residual solvent is still present and there is a complex equilibrium of self-associated and polymer/solvent complexes present.

Registry No. (PMDA)(4,4′-oxydianiline) (copolymer), 25038-81-7; (PMDA)(4,4′-oxydianiline) (SRU), 9043-05-4.

References and Notes

(1) Matsuo, T. *Bull Chem. Soc. Jpn.* **1964**, *37*, 1844.
(2) Vanclef, A.; Bouche, R. *Spectrosc. Lett.* **1979**, *12*, 371.
(3) Bower, G. M.; Frost, L. W. *J. Polym. Sci. A-1* **1963**, *1*, 3135.
(4) Suzanov, Y. N.; Sekeji, T.; Antonova, T. A.; Jakab, E.; Blazso, M.; Dauengauer, S. A.; Shibaev, L. A. In *Proceedings of Second International Conference on Polyimides*; Oct 1984, Ellenville, NY.
(5) Hodgkin, J. *Appl. Sci.* **1976**, *20*, 2339.
(6) Frayer, P. D. In *Polyimides*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; Vol. 1, p 273.
(7) Brekner, M. J.; Feger, C. *J. Polym. Sci.; Part A* **1987**, *25*, 2005.
(8) Brekner, M. J.; Feger, C. *J. Polym. Sci., Part A* **1987**, *25*, 2479.
(9) Ardashvikov, A. Ya.; Kardash, I. Ye.; Pravednikov, A. N. *Polym. Sci. USSR* **1971**, *13*, 12092.
(10) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco and London, 1960.
(11) Kreuz, J. A.; Endrey, A. L.; Gay, F. P.; Scroog, C. E. *J. Polym. Sci. A-1* **1966**, *4*, 2607.
(12) Kardash, I. Ye.; Likhachev, D. Yu.; Nikitin, N. V.; Ardashnikov, A. Ya., Kozlova, N. V.; Pravednikov, A. N. *Polym. Sci. USSR* **1985**, *27*, 1961.
(13) Kretschmer, C. B.; Wiebe, R. *J. Chem. Phys.* **1954**, *22*, 1697.
(14) Renon, H.; Prausnitz, J. M. *Chem. Eng. Sci.* **1967**, *22*, 200; Erratum **1956**, *22*, 1891.
(15) Nagata, I. *Z. Phys. Chem.* (Leipzig) **1973**, *252*, 305.
(16) Acree, W. E. *Thermodynamic Properties of Nonelectrolyte Solutions*; Academic Press: New York, 1984.
(17) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(18) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1989**, *22*, 570.
(19) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1989**, *22*, 580.
(20) Coleman, M. M.; Lichkus, A. M.; Serman, C. J.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(21) Coleman, M. M.; Hu, J.; Park, Y.; Painter, P. C. *Polymer* **1988**, *29*, 1659.
(22) Coleman, M. M.; Lee, J. Y.; Serman, C. J.; Wang, Z.; Painter, P. C. *Polymer* **1989**, *30*, 1298.
(23) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425.
(24) Prigogine, I. *The Molecular Theory of Solutions*; North Holland Publishing: Amsterdam, 1957.
(25) Coleman, M. M.; Hu, J.; Painter, P. C. *Macromolecules*, submitted for publication.
(26) Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1985**, *18*, 1676.
(27) Murthy, A. S. N.; Rao, C. N. R. *Appl. Spectrosc. Rev.* **1968**, *2*, 69.
(28) Novak, A. *Struct. Bonding* **1974**, *18*, 177.
(29) Hadzi, D. *Chimia* **1972**, *26*, 7.
(30) Hadzi, D. *Pure Appl. Chem.* **1965**, *11*, 435.
(31) Odinokov, S. E.; Mashkovsky, A. A.; Glazunov, V. P.; Iogansen, A. V.; Rassadin, B. V. *Spectrochim. Acta* **1976**, *32A*, 1355.
(32) Russell, T. P. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1105.

FTIR Studies of Polyimides: Thermal Curing

R. W. Snyder

IBM Corporation, 1701 North Street, Endicott, New York 13760

B. Thomson, B. Bartges, D. Czerniawski, and P. C. Painter*

Polymer Science Program, The Pennsylvania State University, University Park, Pennsylvania 16802.

Received April 22, 1988; Revised Manuscript Received March 14, 1989

ABSTRACT: In this study the thermal curing of poly(amic acid) films is considered. Analysis of the carbonyl stretching region of the infrared spectrum indicates that in addition to ring-closed imides, some intermolecular links are formed. The relative proportion of these species changes with conditions of cure.

Introduction

Infrared spectroscopic studies of polyimide films can be roughly divided into two categories. In the first, ring closure is implicitly assumed and various bands used as a measure of the degree of imidization.[1-5] The second category involves the use of infrared spectroscopy as a tool for identifying the species actually formed (for example, see ref 6–11). In this context, a distinction between the products obtained by chemical as opposed to thermal curing can also be made. Because normal coordinate calculations of polyimide molecules have yet to be reported, identification of structures has been largely based on group frequency assignments of the characteristic carbonyl stretching modes between 1600 and 1800 cm^{-1}.[6,7]

In this study we will also rely on this region of the spectrum to identify the products formed upon thermal curing. Although similar studies have been reported previously, most of these used "thick" (in infrared spectroscopic terms) films and dispersive instruments. As we will show, the sampling and data analysis advantages of FTIR instruments provide new information.

Experimental Section

The poly(amic acid) used in this study is a poly(pyromellitic dianhydride oxydianiline) obtained from Du Pont. Thin films (~1 μm) were prepared by casting from solutions of NMP (*N*-methylpyrrolidinone) onto KBr windows. Samples were cured at low temperatures by using a Micro Star heating cell placed in the sampling compartment of the spectrometer. Samples cured at high temperatures (about 10-μm-thick films) were sprayed onto ceramic substrates and cured in ovens at the IBM laboratories in Endicott, NY. Various curing protocols were used and these are described in the body of the text.

