

## Note

### *Catalytic Activity of Benzimidazole in the Imidization of Polyamic Acids*

Miscibility in systems containing poly-2,2(*m*-phenylene)5,5'-bibenzimidazole (PBI) and a variety of aromatic polyimides (PI) has recently been reported.<sup>1-3</sup> To study the intermolecular interactions in these blends, mixtures of benzimidazole (BI) and other similar aromatic compounds with PI in the polyamicacid (PAA) form have been prepared. In the context of these experiments a catalytic activity of BI on the imidization reaction (which transforms a PAA to the corresponding PI) was observed. Such catalytic activity is also reported in a recent patent.<sup>4</sup>

In the present study, the imidization reactions of three PAAs have been followed in the presence of different aromatic compounds by infrared (IR) measurements.

### EXPERIMENTAL

#### Materials

One of the polyimides studied was the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (DABP) [known as LaRC TPI (an acronym for NASA Langley Research Center thermoplastic polyimide)]. LaRC PAA (Mitsui Toatsu Chemicals, Inc.) was obtained as a 30% (w/v) solution in *bis*(2-methoxyethylether)(diglyme) with an inherent viscosity of 0.54 dL/g at 35°C. This solution was diluted with diglyme, precipitated in water, and the recovered powder was dried to constant weight prior to dissolution in DMAc or DMSO.

The other two PAAs which were considered are condensation products of BTDA and *m*-phenylene diamine (*m*-PDA), and of pyromellitic dianhydride (PMDA) and 3,3'-diaminodiphenylether (3,3'-ODA). For convenience, the latter two PAAs and their PI counterparts will be referred to as BP-P (for benzophenone phenyl) PAA (or PI) and P-ODA (for phenyl oxydianiline) PAA (or PI), respectively. The BP-P and P-ODA PAAs were supplied (NASA Langley Research Center) as 15% (w/v) solutions in DMAc and were used as received. The solvents and the heterocyclic compounds (Aldrich Chemical) were used as received.

Films were cast from 2 to 3% (w/v) solutions on NaCl windows under nitrogen for 24 h at 50–80°C. At this stage the films, 10–20  $\mu\text{m}$  thick, contained about 15 wt% residual solvent as determined by thermogravimetric analysis (TGA). The films were imidized, and concurrently, the remaining solvent was removed by heating for 1 h under nitrogen at successively higher temperatures.

Infrared spectra were measured at room temperature using an IBM IR/32 FTIR spectrometer at a resolution of 2  $\text{cm}^{-1}$  and were signal-averaged over a minimum of 30 scans.

### RESULTS AND DISCUSSION

The imidization reaction of several PAAs of varying structures has been studied using IR spectroscopy.<sup>5-11</sup> The spectra of the PAAs and their PI counterparts are substantially different, and the extent of cyclization can be followed using either the increase in intensity of the imide bands or the decrease in intensity of the amide bands. Curves *a* and *b* in Figure 1 show IR spectra in the region 2000–600  $\text{cm}^{-1}$  for films of pure LaRC PAA and a 50/50 wt% LaRC PAA/BI blend cast at 80°C, respectively. The spectrum in curve *a* is typical of LaRC PAA, while the spectrum in curve *b* closely resembles that of fully imidized LaRC TPI.<sup>3,9</sup> For comparison, curve *c* in Figure 1 shows the spectrum of a pure LaRC TPI sample prepared by curing at 170°C for 1 h. The spectra in curves *b* and *c* are essentially identical; the small differences are attributed to some BI bands (e.g., at 745  $\text{cm}^{-1}$ ) and to some residual DMAc bands (e.g., at 1620

