

## Thermo-base Generator for Low Temperature Solid-phase Imidation of Poly(amic acid)

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Efficient thermo-base generators (TBGs) which can release an secondary alicyclic amine (e.g. 2,6-dimethylpiperidine; DMP) have been developed for low temperature solid-phase imidation of poly(amic acid) (PAA). Such latent thermo-sensitive catalysts promote thermal imidation of PAA film smoothly up to 200 °C, without the salt formation and storage instability of PAA solution.

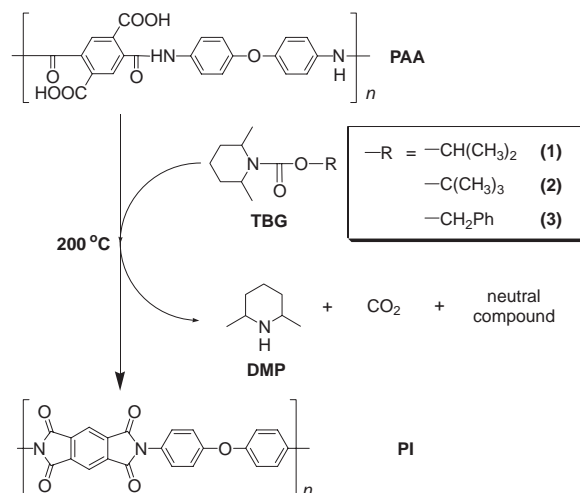
Polyimide (PI), a class of super-engineering plastics, possesses outstanding key properties such as high thermal and chemical stabilities and excellent mechanical and electrical properties, being used as protection and insulation materials in microelectronics.<sup>1</sup> Generally, PIs are prepared from a poly(amic acid) (PAA) by thermal imidation nearly at 350 °C, or by chemical imidation with acetic anhydride and pyridine mixture. However, such a high thermal treatment limits the wide application of PIs in parallel with thermally unstable components.

Recently, we reported efficient base-catalysts, 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), for low temperature imidation of PAA up to 200 °C.<sup>2</sup> The prediction of a proper imidation mechanism seems to be difficult because several elemental reactions are integrated during the imidation process including dynamic changes of diffusion rate, chain mobility, polarity, etc.<sup>3-7</sup> We presume that DABCO and DBU enhance a nucleophilic attack of a carboxylate ion on an amide carbonyl unit through a formation of ammonium salt, giving an isoimide, which is finally isomerized into an imide by the bases. These base catalysts easily form salts with PAAs in polar amidic solvents (e.g. *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), etc.), and dissolution of these salts takes a long time. Furthermore, bases induce the storage instability of PAA solution.

For practical use of these bases in the industry, development of latent base-catalysts for low temperature imidation of PAA is more desirable. Latent catalysts are a group of stable compounds at ambient condition, which acts only under appropriate external stimulation like heating or photoirradiation. Therefore, a latent thermo-sensitive base-catalyst will enhance both storage stability and processability of PAA solution due to non-reactivity at normal temperature, while the imidation of PAA is promoted on a certain range of elevated temperatures.

Here, we present a series of efficient thermo-base generators, from which a secondary aliphatic amine such as 2,6-dimethylpiperidine (DMP) is formed (Scheme 1). To improve the solubility and effectiveness of the latent imidation catalysts, the design of thermo-base generators (TBGs) is based on carbamate (urethane) compounds that are apt to decompose thermally with releasing carbon dioxide and carbocation species, giving neutral compounds, such as olefins and DMP.

TBGs, compound (1) and (3) were prepared by the reaction



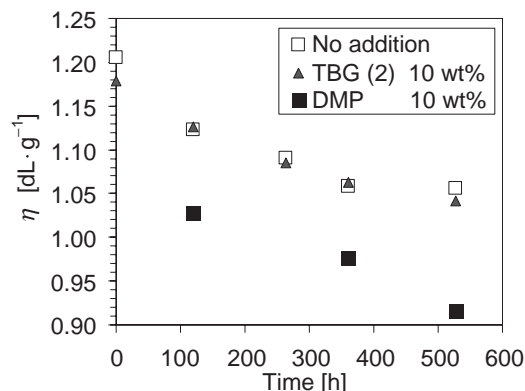
**Scheme 1.** Thermal imidation of PAA to PI with a TBG at lower than 200 °C.

of DMP with isopropyl or benzyl chloroformate in tetrahydrofuran/pyridine mixture. Compound (2) was synthesized from DMP with di-*tert*-butyl dicarbonate. Purification of the obtained TBGs was carried out by vacuum distillation (Supporting Information).