Spectra were recorded on a Digilab FTS 60 spectrometer at a resolution of 2 cm^{-1}. Samples of "thick" films (~10 μm) were prepared by taking a small piece (~1–2 mm) and placing it on top of a KBr underlayer (~300 mg) in a diffuse reflectance cup. The diffuse reflectance spectra were then obtained in the usual fashion. Spectra of model compounds were obtained by dispersing

---

* To whom correspondence should be addressed.

0024-9297/89/2222-4166$01.50/0

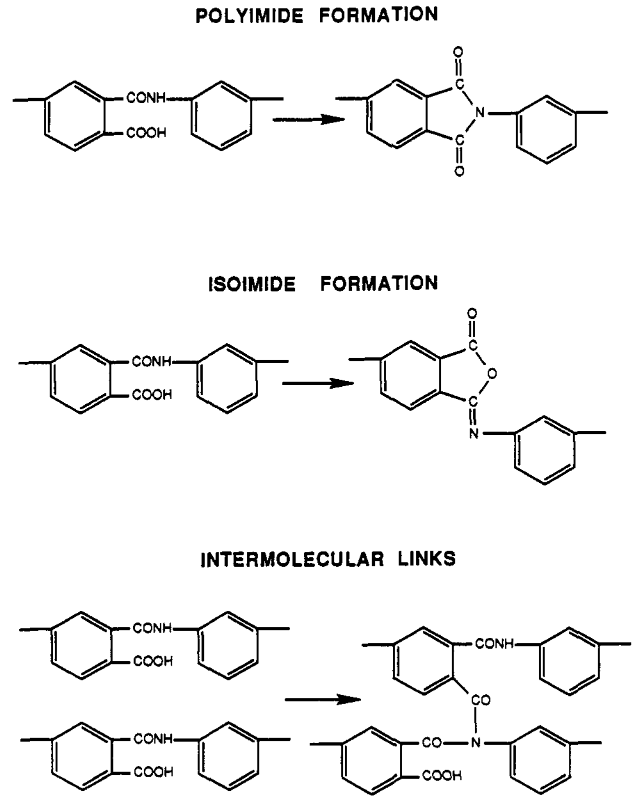

Figure 1. Comparison of some of the products formed during the curing of poly(amic acid)s.

in KBr for conventional diffuse reflectance studies or by preparing 10% (w/v) solutions and using a Spectra Tech Circle Cell.

Results and Discussion

Before we proceed to a discussion of the curing of poly(amic acid) films, it is necessary to place band assignments in the carbonyl stretching region on a firm footing. As we have mentioned above, in many studies of polyimide films it is implicitly assumed that the structures present are predominantly ring-closed species, although in some studies anhydrides have been identified.$^{10-12}$ It has been noted in the chemical literature, however, that isoimides and intermolecular links can also form, the relative proportions depending upon the reaction conditions and the type of imide molecule being cured.^{13,14} Typical structures are illustrated in Figure 1. These various species are distinguishable by their characteristic carbonyl stretching modes. Cyclic anhydrides are identified by bands near 1850 and 1780 cm^{-1}, while isoimides have C=O and C=N stretching modes near 1800 and 1710 cm^{-1}.^{9} Phthalimides are characterized by a characteristic pair of carbonyl bands; the higher frequency and less intense mode is usually found near 1780 cm^{-1}, while the more intense stretching mode is located in the range 1720–1740 cm^{-1}, its precise frequency depending upon the nature of the substituent on the nitrogen atom.$^{6-8}$ Finally, intermolecular links of the type illustrated in Figure 1 are also characterized by a pair of carbonyl stretching modes, but these are located at lower frequencies than the corresponding cyclic imide modes (where ring strain plays a role). The precise frequencies again depend upon the nature of the substituents but are usually located in the 1750–1700-cm^{-1} range. These spectroscopic characteristics are illustrated in Figure 2, where the spectra of the model compounds phthalimidoacetaldehyde diethyl acetal and diacetamide are compared. (Note: These spectra were obtained from 10% solutions in THF. In the solid state effects due to water absorption, crystal field splitting, and alternative crystal forms (of diacetamide) complicate the spectra.)

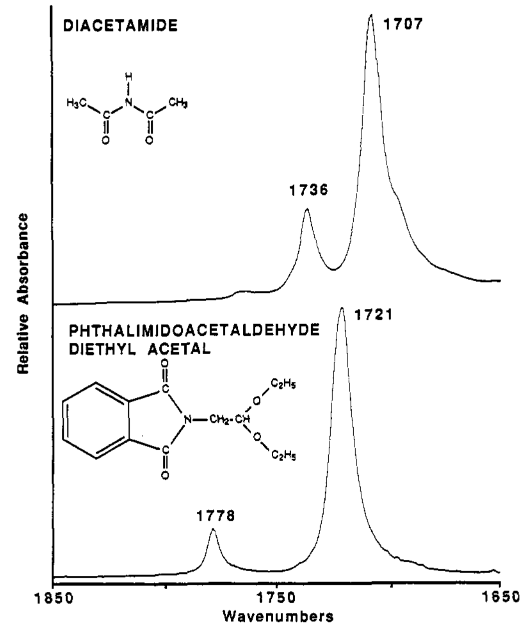

Figure 2. Comparison of the carbonyl stretching region of the infrared spectra of diacetamide (top) and phthalimidoacetaldehyde diethyl acetal (bottom). (Spectra of 10% solutions in THF.)

