Efficient Catalyst for Low Temperature Solid-Phase Imidization of Poly(amic acid)

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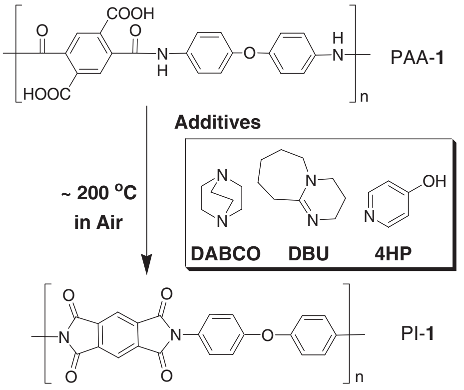
Efficient base-catalysts for low temperature solid-phase imidization of poly(amic acid) (PAA) have been found. Thermal imidization of PAA proceeded smoothly in the presence of 1 wt % of strong bases such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 200 °C in a short time, and no residues of DBU remained in the polyimide film.

Polyimides (PIs) are a class of polymers used extensively in microelectronics because of their outstanding key properties such as high thermal stabilities, chemical resistance, and good mechanical and electrical properties.[1] They are used as interlayer dielectrics in integrated circuit fabrication. Commercial PIs are prepared from diamines with tetracarboxylic dianhydrides to form soluble PIs precursors, namely "poly(amic acid)s" (PAAs), which are then converted thermally, or chemically with acetic anhydride, into the corresponding PIs. Because thermal treatment around 350 °C is generally employed for imidization process, their wide applications in conventional electronic industries containing at least one or more thermally unstable organic compounds are interfered so far. Recently, catalysts such as hydroxypyridine and benzimidazole to accelerate the imidization of PAA were reported, where 0.5 molar equivalent or more catalysts to a repeating unit were required.[2] Therefore, finding more efficient catalysts are important for broadening industrial applications.

Here, we present excellent imidization catalysts of PAA, where only 1 wt % of base-catalyst is enough to complete the imidization at 200 °C in a short time. Furthermore, no residues of the catalysts remain in a PI film after the thermal treatment.

The imidization process involves several interrelated elemental reactions, and dynamic changing physical properties such as diffusion rate, chain mobility, solvation, and acidity.[3–7] Thus, it is very difficult to predict a proper imidization catalyst. In this work, very strong basic catalysts such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were employed because these catalysts would accelerate the nucleophilic attack of a carboxylate ion on an amide carbonyl unit through the formation of ammonium salt, producing an isoimide intermediate, which is then isomerized into an imide by these base-catalysts.

PAA-**1** was prepared by ring-opening polyaddition of pyromellitic dianhydrides with an equivalent of 4,4′-oxydianiline in *N*,*N*-dimethylacetoamide (DMAc) at room temperature. The number average molecular weight and polydispersity index of PAA-**1** were determined by GPC (DMF, PSt standard) to be 5.4×10^5 and 1.9, respectively. One of the bases, DABCO, DBU or 4-hydroxypyridine (4HP) was then added to a PAA-**1** solution and stirred overnight at room temperature (Scheme 1). The resulting solution was retained homogeneous and cast on a silicon wafer, baked at 100 °C for 5 min, and then dried at 100 °C for 1 h under vacuum. Because remained solvent in the film is also effective for the imidization as a plasticizer.[1] The film thickness was around 0.2–0.3 µm. Upon the study of imidization with infrared resonance (IR) spectroscopy, PAA-**1** films were baked on a hotplate at each temperature for 15 min up to 200 °C. A reference PI film was prepared by heating of PAA-**1** at 200, 250 °C for 0.5 h and 350 °C for 1 h, respectively in air.



Scheme 1. Imidization at lower temperature than 200 °C.

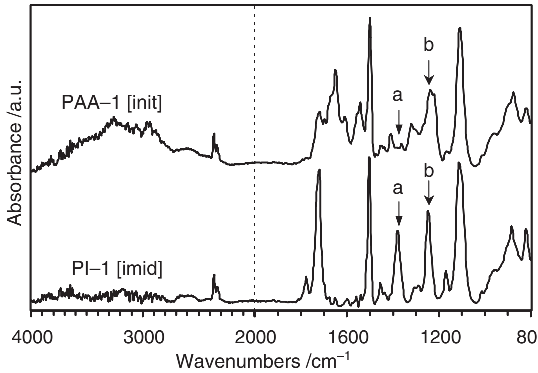


Figure 1. IR spectra of PAA-**1** and corresponding polyimide, PI-**1**. The peaks marked **a** (C–N stretch of imide) and **b** (C–O stretch of phenyl ether) are corresponded to Eq 1.