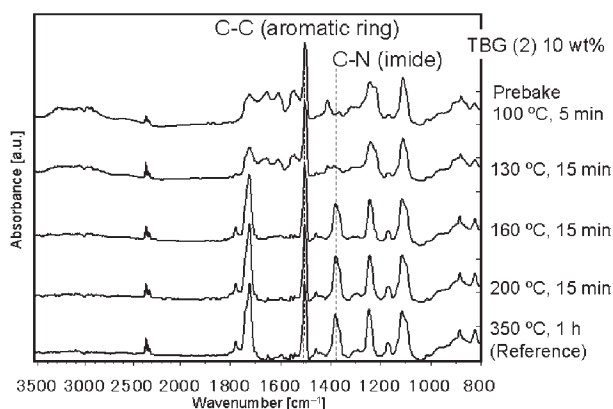
PAA was prepared by ring-opening polyaddition of pyromellitic dianhydrides with an equivalent of 4,4'-oxydianiline in DMAc at room temperature for 12 h to give a viscous clear solution. An inherent viscosity of the polymer in DMAc was 1.2 dL/g at a concentration of 0.5 g/dL in DMAc at 30 °C. TBGs are easily and completely soluble in PAA polymerization solution unlike in case of DABCO or DBU.

To clarify a stability of the PAA solution, viscosity change was investigated as a function of time (Figure 1). The viscosity behavior of the solution with 10 wt % TBG (2) is the same with that of non-additive PAA solution when these solutions were stored at 5 °C. Slow decrease of the viscosity of the solution is explained by the hydrolysis of PAA in the presence of small amount of water in the solution. In contrast, the viscosity of solution containing 10 wt % DMP decreases rapidly even the salt formation of PAA and DMP, which generally increases the viscosity. Hydrolysis of the PAA is accelerated in the presence of DMP in which the carboxylate anion acts as a base catalyst. The difference of the viscosity between protected and unprotected amine in the PAA solution prompts utility of the TBG based on carbamate structure as a latent base catalyst.

The study on a degree of imidation (DI) of the PAA film containing one of TBGs was carried out with infrared (IR) spectroscopy up to 200 °C in a similar manner as reported previously.<sup>2</sup> In this study, two bands at 1500 and 1375 cm<sup>-1</sup>



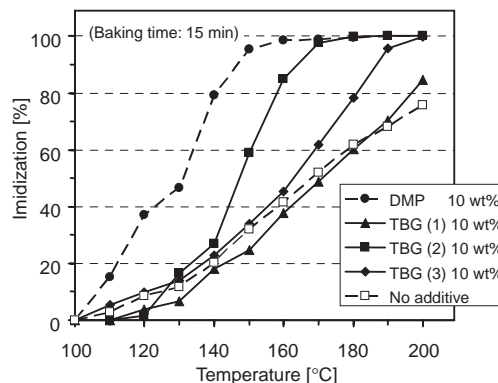
**Figure 1.** Viscosity changes of PAA solution in DMAc with DMP (■), TBG (2) (▲), and additive-free (□), with 10 wt % additive of PAA and stored at 5 °C.



**Figure 2.** IR spectra of PAA films containing 10 wt % TBG (2) baked at various temperature for 15 min and a reference PI film.

due to aromatic C=C and imide C-N stretchings, respectively, were used for calculation of DI. PAA films containing 10 wt % TBG (2) were pre-baked at 100 °C for 5 min, and then baked at each temperature for 15 min up to 200 °C. A reference PI film was prepared by heating PAA at 350 °C. The results are shown in Figure 2, which indicate that the DI increases with increasing the cure temperature, reaching 100% at 200 °C.

The DI for PAA films containing various additives (10 wt %) upon heating is shown in Figure 3 with a comparison to an additive-free PAA film that reaches 75% of imidation at 200 °C. A PAA film containing 10 wt % DMP significantly accelerates the DI even in lower heating level, resulting in completion of the imidation at 180 °C. In the case of TBG (2), the imidation is completed at 180 °C, indicating the most efficient catalyst among the TBGs. On the other hand, TBG (1) is not effective compared with the other TBGs. All the TBG-containing PAA films show a similar trend of imidation as additive-free at lower temperature levels (e.g. up to 190 °C for (1), 140 °C for (2), and 160 °C for (3)). Efficiency for the imidation of PAA is related to



**Figure 3.** DI of PAA with DMP (●), TBG (1) (▲), TBG (2) (■), TBG (3) (◆), and additive-free (□), with 10 wt % additive of PAA.

thermal stability of each TBG. TBG (2) easily decomposes and forms isobutene and DMP because of the formation of the most stable tertiary carbocation in the TBGs. Thermal decomposition behavior of TBG (2) in PAA film was traced by <sup>1</sup>H NMR spectroscopy. TBG (2)-containing PAA film, which was prepared by spin-cast on a silicon wafer and then pre-heated at 100 °C for 5 min, was heated at 180 °C in a glass-tube for 1 h with nitrogen flow. The fraction was collected out of the tube and then dissolved in deuterated chloroform (CDCl<sub>3</sub>) for the measurement. A characteristic signal at 2.65 ppm assignable as methine proton of DMP was detected in the <sup>1</sup>H NMR spectrum.

In summary, we developed new TBGs, which decompose up to 200 °C, producing DMP. These TBGs act as catalysts for the thermal imidation of PAA films at low temperature. Especially, 10 wt % or less of TBG (2) is enough to complete the imidation at 200 °C in a short time. Moreover, the PAA solution containing TBG (2) is stable for a long period. This process will provide a potentially efficient and versatile route for the low temperature solid-phase imidation of PAAs.

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