Notes

Absence of Noncyclic Imide Formation in PMDA−ODA Polyimide

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Introduction

Intermolecular noncyclic imide cross-link formation is a possible side reaction that can accompany the intramolecular ring closure reaction of polyimides.[1−3] A number of authors have argued against the occurrence of this reaction.[4−6] The formation of a noncyclic imide cross-link, shown in Figure 1, would leave residual or "widow" carboxylic acid and amide functional groups along the polymer chain. Therefore, four carbonyl bands are expected from a noncyclic imide cross-link, one each from the residual carboxylic acid and amide and two from the imide, an in-phase and an out-of phase mode. As in the case of the cyclic imide, only the higher frequency (symmetric) in-phase mode of the noncyclic imide may have sufficient intensity to be observed in the Raman spectrum and the lower frequency (antisymmetric) out-of phase mode may only be present in the IR spectrum. However, unreacted starting material is also expected to have vibrations in this same spectral region and band assignments are complicated by hydrogen-bonding interactions.

Recently, weak shoulder bands at 1738 cm^{-1} observed in the second-derivative profiles of FT-IR spectra of the polyimide formed from pyromellitic dianhydride and oxydianiline were attributed to noncyclic imide cross-links.[1] This assignment was based on (i) band assignments from the noncyclic imide model compound diacetamide that exhibited C═O stretches at 1707 cm^{-1} (more intense) and 1736 cm^{-1} (less intense) in 10% THF solution and on (ii) the decrease in intensity observed for the 1738 cm^{-1} shoulder band compared with the intensity of the 1724 cm^{-1} cyclic imide mode as the imidization was carried out in increasingly dilute NMP solution. Solution curing the polyimide is believed to result in a higher degree of cyclic imide formation and a reduction in the occurrence of side products. In fact, NMP, through its complexes has been speculated to completely block interchain reactions.[2] Thus the amount of noncyclic to cyclic imide is expected to decrease with increasing dilution.

Raman spectra are generally less complex than IR spectra, simplifying interpretation. Improvements in near-IR detection now allow the routine acquisition of FT-Raman spectra with high signal to noise ratios.[7] This permits detection of previously unobserved weak features in the Raman spectrum of polyimides that can originate from unreacted starting material or side products.

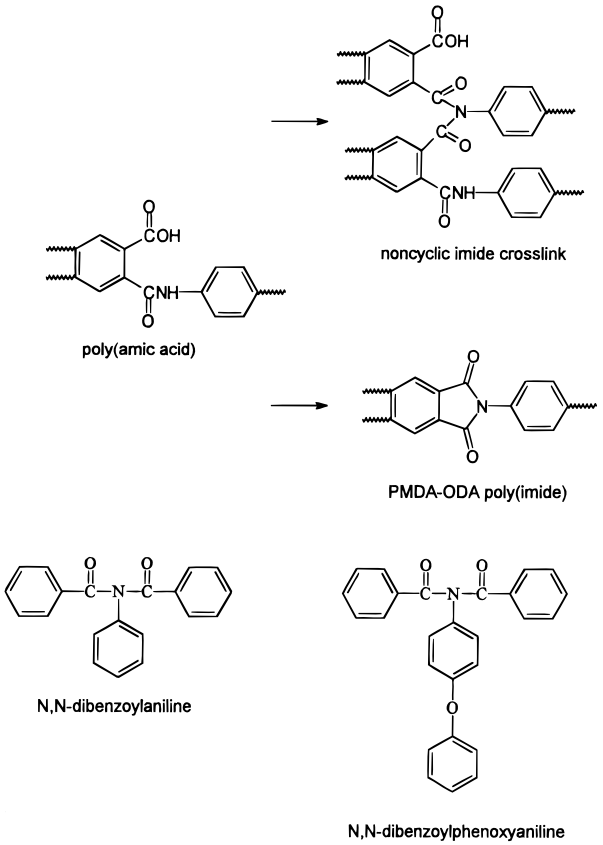

Figure 1. Chemical structures of the compounds involved in this study.

In this report, the FT-Raman spectra of two aromatic noncyclic model compounds, *N*,*N*-dibenzoylaniline and *N*,*N*-dibenzoyl-4-phenoxyaniline, shown in Figure 1, were obtained and compared with the spectra of thermally cured polyimides. The detection of noncyclic imide cross-links was believed to be most straightforwardly accomplished by the observation of modes directly attributable to the noncyclic imide, since the amide and carbonyl vibrations could arise either from the cross-link or from unreacted starting material. In addition, the FT-Raman spectra of PMDA−ODA poly(amic acid) cured at different solution concentrations were compared, to determine if the same trends observed in the IR could be observed in the Raman spectra of the polyimides.

