchronous spectrum in the region from 1800 to 1550 cm$^{-1}$. Basically, an asynchronous spectrum with cross peaks provides information about the order or priority of the modes of variables $v_1$ and $v_2$.[23-24,29] A positive cross peak indicates that $v_1$ occurs predominantly before $v_2$, while a negative cross peak indicates that $v_2$ occurs first. This rule is reversed when the sign of the corresponding cross peak in the synchronous spectrum is negative. Strong positive cross peaks in the asynchronous spectrum in Figure 4(b) are observed at 1606, 1788; 1565, 1788 cm$^{-1}$. According to the rules just introduced, the modes responsible for the amide at 1606 and 1565 cm$^{-1}$ indicate a change before the imide mode at 1788 cm$^{-1}$ if the related cross peaks of the synchronous spectrum are positive. However, the situation is reversed because the corresponding cross

peaks of the synchronous spectrum (Fig. 4(a)) are negative, indicating that the imide ring was formed before release of the amide proton (pathway 1 in Fig. 3). The negative cross peaks in the asynchronous spectrum in Fig. 4(b) are positioned at 1788, 1606; 1788, 1565 cm$^{-1}$. The 2D rules introduced previously suggest that the amide modes at 1606, and 1565 cm$^{-1}$ changed before the imide mode at 1788 cm$^{-1}$. However, the priority is reversed since the corresponding cross peaks in the synchronous spectrum are negative. Therefore, it is obvious that the imide ring closure occurred before abstraction of the amide proton.

Figure 5 shows the 2D correlation spectra in the region of 1800-1350 cm$^{-1}$. The synchronous spectrum in Figure 5(a) yields positive cross peaks at 1565 and 1606 cm$^{-1}$, and negative cross peaks at 1394, 1606; 1394, and 1565 cm$^{-1}$. The presence of the positive cross peaks indicates that the intensities of the amide II and carboxylic acid bands changed together in the same direction. The negative cross peaks reveal that the amide II mode varied in the opposite direction to the imide II mode as a function of the heating temperature.

In order to investigate the order of the ring closing process more closely, an asynchronous spectrum was obtained and is
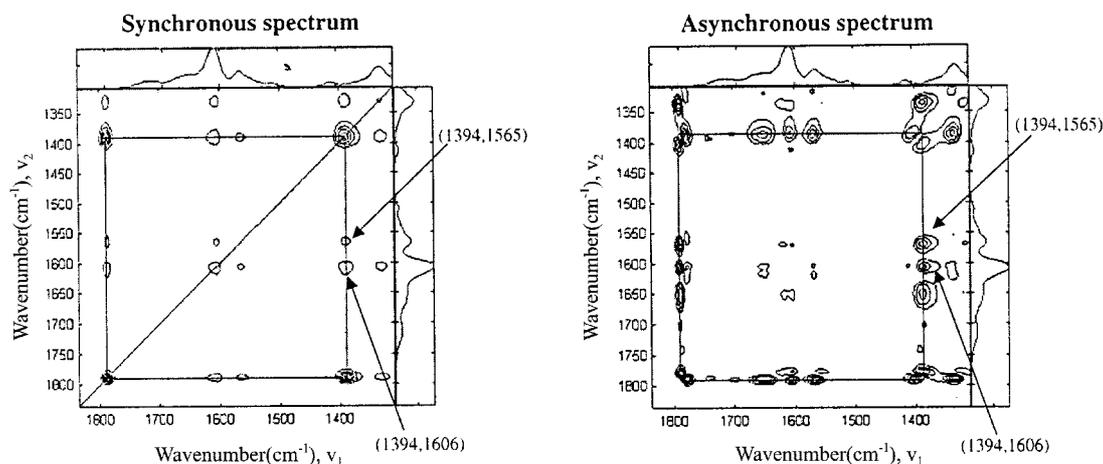


