as the catalyst, and NaI as the co-catalyst, were dried at a specified temperature and put into an autoclave. By substituting the atmosphere in the reactor with carbon dioxide gas, thermal treatment was applied to the mixture at a specified temperature for a specified period. After completing the reaction, the reactant was analyzed by high performance liquid chromatography to evaluate the product composition and yield. The yield of NTCDA was defined as the percentage of NTCDA formed to the theoretical quantity of NTCDA obtained from the starting material:

$$Y = nP_{\text{NTC}} / P_{\text{NCAs}} \times 100$$

where Y is the yield of NTCDA (%), P_{NTC} is the quantity of NTCDA formed or P_{NCAs}

unstable and so most of the formed $NTCCd_2$ is immediately decomposed. In the presence of NaI, however, a metal interchange occurs between the formed $NTCCd_2$ and NaI, and NTC presumably becomes a Na salt ($NTCNa_4$) which is thermally stable.

Various reaction conditions were investigated to improve the NTC yield, and the highest yield was as low as 30% for all the tested conditions. To identify the cause of the limit of 30% yield, X-ray diffraction of the reaction product was analyzed (**Fig. 2**). The analysis showed a different diffraction pattern for the reaction product from that of $NTCNa_4$ and of $NDCNa_2$. From the X-ray diffraction pattern, t t l   dif5   t rom th   t

and $ZnCl_2$ as the zinc compound, no NTC formation was observed. With $ZnCl_2$ as the zinc compound, the yield was 0.5% at the highest.

As described above, in view of the fact that the activity of zinc catalyst in the Henkel Reaction using sodium naphthalene carboxylate as the raw material was low, and that there are many examples of starting materials of potassium aromatic carboxylate, such as the rearrangement of dipotassium 1,8-naphthalate $(1,8-NDCK_2)$ to $2,6-NDCK_2$ and of dipotassium phthalate to dipotassium terephthalate[4–7], the authors conducted the reaction described below. Speculating that the coexistence of potassium carboxylate in the raw material forms a zinc naphthalenecarboxylate, and that NTC can be synthesized in the presence of zinc catalyst, the reactions upon adding various potassium carboxylates to $2,6-NDCNa_2$ were tested. The result ere t   e t   e wprl   er   ng vario

reaction of the small-scale test was well reproduced in the autoclave, and the production of NTCDA at 1 kg/d has started. The products are being supplied to customers, and also used for evaluating the properties of polyimide as described below.

3.

hydrolysis resistance, and the market requires higher preservation stability[9]. **Figure 9** shows the measurements of hydrolysis resistance of various polyamic acids after thermal treatment at 80°C[10]. Generally, thermal treatment of polyamic acid as the precursor of polyimide enhances the hydrolysis reaction, thereby decreasing the intrinsic viscosity and stabilizing the intrinsic viscosity at a certain level. This occurs because the amic acid forming reaction is an equilibrium reaction, as shown in **Fig. 10**. The polyamic acid using NTCDA shows a slow decrease in the intrinsic viscosity and has high hydrolysis resistance compared with those of polyamic acids using PMDA and BPDA. Hence, NTCDA has the potential to solve the issue of preservation stability.

3.3 High Performance Reforming of NTCDA

The properties required of polyimide for next-generation electronic boards were described earlier in this paper. The polyimide using NTCDA has suffcient heat resistance, small coeffcient of linear thermal expansion, and large modulus of elasticity, and also has excellent hygroscopic resistance. Furthermore, this type of polyimide provides high stability in the raw material stage and also in the polyamic acid stage as the precursor of resin a   a%   s