Experimental Section

Equipment and Materials. FT-Raman spectra were obtained using a Mattson Cygnus FT-IR spectrometer equipped with near-IR optics and a liquid nitrogen cooled Ge detector. All spectra were taken at 4 cm^{-1} resolution and were ratioed with the instrument response. IR spectra were recorded with a Mattson RS/1 FT-IR spectrometer at 4 cm^{-1} resolution.

All starting materials were purchased from Aldrich. DMAc was vacuum distilled and stored over molecular sieves. Benzanilide was recrystallized from ethanol. Sodium hydride (60 wt % in mineral oil) was washed with freshly distilled hexane immediately prior to use. Aniline and benzoyl chloride were

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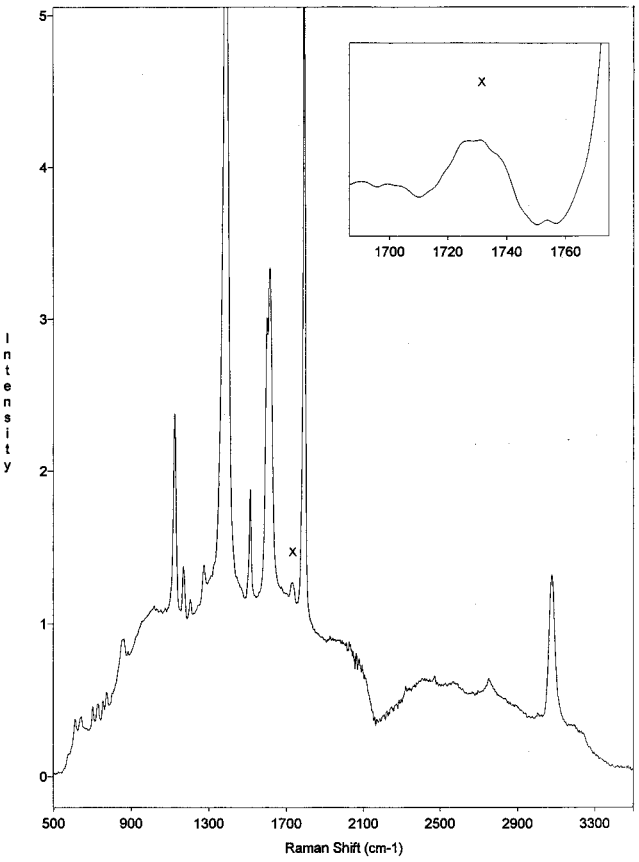

Figure 2. FT-Raman spectrum of PMDA−ODA polyimide; insert is scale expanded in the 1730 cm^{-1} region.

each purchased at the highest purity available and used as received; 4-phenoxyaniline was sublimed prior to use.

The PMDA−ODA poly(amic acid), from pyromellitic dianhydride and 4,4′-oxydianiline, is available commercially from E. I. du Pont as PI2545.

Preparation of *N,N*-Dibenzoylaniline and {*N,N*-Dibenzoyl-4-phenoxyaniline}. Washed NaH, 1.662 g {0.977 g} of a 60% suspension in mineral oil, was added to 150 mL {100 mL} of DMAc in a three-neck flask equipped with a magnetic stirring bar, dropping funnel, inert gas inlet, and drying tube. Anilinebenzoyl, 7.394 g {phenoxyanilinebenzoyl, 7.068 g (prepared by mixing 20.730 g of phenoxyaniline with 15.732 g of benzoyl chloride, precipitated and washed in water, and dried under vacuum)} was dissolved into 30 mL of DMAc and added dropwise to the NaH suspension with gas evolution. The reaction was allowed to proceed for 1 h. Then, 5.865 g {3.434 g} of benzoyl chloride was added dropwise and this reaction was allowed to proceed for 1 h. The resulting solution was slowly poured into 400 mL of ether {ice}, filtered, and recrystallized from methanol {extracted into ether and recrystallized from ethanol}. Clear crystals, 50% yield {75%}, were obtained.

Preparation of Polyimides. PMDA−ODA poly(amic acid) was heated to 350 °C for 30 min under nitrogen in the solid state to form the polyimide. Solution-cured polyimides were prepared from 2% and 10% poly(amic acid) in NMP. The solutions were heated for 3 h at 180 °C, and the orange precipitate which formed after ∼30 min was filtered off. The material was washed with DMF and methanol and then vacuum dried at 100 °C.