Figure 1 shows IR spectra of PAA-**1** film containing 5 wt % (0.19 molar equivalent) DABCO after vacuum drying at 100 °C and the corresponding PI-**1** film cured at 350 °C for 1 h in air as references. An absorbance of peak (**a**) at 1375 cm^{-1} assignable as C–N stretch of imide group increased with increasing curing temperature, while that of (**b**) at 1235 cm^{-1} assignable as C–O stretch of phenyl ether had no influence by the catalyst and solvent as reported the literature.[2] From those two absorbencies in IR spectra, the degree of imidization was determined using the following equation,

$$\textbf{Degree of Imidization}\ (\%) = \frac{\mathbf{a}/\mathbf{b}_{[\mathrm{samp}]} - \mathbf{a}/\mathbf{b}_{[\mathrm{init}]}}{\mathbf{a}/\mathbf{b}_{[\mathrm{imid}]} - \mathbf{a}/\mathbf{b}_{[\mathrm{init}]}} \times 100 \qquad (1)$$

Subscripts between brackets followed **a**/**b** in the equation indicate states of polymer films; e.g. [samp] is the polymer sampled at each heating temperature level (110–200 °C); [init] is initially prebaked PAA at 100 °C under vacuum; [imid] is the fully cured PI at 350 °C for 1 h in air.

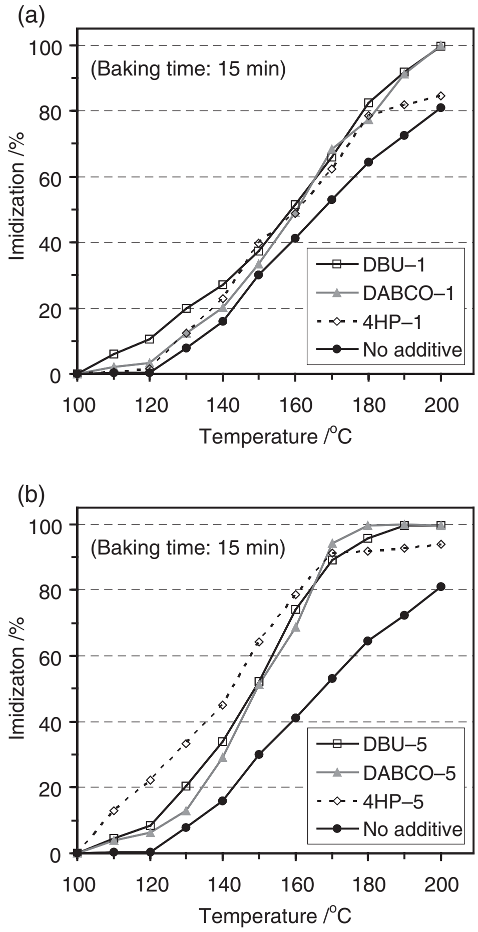


Figure 2. Degree of imidization of PAA-**1** with DBU (solid line with open square, □), DABCO (gray line with triangle, ▲), 4HP (dashed line with open diamond, ◇) and additive-free (solid line with closed circle, ●). Each additive was added (a) 1 wt % or (b) 5 wt % of PAA-**1**.

The degree of imidization for PAA-**1** films containing various bases upon heating is shown in Figure 2. The degree of imidization is 80% for the base-free PAA-**1** at 200 °C. Even in the presence of 1 wt % of DBU and DABCO the imidization is accelerated, producing the fully cyclized PI at 200 °C. On the other hand, 4HP is not effective compared to DBU and DABCO. An addition of 5 wt % of DBU and DABCO further accelerates the imidization that reaches 100% at 190 and 180 °C, respectively. In the presence of 5 wt % of 4HP the imidization can not be completed up to 200 °C, though the addition of 1 molar equivalent (ca. 18 wt %) of 4HP to a repeating unit of the PAA-**1** accelerates imidization quite well even at lower temperature (140 °C) as described in a previous report.[2]

The residual catalysts influence the properties of PI films. Thus, the residues of these bases in the imidized films were traced by thermal desorption spectrometer. The measurement was carried out at a heating rate of 1 °C/min from 60 to 300 °C under 10^{-10} Torr. When PAA-**1** films containing 5 wt % DABCO, or DBU were cured at 200 °C for 40 min, a trace amounts of DABCO were detected, but no DBU was found.

In summary, strong bases such as DABCO and DBU accelerate the thermal imidization of PAA films at low temperature based on IR spectroscopic study. Furthermore, no residues of DBU remained in the PI film. This process will provide a potentially efficient and versatile route for the low temperature solid-phase imidization of PAAs. The mechanism of imidization catalyzed by these strong bases is now under investigation.

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