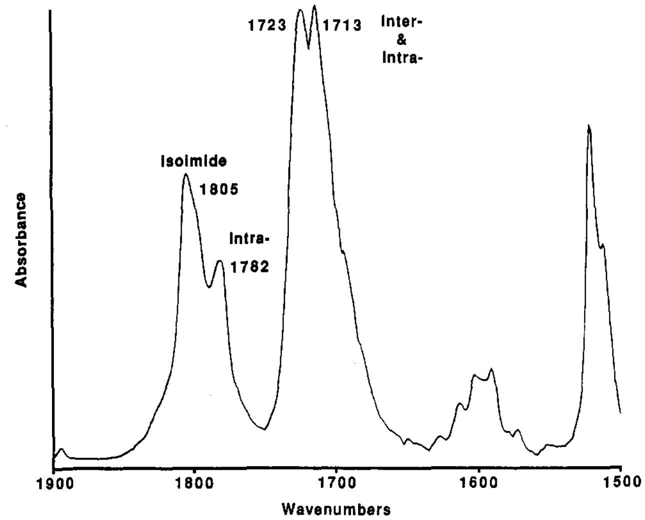

Figure 3. Infrared spectrum (carbonyl region) or the products of curing the amic acid obtained from reaction of pyromellitic dianhydride and *p*-anisidine.

Bands due to isoimides are illustrated in Figure 3, where the spectra of the mixed products obtained by curing the amic acid produced by condensation of pyrometallitic dianhydride (PMDA) and *p*-anisidine in solutions of acetic anhydride with a few drops of pyridine are shown.

Having confirmed band assignments, we can now turn our attention to the products obtained when poly(amic acid) films are thermally cured. This is not a straightforward process and depends upon temperature of cure and film thickness, due to the effect of residual hydrogen-bonded solvent.^{5,10,11} Because the imide carbonyl band near 1730 cm^{-1} absorbs strongly, "thick" films (i.e., thick in infrared terms, usually greater than about 2–3 μm) cannot be studied by the same simple transmission methods used to study "thin" films. We therefore adapted a diffuse reflectance procedure (see the Experimental Section). Unfortunately, this can result in changes in relative intensities that are frequency dependent, so that

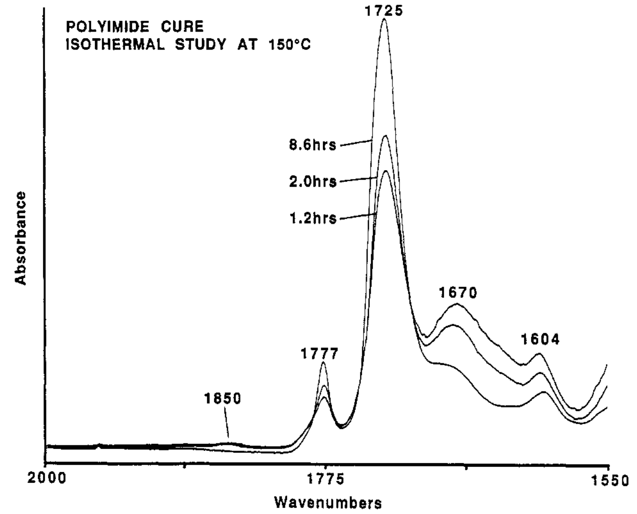

Figure 4. Carbonyl region of the infrared spectrum of a poly(amic acid) cured for 1.2, 2.0 and 8.6 h at 150 °C.

a quantitative comparison of the results obtained by the two procedures cannot be made with any confidence. Nevertheless, a qualitative identification of products can be made. We will initially consider the curing of thin films (about 1 μm thick).

The spectra obtained from a poly(amic acid) cast film cured isothermally for various times at 150 °C are compared in Figure 4. Initially, the uncured poly(amic acid) is characterized by three bands in the 1800–1600-cm^{-1} region; a mode near 1700 cm^{-1} assigned to hydrogen-bonded carboxylic acid pairs, a mode near 1660 cm^{-1} assigned to hydrogen-bonded amide groups, and a weaker aromatic ring stretching mode near 1600 cm^{-1} (see the preceding paper). Upon curing, a strong band near 1725 cm^{-1} quickly becomes apparent, together with a weaker characteristic imide mode near 1777 cm^{-1}. A careful examination of the scale-expanded spectra also shows the presence of a weak anhydride band near 1850 cm^{-1}. These results are straightforward and have been observed in numerous other studies. We are principally interested in two other features: first, the width of the 1725-cm^{-1} absorption and the suggestion of the presence of shoulders due to unresolved overlapping bands; second, the gradual shift of the amide mode near 1670 cm^{-1} to higher frequencies with increasing degree of cure.

The model compound studies discussed above demonstrate that isoimides, ring-closed imides, and intermolecular diacetamide-type links all have strong bands between 1750 and 1700 cm^{-1}. The absence of a detectable band near 1800 cm^{-1} suggests that negligible amounts of isoimides are present under these conditions of cure, however. In contrast, intermolecular links, formed by the condensation of carboxylic acid and amide groups on adjacent chains, would result in a pair of bands between 1750 and 1710 cm^{-1} that would overlap significantly with the strong imide mode found in this same frequency range. Bands that are separated by less than half their half-width are not usually detectable by techniques such as self-deconvolution or the second derivative of the spectral profile. Because of the inherent breadth of polymer bands, we would not therefore anticipate being able to identify all the modes contributing to the peak centered near 1725 cm^{-1} and neither would we anticipate being able to measure quantitatively their relative contributions. Nevertheless, the second derivative of the sample cured 8.6 h, shown in Figure 5, suggests that there is at least one other band contributing to the profile. Of course, this does not necessarily mean that there are intermolecular links as well as intramolecular ring-closed species; the imide carbonyl modes could be split as a result of dipole–dipole intermolecular interactions (indeed, the 1777-cm^{-1} band has a high-frequency shoulder that could be due to such effects, but more on this later). Fortunately, these possibilities can be tested by curing under different conditions. For the spectra shown in Figures 4 and 5, the film was placed in the spectrometer and the heating cell was then turned on and allowed to reach 150 °C over a period of time (~30 min). In this time period a significant quantity of solvent was driven off and this can affect imidization.[10,11] We therefore took a sample and placed it in a heating cell that was already at 150 °C. After 2.75 h at this temperature, the spectrum shown in Figure 6 was obtained. The band near 1777 cm^{-1} clearly shows the formation of ring-closed species, but in the second derivative of this spectrum it is now clear that a band near 1738 cm^{-1} is much more prominent than one near 1724 cm^{-1}, a reversal of the intensity relationship obtained for the slowly