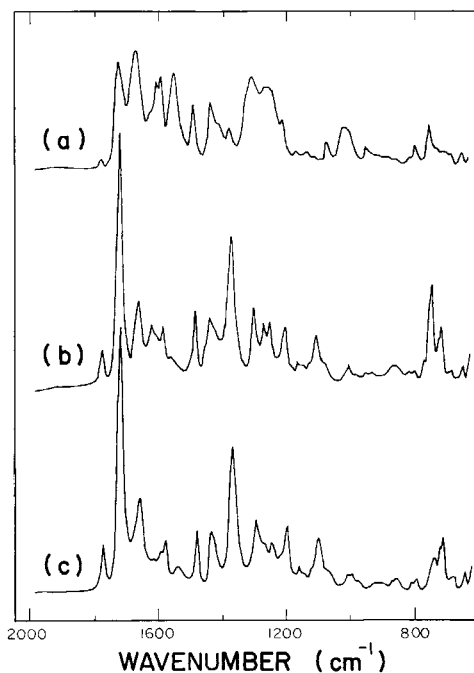


Fig. 1. IR spectra, 2000–600  $\text{cm}^{-1}$ , *a*: LaRC PAA cast at 80°C, DMAc solution; *b*: LaRC PAA/BI 50/50 wt% blend, cast same conditions as *a*; *c*: LaRC PAA cast at 80°C, DMAc solution, cured at 170°C, 1 h.

$\text{cm}^{-1}$ ). Thus it is immediately apparent that BI increases the degree of imidization (24 h at 80°C) to levels that can be reached, in its absence, only by curing at much higher temperatures (170°C).

As in the previous study of the imidization of LaRC in PBI blends,<sup>12</sup> the increase of the two phthalimide carbonyl stretching bands, located near 1780 and 1720  $\text{cm}^{-1}$  was followed as a function of cure temperature, with a 1 h anneal at each temperature. The benzophenone carbonyl band near 1670  $\text{cm}^{-1}$  was used as reference band for LaRC PAA. This choice was made because, in this region, the absorbance of BI is low<sup>13</sup> (as it is for PBI) and does not interfere with the carbonyl bands. Mole percent imidization is conveniently defined using the relative absorbances of the 1780  $\text{cm}^{-1}$  and 1670  $\text{cm}^{-1}$  bands, and is shown on the ordinates of Figures 2–5. Consistent imidization values are also obtained using the relative absorbances of the 1724  $\text{cm}^{-1}$  and 1670  $\text{cm}^{-1}$  bands.

The absorbances of the two phthalimide carbonyl bands relative to the absorbance of the benzophenone carbonyl band are reported as a function of the curing temperature in Figures 2(A) and 2(B) for samples cast from DMAc solutions in which the LaRC PAA/BI weight ratio varied from 95/5 to 50/50. In each case, the casting temperatures are those of the first data point. The sigmoidal curves associated with the imidization of the polyamic acid are shifted downward by up to 100°C. In particular it is noted that the 50/50 wt% LaRC PAA/BI sample was already 65% imidized after the casting procedure carried out at 80°C.

The as-cast samples still contain residual solvent (nearly 15 wt%, as determined by TGA), which in practice cannot be removed prior to imidization; this solvent is gradually removed during imidization. It is well known that the nature of the residual solvents may affect the imidization rate.<sup>14,15</sup> Figure 3 shows data analogous to those of Figure 2, for 50/50 wt% LaRC PAA/BI samples cast from dimethyl sulfoxide (DMSO). Retardation of the imidization reaction relative to that found with DMAc is observed both in the presence and absence of BI, but the catalytic activity of the latter is still apparent.

Figures 4(A) and 4(B) show the absorbances of the minor phthalimide carbonyl stretching band relative to the aromatic C—C stretching band for the BP-P and P-ODA PAA/PI samples cast from DMAc, respectively. The strong influence of BI on the rate of the imidization reactions is

