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# A Novel Polymerization Process of Poly(4,4′-oxydiphenylenepyromellitamic acid)

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Poly(4,4′-oxydiphenylenepyromellitimide) (PI) is one of the most useful polyimides because of its high thermal stability and good mechanical strength. Poly(4,4′-oxydiphenylenepyromellitamic acid) (PAA), a typical precursor of PI, is conventionally prepared from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) by solution polymerization in aprotic polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and the like, which are characterized generally by high dipole moments and high boiling temperatures.[1] These aprotic polar solvents strongly associate with PAA which is the solute in the resulting solution.[2–4] Due to this solvent–solute interaction, the solvents cannot be easily removed from PAA when a PI product is prepared by thermal curing.

In view of the above, a solution polymerization process which does not utilize aprotic polar solvents has been investigated. As a result, we discovered that a mixture prepared by mixing tetrahydrofuran (THF) and methyl alcohol (MeOH) in a particular ratio is capable of dissolving PAA and can be applied for the synthesis of PAA, while THF or MeOH alone does not dissolve PAA. Interestingly, in fact, the reaction of PMDA with ODA smoothly proceeds in the mixed solvent of THF/MeOH to afford an entirely homogeneous solution containing highly polymerized PAA.

The polymerization process is presented in Scheme 1. The ratio of THF/MeOH needs to be between 9/1 and 4/6 by weight or else a homogeneous PAA solution cannot be obtained.

A typical polymerization procedure is as follows:

Into a reaction flask fitted with a mechanical stirrer and thermometer were charged 28.57 g (0.143 mol) of ODA, 272.0 g of THF, and 68.0 g of MeOH (THF/MeOH = 8/2 by weight). Stirring was begun, and after the ODA has almost dissolved, 31.43 g (0.144 mol) of PMDA powder was added gradually to the stirring solution of the diamine over 40 min. The temperature of the solution was maintained between 20 and 25 °C during the addition of PMDA. Stirring was continued at room temperature for 20 min. A viscous, homogeneous, yellow solution resulted.[5] Thereafter, in order to equilibrate the PAA to a most probable molecular weightdistribution ($M_w/M_n$), the temperature was maintained at room temperature for 24 h. The solid concentration and the solution viscosity[6] of the resulting solution were 15.0 wt % and 206 P, respectively. The intrinsic viscosity,[7] the weight-average molecular weight ($M_w$), and $M_w/M_n$[8] of the obtained PAA were 1.49, 191 000, and 2.51, respectively.

PMDA reacts with MeOH under reflux to produce pyromellitic acid dimethyl ester (PMDE),[9] and MeOH is a component of the present solvent system. Therefore, a possibility of a two-stage polymerization, in which PMDE is initially formed as an intermediate and then PMDE reacts with ODA to afford PAA, should be considered. In order to clarify the reaction mechanism, separately synthesized PMDE was added to the mixture of THF and MeOH (THF/MeOH = 85/15 by weight) containing a stoichiometric amount of ODA, and the temperature was maintained at room temperature for more than 50 h. However, the reaction between PMDE and ODA scarcely proceeded in the mixed solvent. Consequently, we confirmed that ODA directly reacts with PMDA in THF/MeOH to afford PAA.

**Scheme 1**

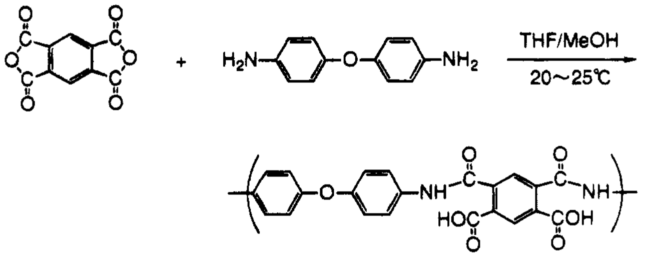

**Table 1. Mechanical Properties of the PI Film**

| thickness (μm) | density (g/cm³) | tensile strength (kg/mm²) | tensile modulus (kg/mm²) | elongation (%) |
|---|---|---|---|---|
| 35 | 1.42 | 17 | 286 | 85 |

A free-standing PAA film was prepared from the present PAA solution by doctorblading onto a glass plate, followed by drying at 80 °C for 2 h. A dynamic mechanical thermal analysis pointed out that the PAA film was hardly plasticized during the thermal cure. On the contrary, when aprotic solvents such as NMP are used, the residual solvents cause the PAA film to be plasticized. These results suggest that the association of THF/MeOH with PAA is relatively weak so that the solvents can be easily removed from PAA during the thermal cure.[10]

The PAA film was cured thermally at 300 °C for 3 h under a nitrogen atmosphere to yield a transparent PI film which exhibited IR spectra in accordance with assigned structures and had good mechanical properties[11] as demonstrated in Table 1. Further properties of the PI films will be presented in the near future.

Since there appeared no reports concerning a solution polymerization of PMDA with ODA without using aprotic solvents, the present polymerization process using THF/MeOH, in which high molecular weight PAA can be produced, is novel and unique. In addition, it should be noted that the present PAA solutions are quite useful in practical applications for various PI products because the mixed solvent is easily removed from PAA.

## References and Notes

(1) Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* **1976,** *11,* 161.
(2) Kreuz, J. A.; Endrey, A. L.; Gay, F. P.; Sroog, C. E. *J. Polym. Sci.* **1966,** *4,* 2607.
(3) Brekner, M.-J.; Feger, C. *J. Polym. Sci., Polym. Chem.* **1987,** *25,* 2005.
(4) Brekner, M.-J.; Feger, C. *J. Polym. Sci., Polym. Chem.* **1987,** *25,* 2479.
(5) Polymerization-grade PMDA and ODA were purchased from commercial sources and were used as received. THF and MeOH were reagent-grade materials and were used as received.
(6) Solution viscosity measurements were performed at 20 °C using a TOKIMEC Model DVL-BII.
(7) Intrinsic viscosity measurements were performed in NMP at 25 °C using an Ubbelohde suspended level viscometer. The concentration was 0.5 g/100 mL.

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(8) Molecular weights and molecular weight distributions were determined using a Hitachi GPC system equipped with a Hitachi RI detector and a Hitachi Kasei column (GL-S300MDT-5) in DMF/LiBr/$H_3PO_4$/THF at 35 °C. Molecular weight calculations were based on polystyrene standards.

(9) Wagner, R. B.; Zook, H. D. *Synthetic Organic Chemistry*; John Wiley & Sons: New York, 1953; Chapter 14, p 482.

(10) Details of the curing process will be presented in the near future.

(11) Mechanical properties were measured at 20 °C according to JIS (Japanese Industrial Standard) K 7127 on a INTESCO Model 2020.

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