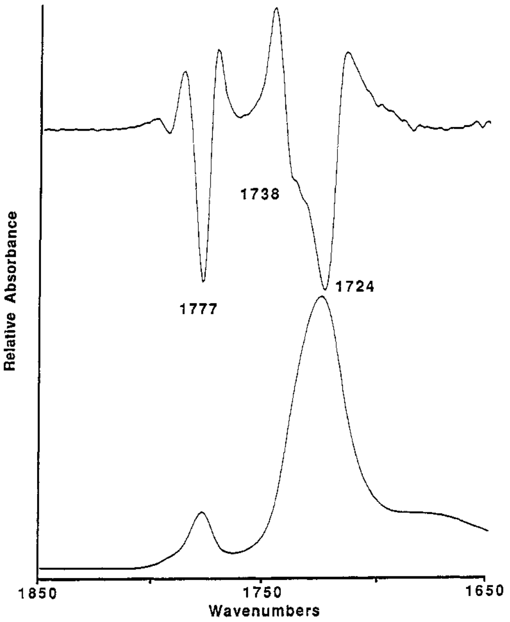

Figure 5. Carbonyl region of the poly(amic acid) cured at 150 °C for 8.6 h compared to its second derivative.

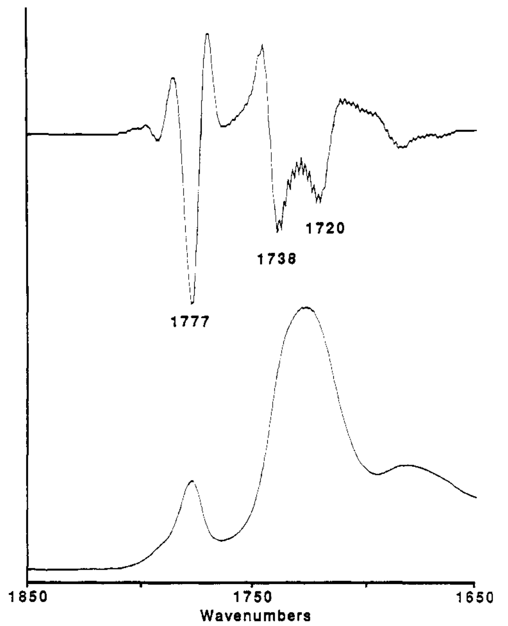

Figure 6. Infrared spectrum of a poly(amic acid) film heated quickly to 150 °C and held at this temperature for 2.75 h, compared to its second derivative.

heated samples. As we will see below, changing the temperature of cure also affects the relative intensities of these bands. Before considering this evidence, however, we will discuss the other feature of Figure 4 that interests us, the gradual shift to higher frequency of the amide carbonyl mode with increasing degree of cure.

In solvent-free amic acid or poly(amic acid) films this band appears near 1650 cm^{-1}, characteristic of amide modes in hydrogen-bonded chains (see the preceding paper). Solvents such as NMP lead to more complicated spectra, in that they hydrogen bond to amide N–H groups, freeing an equal number of carbonyl groups, which then appear at a higher frequency. Accordingly, the broad band near 1670 cm^{-1} in Figure 4 can be assigned to a composite of such overlapping contributions. As the cure proceeds, amide groups are consumed and residual solvent is driven off, so that unreacted amide groups find it increasingly difficult to find hydrogen-bonding partners of any description. This would lead to the appearance of a higher frequency true "free" carbonyl, a band characteristic of an amide group where neither the carbonyl nor N–H is hydrogen bonded to any other species. Accordingly, as the poly(amic acid) is cured the amide mode *apparently* shifts to the 1680–1700 cm^{-1} range, as a band due to "free" carbonyl groups increases in intensity, while overlapping lower frequency bands associated with various hydrogen-bonded amide groups decrease in intensity.

The appearance of a band due to non-hydrogen-bonded amide groups suggests that we are observing "widow" effects in the curing process, and in turn this indicates a more complicated mechanism of curing than simple ring closure. If intermolecular links (see Figure 1) are formed randomly, a residual acid and amide group would remain in the two intermolecularly adjacent repeat units involved. As the curing process proceeds, chain mobility decreases and such units would find themselves isolated by completely reacted species. The isolated COOH groups would absorb near 1750 cm^{-1} and be subsumed under the broad band centered near 1725 cm^{-1}, while the amide group would appear, as observed, near 1680–1700 cm^{-1}. Alternatively, we could simply be observing a kinetic effect and the presence of free amide (and presumably carboxyl) groups represents unreacted species next to one another in the same repeat unit, as opposed to those incapable of reacting through loss of an adjacent partner. We do not believe this to be the case, for a number of reasons. The most important of these is that results obtained from samples cured under a variety of conditions are also consistent with the formation of intermolecular links. Furthermore, the formation of certain types of anhydrides could also lead to the "isolation" of amide groups and a brief discussion of the formation of these species is in order here.