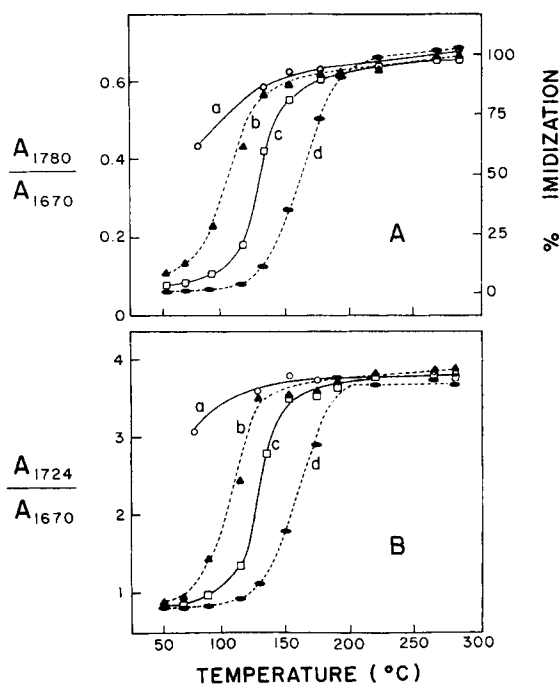


Fig. 2. Absorbancies of the two phthalimide carbonyl bands, relative to the  $1670\text{ cm}^{-1}$  benzophenone carbonyl band, as a function of curing conditions. 1 h anneal at indicated temperature for mixtures of LaRC/BI: *a*: 50/50 wt%, *b*: 80/20 wt%, *c*: 95/5 wt%; and *d*: 100/0 wt%; the solvent is DMAc. Figures 2A and 2B are for the phthalimide carbonyl bands located at  $1780\text{ cm}^{-1}$  and  $1724\text{ cm}^{-1}$ , respectively.

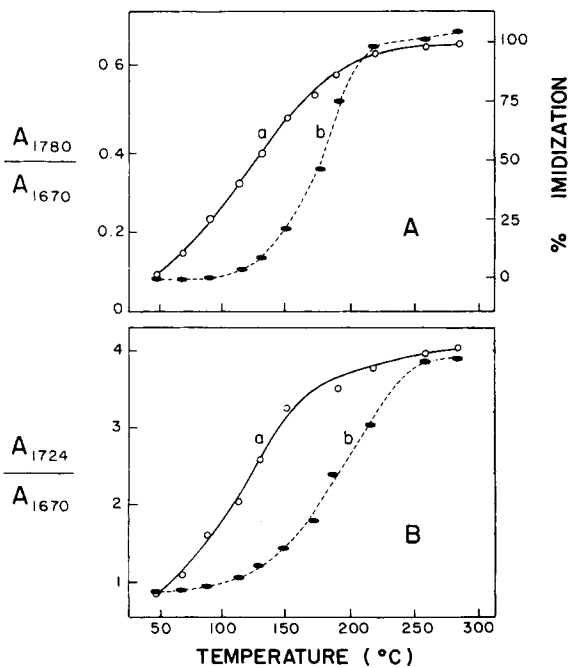


Fig. 3. As in Figure 2, DMSO solvent, *a*: a 50/50 wt% LaRC PAA/BI mixture and *b*: pure LaRC PAA.

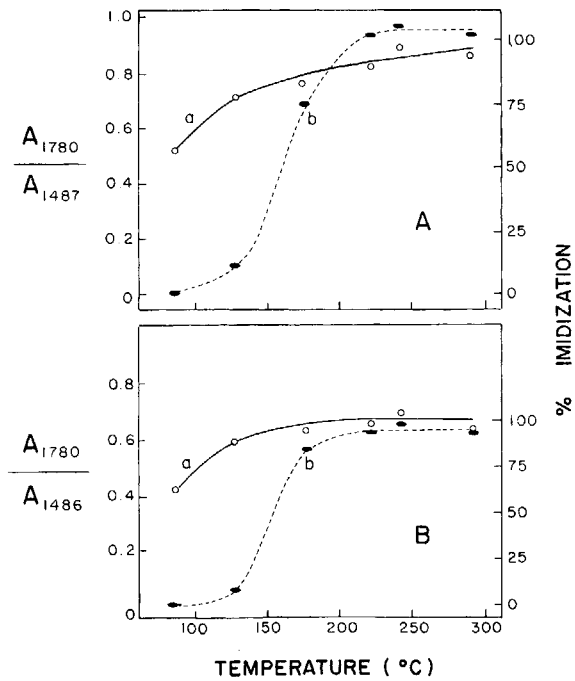


Fig. 4. Absorbance of the minor phthalimide carbonyl band ( $1780\text{ cm}^{-1}$ ) relative to the aromatic C—C band as a function of curing conditions. 1 h anneal at indicated temperature; *a*: a 50/50 wt% PAA/BI mixture and *b*: pure PAA. 4A: BP-P system; 4B: P-ODA system.