**Figure 5**. The 2D Raman correlation spectra in the region of 1800-1350 cm$^{-1}$, (a) synchronous and (b) asynchronous.
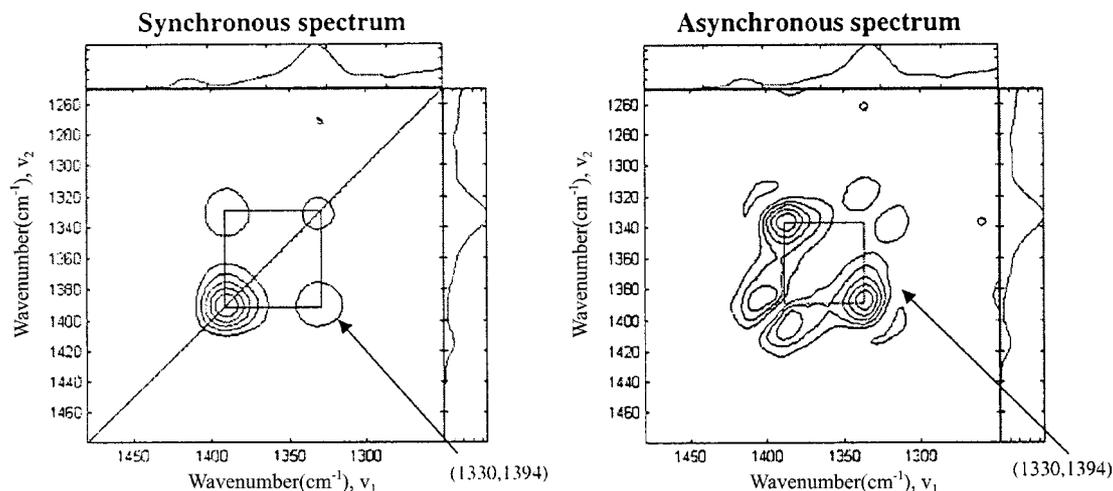
**Figure 6**. The 2D Raman correlation spectra in the region of 1400-1300 cm$^{-1}$, (a) synchronous and (b) asynchronous.

shown in Figure 5(b). The negative sign of the cross peaks at 1394, 1606; 1394, 1565 cm$^{-1}$ suggests that the amide modes (1606 and 1565 cm$^{-1}$) changed before formation of the imide ring. However, the negative sign of the peaks in the synchronous spectrum (Fig. 5(a)) reverse the situation, indicating that the imide ring closed before the proton was released, which Fig. 4(b) confirms.

Studies of imidization in 1D Raman spectra are often based on the disappearance of the carboxylic group band at 1330 cm$^{-1}$ and the appearance of the corresponding imide band at 1394 cm$^{-1}$.[32] Therefore, it is valuable to monitor the intensity changes and relationships of these bands in the 2D contour maps. The 2D correlation spectra in the region 1400 to 1300 cm$^{-1}$ are shown in Figures 6 (a) and (b). Figure 6(a) is the synchronous spectrum, and the negative cross peak at 1330, 1394 cm$^{-1}$ suggests the opposed correlation of the carboxylic group and imide II. The positive cross peak at 1330, 1394 cm$^{-1}$ in the asynchronous spectrum (Fig. 6(b)) and the negative sign of that peak in the synchronous spectrum reveal that the imide mode changed before the amide mode. In other words, cyclization occurred before the proton attached to the amide nitrogen was removed.

The thermal imidization of PAA into PI was easily confirmed from the signs of the synchronous spectra, and the order of cyclization during the thermal imidization was determined from the asynchronous spectra, and is summarized in Table 2.

**Table 2**. Order of events during thermal imidization of poly(amic acid)

| $\varphi$ (synchronous at $v_1$, $v_2$) | $\Psi$ (asynchronous at $v_1$, $v_2$) | Order[a] |
|---|---|---|
| 1606, 1788 < 0 | 1606, 1788 > 0 | after |
| 1565, 1788 < 0 | 1565, 1788 > 0 | after |
| 1394, 1606 < 0 | 1394, 1606 < 0 | before |
| 1394, 1565 < 0 | 1394, 1565 < 0 | before |
| 1330, 1394 < 0 | 1330, 1394 > 0 | after |

[a]before means that the intensity change of the band at $v_1$ occurs prior to $v_2$ for the asynchronous peak at $v_1$ and $v_2$.

**Conclusion**

The detailed pathway of the thermal imidization of film-type PAA into PI was thoroughly investigated using 2D Raman correlation spectroscopy, which produces dynamic information that is not possible from 1D Raman spectroscopy. The positive sign of the cross peaks at 1565, 1606 cm$^{-1}$ in the synchronous spectra indicates that the amide-related bands varied together in the same direction. The negative sign of the cross peaks positioned at 1606, 1788; 1565, 1788; 1394, 1606; 1394, 1565 cm$^{-1}$ in the synchronous spectra shows that the changes between the amide and imide modes occurred in opposite directions. Positive cross peaks in the asynchronous spectra appeared at 1606, 1788; 1565, 1788; 1565, 1394; 1606, 1394; 1394, 1330 cm$^{-1}$ and negative peaks at 1788, 1606; 1788, 1565; 1394, 1606; 1394, 1565; 1394, 1330 cm$^{-1}$. These provide a very useful guide for determining the order of cyclization in thermal imidization. These results are summarized in Table 2, and suggest that the imide-related bands varied before the amide bands started to change in intensity. In conclusion, ring closure occurred before removal of the amide proton, which follows the suggested pathway 1 in Figure 3. Two-dimensional correlation Raman spectroscopy is a powerful technique for investigating reaction pathways that cannot be followed by conventional spectroscopic methods. The precise cyclization pathway for solution type PAA should also be studied, and we will do so in the future.

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