Brekner and Feger[10,11] have discussed one mechanism, which essentially results in the regeneration of cyclic anhydrides. The infrared spectroscopic evidence for this is good and, as we mentioned above, if the spectra shown in Figure 4 are carefully examined a characteristic weak band near 1850 cm^{-1} can be perceived in the spectra of the samples cured 1.2 and 2.0 h. Such cyclic anhydrides also have a more intense band near 1780 cm^{-1}, and a shoulder on the high wavenumber side of the 1777-cm^{-1} imide peak that decreases with increasing degree of cure is also apparent. The formation of such species involves the simultaneous loss of intramolecularly adjacent carboxylic acid and amide groups, however, and thus would not result in the isolation of unreacted amides. In contrast, the formation of linear anhydrides would result in the formation of such isolated amide groups and it is well-known that both types of anhydrides are readily formed in acid-containing polymers upon heating above a temperature of about 140 °C.[15-17] In recent work in this laboratory on ethylene–methacrylic acid copolymers, we have observed bands characteristic of both species.[18] The formation of intermolecular linear anhydrides would be influenced by the propensity of the acid groups to form hydrogen-bonded pairs. We have demonstrated in the preceding paper that in the absence of solvent the carboxylic acid groups in poly(amic acid)s also form such pairs, so it is to be expected that there would be at least some noncyclic intermolecular anhydrides formed at certain points in the usual curing processes. This would, of course, result in the observed local isolation of amide groups that could not then engage in ring-closing reactions. Unfortunately, the formation of such species cannot be readily demonstrated, because noncyclic conjugated anhydrides are characterized by a pair of bands at 1780 and 1720 cm^{-1}, with the latter being the more intense. These modes would thus almost completely overlap the strong imide modes at approximately the same frequencies. Nevertheless, there is qualitative evidence for the occurrence of such side reactions in the observation of an apparent complex of overlapping bands between 1700 and 1800 cm^{-1}. As we have noted above, intermolecular imides could also contribute to the modes observed in this region, and we now return to a consideration of this subject.

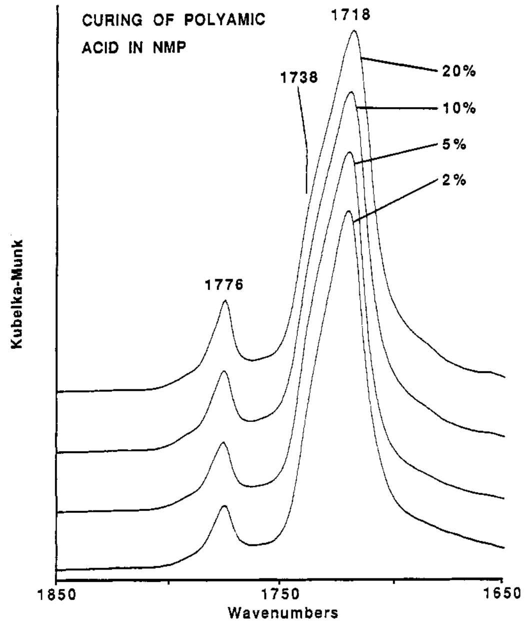

Figure 7. Carbonyl region of the infrared spectrum of a poly(amic acid) cured in dilute solution of NMP (concentrations shown on figure).

In order to address the problems of interpretation raised above, it would clearly be useful to cure in a fashion that would change the relative amounts of imide rings and the products of competing intermolecular reactions. We therefore heated solutions of poly(amic acid) in NMP to 180 °C. After about $^1/_2$ h, a fine precipitate formed. After curing for an additional period of 1 h the products were filtered, washed with water, and dried in a desiccator. The fine powder was dispersed in KBr and a spectra obtained in diffuse reflectance; the 1850–1650-cm^{-1} region is shown in Figure 7. (Spectra of thin mats of the precipitate cast onto KBr windows were also obtained and showed the same bands and relative intensities). There are a number of interesting features. First, the shoulder near 1738 cm^{-1} in the solution-cured spectra is apparently weaker than

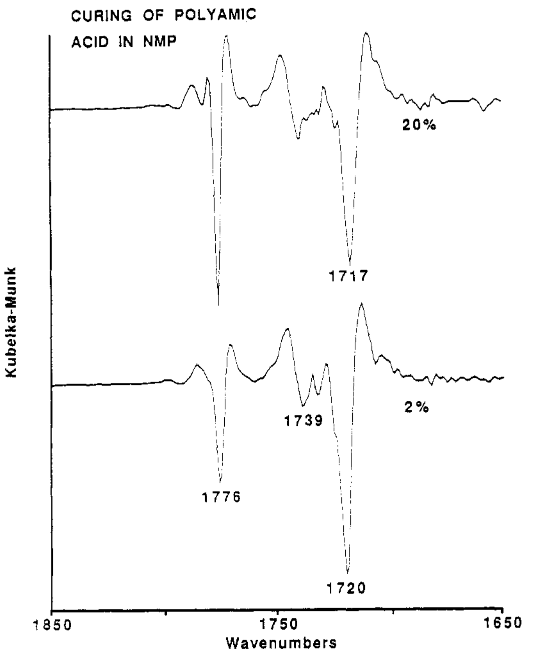

Figure 8. Second derivative of spectra of samples cured in solution (concentrations of 2% and 20%).

in the spectra of cured films and increases with the concentration of poly(amic acid) in the solution. If this mode were solely due to dipole-dipole intermolecular interactions, then we would anticipate little change in intensity relationships (assuming equivalent average local arrangements of carbonyl groups). Furthermore, the band assigned to residual "widowed" amide groups now appears as a weak broad shoulder near 1690 cm^{-1}. Because the initial products of curing precipitate, we would not anticipate a complete absence of, for example, intermolecular reactions relative to ring-closing reactions, just a change in their relative proportions.