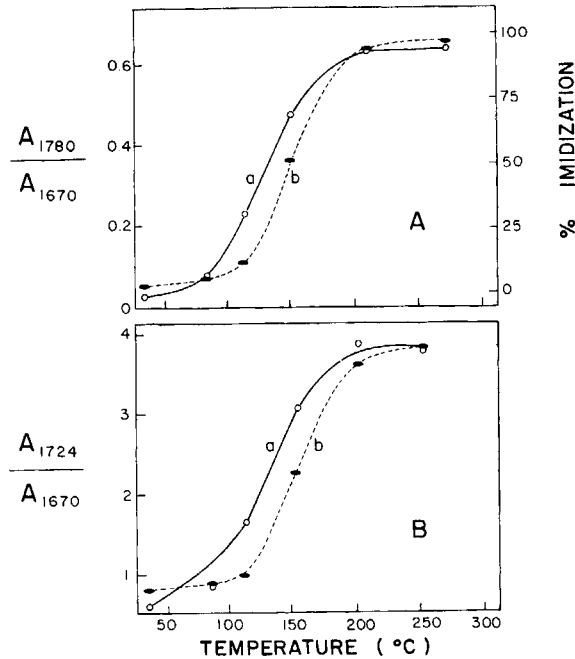


Fig. 5. Same as Figure 2, *a*: 50/50 wt% LaRC PAA/imidazole mixture, *b*: pure LaRC PAA.

again apparent with a maximum temperature shift of nearly 100°C for the 50/50 wt% PAA/BI samples.

Similar studies were carried out using compounds with structural similarities to BI; imidazole, indazole, indole, and indene. Figures 5(A) and 5(B) show that imidazole at a 50/50 wt ratio of LaRC PAA/imidazole produces a smaller effect on the imidization reaction, a result consistent with earlier work that reported the lowering of the temperature of onset of solid-state imidization of a polyamic acid by 20°C<sup>16</sup> in the presence of imidazole. The other three compounds tested at the same weight ratio do not affect the imidization reaction.

Chemical (as distinct from thermal) imidization of PAAs is generally accomplished by using dehydrating agents such as aliphatic anhydrides, ketenes, and *N,N*-dialkylcarbodiimides, usually in conjunction with tertiary amine catalysts.<sup>11,17</sup> Strong inorganic acids such as HCl or H<sub>3</sub>PO<sub>4</sub> have also been suggested as catalysts for the imidization of PAAs.<sup>18</sup> In the case of imidization in the presence of BI, no dehydrating agent or strong acid is necessary and a different mechanism which may involve the complexation of amic acid and/or the imide or phthalimide rings appears to be operating. Polymer complex formation has been recently proposed for PAAs with amines,<sup>19</sup> on the other hand, a number of molecular complexes containing BI, as well as other azoles, have also been reported. Some examples of substrates for BI are benzophenone,<sup>20</sup> dimethyl sulfoxide,<sup>20</sup> furan,<sup>20</sup> naphthalene,<sup>21</sup> trinitrophenol,<sup>22</sup> and trinitroanisole.<sup>22</sup> In several cases the formation of hydrogen bonds in the complexes has been suggested.<sup>20,22</sup> However, the specific effect of BI on the imidization reaction, as well as the broad conditions of miscibility for PBI/PI blends,<sup>1-3,12</sup> suggests that some specific interaction or complexation between BI and the phthalimide rings could be involved.

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