Results and Discussion

The FT-Raman spectrum of PMDA−ODA poly(amic acid) heated to 350 °C for 30 min is shown in Figure 2. This thermal treatment was believed to result in full conversion to cyclic imide, based on IR spectra which show the absence of any features attributable to unreacted poly(amic acid).[4] In Figure 2 there are weak carbonyl modes present near 1730 cm^{-1} that have not been observed in previously published Raman spectra acquired with lower signal to noise ratios. If this region is carefully inspected, Figure 2 (insert), three bands appear to contribute to the profile. There is a central peak at 1730 cm^{-1} with a low-frequency shoulder near 1715−1720 cm^{-1} and a high-frequency shoulder near 1735−1740 cm^{-1}.

The frequency of the amide I mode is near 1650 cm^{-1} in the poly(amic acid) but shifts up to 1695 cm^{-1} as the imidization progresses, before it disappears.[1,8] These frequencies may still be due to the hydrogen-bonded amide, and the free amide could appear near 1715−1720 cm^{-1} as part of the residual set of bands observed in the highly cured material. The amide I mode is expected to have a frequency near its free or non-hydrogen-bonded value since there are relatively few amide functions remaining at high degrees of conversion in an essentially amorphous polyimide matrix. The carboxylic acid carbonyl appears in the poly(amic acid) at 1720 cm^{-1} and increases in frequency by 10 cm^{-1} as the imidization proceeds.[1,8] The carboxylic acid carbonyl band is also expected to have a frequency near its non-hydrogen-bonded value. The noncyclic imide, because of the lack of ring strain, should have a frequency lower than that of the cyclic imide (1725 cm^{-1} IR active, 1790 cm^{-1} Raman active). Thus one of the two higher frequency bands between 1730 and 1740 cm^{-1} could be the noncyclic imide mode.

In order to determine the frequency of an aromatic noncyclic imide function, the FT-Raman and IR spectra of the model compounds *N,N*-dibenzoylaniline and *N,N*-dibenzoylphenoxyaniline (Figure 1) were obtained. The solid-state Raman spectra of *N,N*-dibenzoylaniline, shown in Figure 3A, and *N,N*-dibenzoylphenoxyaniline, not shown, are complicated by crystallinity effects. In dilute chloroform solution there is a single broad band at 1705 cm^{-1} for both compounds, shown in Figure 3B for *N,N*-dibenzoylaniline. These results indicate that in a highly cured, amorphous, polyimide matrix only a single Raman frequency near 1705 cm^{-1} would be expected for the aromatic, noncyclic, symmetric imide carbonyl. This frequency is significantly lower than the value of even the low-frequency shoulder of the triplet of residual bands centered at 1730 cm^{-1}. In the infrared, the antisymmetric imide carbonyl appears at 1692 cm^{-1} in dilute chloroform solution (Figure 3C).

Ishada et al., and others, have discussed the effect of conjugation between the imide carbonyls and the phenoxy oxygen in PMDA−ODA polyimide.[9] This conjugation tends to lower the carbonyl frequency. We have not observed this effect in going from *N,N*-dibenzoylaniline to *N,N*-dibenzoylphenoxyaniline in solution. Nevertheless, if this type of conjugation were to develop in the polyimide, the noncyclic imide carbonyl frequency would be lowered even further, precluding the assignment of the 1730 cm^{-1} band to noncyclic imide.

The FT-Raman spectra of poly(amic acid) samples cured at 2 and 10% concentration in NMP are shown in Figure 4. The residual bands between 1650 and 1750 cm^{-1} do not overlap with the cyclic imide features and are virtually identical in intensity for both polyimides. This result is inconsistent with assignment of the vibrations to noncyclic imide species but instead supports the assignment to unreacted starting material.