The spectra shown in Figure 7 have to be carefully examined in order to discern our claimed variation in the relative intensities of the 1738- and 1718-cm^{-1} peaks. It is easier to see when the spectra are directly superimposed or when the second derivative of the spectra are examined, as in Figure 8. What is equally important, however, is that the bands of the polymers cured in solution are somewhat sharper and the multitude of peaks that contribute to the broad profile centered near 1720–1730 cm^{-1} in the original spectra are now much more apparent. Because of the noise level characteristic of second-derivative profiles, we cannot assign specific peaks with any confidence, but it is clear from Figure 8 that there are at least three bands superimposed between 1740 and 1715 cm^{-1}.

If we summarize the cumulative evidence for the occurrence of intermolecular links in the curing of polyamic acid presented so far, we believe it to be persuasive. First, it has been proposed that such reactions occur in low molecular weight materials. In fact, Kolesnikov et al.[14] state that the activation energy for the intramolecular reaction is higher than the intermolecular reaction and on this basis suggest that imidization be carried out at the highest possible temperature. Second, the acyclic imide structures formed between polymer molecules would have characteristic bands in the 1740–1720-cm^{-1} region of the spectrum; these should overlap with the strong cyclic imide mode in the same range. Because polymer bands are inherently broad, these are difficult to resolve. Nevertheless, second-derivative techniques demonstrate the presence of more than one band. The relative intensities of these bands change with conditions of cure, indicating that they are not a result of intermolecular interactions or due to other vibrational effects (e.g., Fermi resonance interactions). Finally, interchain reactions should result in the appearance of "widows", those groups that become isolated due to the complete reaction of spatially local functionalities. These are observed and their concentration varies with conditions of cure.

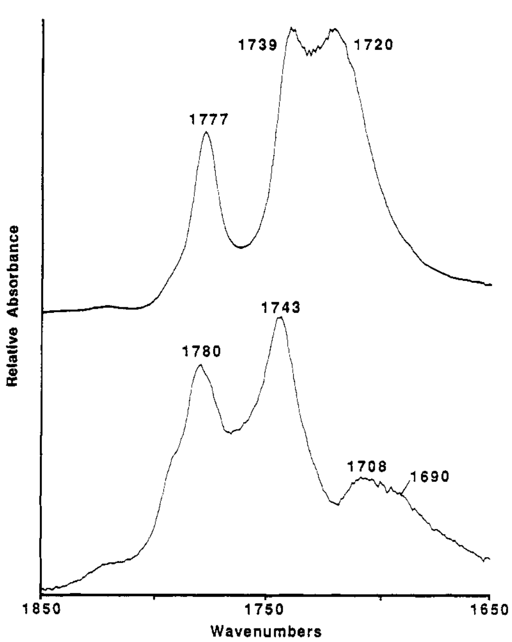

Figure 9. Diffuse reflectance spectrum of a sample cured on a ceramic substrate (bottom) compared to the spectrum obtained in transmission of a small piece of the same film.

These conclusions are supported by additional evidence, notably by curing at higher temperatures where the observations of Kolesnikov et al.[14] suggest that we should observe a higher degree of ring-closing imidization. We have chosen to discuss this evidence separately because the bulk of it concerns thicker films (~10 μm) whose spectra were obtained by a diffuse reflectance technique (see the Experimental Section). As a result of the specific methodology employed, the relative intensities of the bands are not directly comparable to those from transmission studies.

Figure 9 (bottom) shows the spectrum of an (approximately) 10-μm polyimide film cured on a ceramic substrate by heating successively at temperatures of about 130, 200, and 350 °C for 1 h (each). This spectrum was obtained by the diffuse reflectance procedure described in the Experimental Section and is typical of those of a number of films we studied that were cured under the same conditions. The use of diffuse reflectance in this fashion (as opposed to examining a dispersion of a finely powdered sample) often results in intensity anomalies; weaker bands appear to be intensity enhanced relative to spectra obtained in transmission. Furthermore, curing polyimide films on a substrate can result in an in-plane orientation,[19] which could also influence the relative intensities of bands. For whatever reason, we consistently observe a strong ring-closed imide mode at 1780 cm^{-1}, while the broad composite band centered near 1725 cm^{-1} in thin films cured at lower temperatures is replaced by a sharper band centered near 1743 cm^{-1}. These frequencies are similar to those observed in many phthalimide model compounds.[6-8] There are two weaker bands observed near 1708 and 1690 cm^{-1}. The latter can be assigned to "widowed" amide groups, but the assignment of the 1708-cm^{-1} mode is more tentative. It could be attributed to a small amount of intermolecular links; the stronger, lower frequency carbonyl stretching mode of diacetamide is observed at 1707 cm^{-1} (see Figure 2). Alternatively, a weak shoulder can be observed in the 1800–1820-cm^{-1} range, which could be attributed to a small amount of isoimide; these structures have strong C=N stretching modes near 1710 cm^{-1}. One or both of the above could contribute to the band near 1710 cm^{-1}; the important observation in terms of this study is that bands due to ring-closed imides are more prominent after prolonged treatment at higher temperature.

Most of the films cured on ceramic substrates were too thick for transmission studies. In the case of the film whose diffuse reflectance spectrum is shown in Figure 9, however, we did manage to obtain a transmission spectrum; this is shown in the same figure. The absorbance values (greater than 2.0) are at the limit for accurate reproducibility, but they display a surprising result. Bands at 1739 and 1720 cm^{-1} are separately resolved, unlike the situation observed in thin films (including those cured at the same temperatures as these films). We presume that this is at least in part due to the enhanced retention of solvent in thicker films. There are also clear differences in the results obtained by diffuse reflectance and transmission that are unlikely to be solely due to intensity variations in scattering as opposed to transmission-type studies. Instead, this must be related to the different regions of the film that are sampled by these techniques; transmission studies produce an average over the entire film thickness, while diffuse reflectance in the mode employed here samples more of the surface layers. If curing mechanisms are related to the presence of residual hydrogen-bonded solvent, then we would anticipate such differences. This is complicated by the possibility of orientation effects, but a more systematic depth profiling study is required before quantitative conclusions concerning this point can be drawn.

The films shown in Figure 9 were initially cured at lower temperatures, where the results presented above indicate side reactions are significant. These reactions are (presumably) somewhat reversible, so that subsequent curing at higher temperatures could result in a degree of additional cyclic imide formation. According to Kolesnikov et al.,[14] however, curing at higher temperatures should favor ring closure. This conclusion is supported by the spectra shown in Figure 10, where the carbonyl bands that appear as a result of curing at 400 °C for 2 min, 450 °C for 2 min, and 500 °C for 1 min in an infrared furnace are compared. It can be seen that high temperatures clearly favor closed-ring imide formation; the spectrum obtained from the 500 °C cured sample, displaying sharp bands near 1780 and 1744 cm^{-1}, is very similar to those observed in model compounds.[6-8] Bands due to unreacted groups and/or the products of side reactions become weaker with increasing temperature of cure.

These results are consistent with the conclusions we reached in the preceding paper concerning the types of hydrogen-bonded species present in the poly(amic acid) precursor. In the absence of solvent, carboxylic acid groups prefer to hydrogen bond to each other as opposed to forming complexes with amide groups. Amide groups self-associate in the form of "chains" of hydrogen-bonded functionalities. Clearly, as Brekner and Feger point out,[10,11] this intermolecular arrangement of groups is not the most conducive to imidization. In the presence of strongly hydrogen-bonding solvents such as NMP, these interchain interactions are broken and replaced with bonds to solvent and this appears to favor imidization as opposed to intermolecular condensations. The type of linkages formed is thus a complex function of temperature-dependent competing reaction rates and loss of solvent; the latter in turn is a function of film thickness and also temperature. In addition, it should be noted that these results deal solely with diamic acids or pyromellitic-type polymers. We have some evidence that monoamic acids ring close more easily, but this observation needs to be confirmed in a more detailed study.

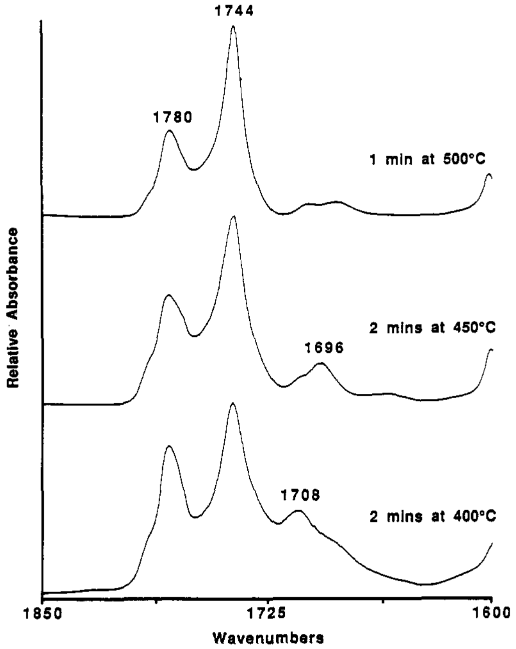

Figure 10. Comparison of the diffuse reflectance spectra of films of a poly(amic acid) cured at high temperatures.

It is unfortunate that because of the considerable overlap of bands and the anomalous intensity behavior observed in the diffuse reflectance studies, it is not possible to determine quantitatively or to estimate the proportion of linear imide (or anhydride) cross-links that are formed. Because the ring-closed imide is thermodynamically more stable, we would expect the concentration of cross-linked species to be (relatively) small and to be determined by factors such as temperature and film thickness. The formation of such links should influence both the solubility and molecular weight of the final imide product, however. Molecular weight measurements of the type of polyimide considered here are made in solutions of 97% sulfuric acid, and Cotts[20] concluded that various temperature-cured polyimides had essentially the same molecular weight as their poly(amic acid) precursors. This is in contrast to earlier studies[21,22] of polypyromellitimides, where considerable degradation of molecular weight was observed as a function of time in sulfuric acid. Cotts attributed the results of Wallach[21] to the presence of isoimides in chemically cured samples, which degrade in strongly protonating solvents.

If the data of Cotts are carefully examined, the conclusions of this author are not quite as clear cut. The weight-average molecular weights of three different polyimides are compared to those of their poly(amic acid) precursors, and for at least two of these samples there appears to be a measurable decrease in molecular weight (for a sample described as Du Pont A the value of $\bar{M}_w$ decreases from 28×10^3 Da for the poly(amic acid) to values between 20×10^3 and 25×10^3 Da for the polyimide, depending upon how the film was cured, while the $\bar{M}_w$ value of sample labeled PAA-3 decreases from 37×10^3 to 30×10^3 Da). Cotts[20] states that these values are within experimental error of one another, but a similar trend is observed in the data reported by Volksen et al.[23] If in-

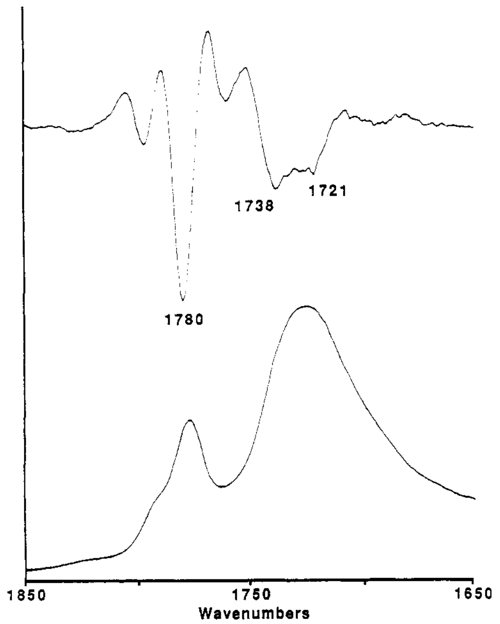

Figure 11. Infrared spectrum of a sample initially cured 8.6 h at 150 °C and subsequently precipitated from an H_2SO_4 solution (bottom) compared to that of its second derivative.

termolecular linear anhydride and imide linkages are formed during cure, then we would anticipate that certainly the former and probably the latter would be susceptible to cleavage in a strongly protonating solvent such as sulfuric acid.