Based on band assignments from the model compounds *N,N*-dibenzoylaniline and *N,N*-dibenzoylphe-

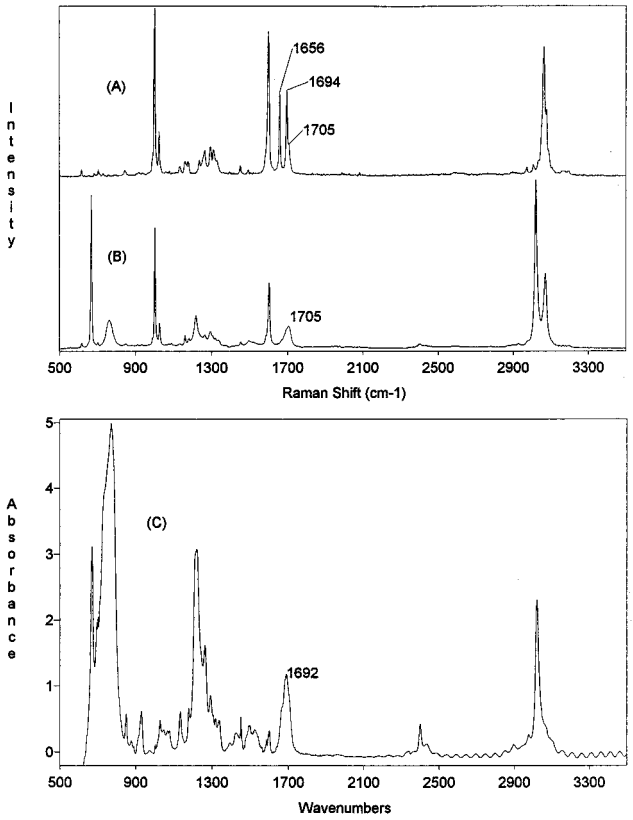

Figure 3. FT-Raman spectra of *N*,*N*′-dibenzoylaniline: (A) in the solid state, showing three bands in the carbonyl region, 1656, 1694, and 1705 cm^{-1}; (B) in 10% chloroform, showing a broad band at 1705 cm^{-1}. (C) A single band appears at 1692 cm^{-1} in the IR spectrum in chloroform; previous IR studies on the noncyclic imide model compound *N*,*N*-dibenzoylaniline indicated that the noncyclic imide modes occurred at even lower frequency, with a singlet at 1670 cm^{-1} in chloroform solution.[12]

noxyaniline and the behavior of the residual Raman carbonyl bands under various imidization conditions, it is concluded that there is no evidence for noncyclic imide cross-linking in the FT-Raman spectra of PMDA−ODA polyimide. The residual bands observed in the FT-Raman spectrum are attributed to unreacted poly(amic acid) that is not capable of fully converting to polyimide.[10] This assignment is consistent with results for this same material using solid-state ^{15}N NMR spectroscopy.[11]

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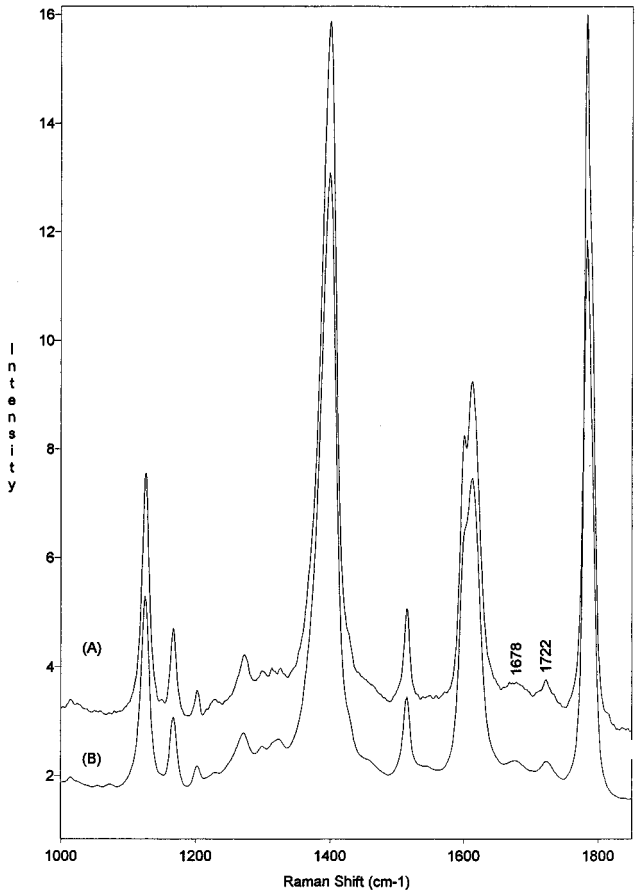

Figure 4. FT-Raman spectra of polyimide cured in (A) 2% NMP and (B) 10% NMP. The spectra were scaled to the 1600 cm^{-1} benzene ring mode. The weak bands are attributable to unreacted amide (1678 cm^{-1}) and carboxylic acid (1722 cm^{-1}) functional groups in both spectra.