Clearly, if intermolecular imide linkages are present and if they are susceptible to cleavage in sulfuric acid, there should be measurable changes in the 1800–1700-cm^{-1} region of the spectra of a sample upon dissolution in this solvent. Figure 11 shows the infrared spectrum of a film cured 8.6 h at 150 °C, which was subsequently precipitated from a concentrated sulfuric acid solution where it had sat for 12 h. The precipitate was ground with KBr and the spectrum obtained by diffuse reflectance. By comparison of the spectrum to that of the original sample (Figure 4), it can be seen that the band originally near 1725 cm^{-1} has broadened considerably and its center of gravity has moved toward 1740 cm^{-1}. This is consistent with the presence of a higher concentration of ring-closed imides relative to intermolecular links.

Conclusions

Curing of poly(amic acid)s at low temperatures (150–200 °C) apparently results in the formation of mixed products; principally ring-closed imides and intermolecular imide links. This mixture of products is difficult to identify in the infrared spectrum because it is characterized by a complex of overlapping bands centered near 1725 cm^{-1}. Because the bands overlap to such an extent, they cannot readily be separated and used for quantitative analysis of the relative proportions of species. That the observed spectroscopic results are indeed due to this mixture of products is clear from the results of curing samples under different conditions and at different temperatures. Higher temperatures favor the formation of ring-closed species relative to intermolecular links.

Registry No. (PDMA)(4,4′-oxydianiline) (copolymer), 25038-81-7; (PDMDA)(4,4′-oxydianiline) (SRU), 9043-05-4.

References and Notes

(1) Kreuz, J. A.; Endrey, A. L.; Cay, F. P.; Sroog, C. E. *J. Polym. Sci. A-1* **1966**, *4*, 2607.
(2) Mikhailova, N. V.; Nikitin, V. N.; Sidorovich, A. V.; Adrova, N. A.; Baklagina, Yu., G.; Dubnova, A. M.; Yefanova, N. V. *Polym. Sci. USSR* **1977**, *19*, 1188.
(3) Krasovskii, A. N.; Antonov, N. P.; Koton, M. M.; Kalnin'sh, K. K.; Kudrysavtsev, V. V. *Polym. Sci. USSR* **1979**, *21*, 1038.
(4) Koton, M. M.; Meleshko, T. K.; Kudrysavtsev, V. V.; Nechayev, P. O.; Kamzolkina, Ye. V.; Bogorad, N. N. *Polym. Sci. USSR* **1982**, *24*, 791.
(5) Kardash, I. Ye.; Likhachev, D. Yu.; Nikitin, N. V.; Adrashinikov, A. Ya.; Kozlova, N. V.; Pravednikov, A. N. *Polym. Sci. USSR* **1985**, *27*, 1961.
(6) Matsuo, T. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1844.
(7) Vanclef, A.; Bouche, R. *Spectrosc. Lett.* **1979**, *12*, 371.
(8) Dine-Hart, R. A.; Wright, W. W. *Makromol. Chem.* **1971**, *43*, 189.
(9) Angelo, R. J.; Golike, R. C.; Tatam, W. E.; Kreuz, J. A. In *Recent Advances in Polyimide Science and Technology*; Weber, W. D., Gupta, M. R., Eds.; Mic-Hudson Section, Society of Plastics Engineer's Inc., 1987; p 67.
(10) Ishida, H.; Wellinghoff, S. T.; Baer, E.; Koenig, J. L. *Macromolecules* **1980**, *13*, 826.
(11) Tsimpris, W. B.; Mayhan, K. G. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1151.
(12) Brekner, M. J.; Feger, C. *J. Polym. Sci., Part A* **1987**, *25*, 2905.
(13) Brekner, M. J.; Feger, C. *J. Polym. Sci., Part A* **1987**, *25*, 2479.
(14) Young, P. R.; Chang, A. C. 30th National SAMPE Symposium, 1985; p 889.
(15) Cotter, R. J.; Matzner, M. *Ring Forming Polymerizations Part B. 2. Heterocyclic Rings*; Academic Press: New York, 1972.
(16) Kolesnikov, G. S.; Fedotova, O. Ya.; Hofbauer, E. I.; Hesein Hamid Mohamed Ali Al'Sufi *Polym. Sci. USSR* **1966**, *8*, 1585.
(17) Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 125.
(18) McGraugh, M. C.; Kottle, S. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 817.
(19) Maurer, J. J.; Eustace, D. J.; Ratcliffe, C. T. *Macromolecules* **1987**, *20*, 196.
(20) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 346.
(21) Russell, T. P. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1105.
(22) Cotts, P. M. In *Polyimides: Synthesis, Characterization and Applications*; Mittal, K. C., Ed.; Plenum Press: New York, 1984; p 223.
(23) Wallach, M. L. *J. Polym. Sci.* **1969**, *A2*, 7, 1995.
(24) Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Olivier, K. L. *J. Polym. Sci.* **1965**, *A3*, 1373.
(25) Volksen, W.; Cotts, P.; Yoon, D. Y. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2487.