

NOTES

Synthesis of Various Polyimides Using Tetrahydrofuran/Methanol as Solvent

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The presence of residual solvent in the polyamic acid precursor films affects processing conditions in the fabrication of polyimide films due to the need to remove it from the system. The aprotic solvents typically used in the manufacture of polyamic acids, dimethylacetamide (DMAc) and *N*-methyl pyrrolidone (NMP), form molecular complexes with polyamic acid making the solvent particularly difficult to remove under ambient conditions.¹⁻⁴ Echigo *et al.*, have created a novel solvent system consisting of tetrahydrofuran (THF) and methanol for the fabrication of ODA-PMDA polyimides.⁵⁻⁷ They found that this solvent system can be used in the synthesis of high molecular weight polyamic acids that can later be thermally cured into polyimides. They developed this system to assist the incorporation of water into the solution mixture which upon curing introduces porosity into the films. This solvent system results in the easy removal of nearly all solvent from the polyamic acid prior to thermal cure. The synthesis of other polyimides using this easy to remove solvent system has heretofore not been attempted. Here is reported the synthesis of a variety of polyimides using the THF/MeOH solvent system.

GENERAL EXPERIMENTAL PROCEDURE

Polyamic acids, as 3—12 wt% solutions were prepared by reacting stoichiometric amounts of diamines and pyromellitic dianhydrides for 2—12 hours. In a three necked flask under a nitrogen purge, the diamine was first dissolved in 40—100 mL solvent, a 80/20 wt% mixture of THF and methanol, by mechanical stirring. Upon complete dissolution of the diamine, addition of the dianhydride as one batch resulted in a curd-like mixture. Continued stirring resulted in complete dianhydride dissolution and homogeneous solutions. Films were then cast from these solutions and after evaporation of the solvent under ambient conditions, subjected to 125°C for one hour and two hours at 250°C to imidize the films. All diamines and dianhydrides were purified by either sublimation or recrystallization from toluene prior to use. THF and methanol were used as received. The generalized reaction scheme is shown in eq 1. Various diamines and dianhydrides are drawn in

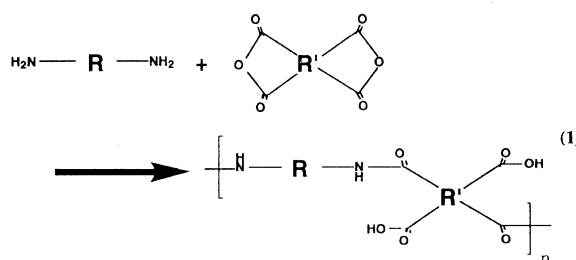


Figure 1. Viscosity measurements were conducted in concentrated sulfuric acid (H_2SO_4) on polyamic acids precipitated from the reaction solutions by pouring the solutions into water. Ubbelohde capillary viscometry using a concentration of 0.5 g/100 mL H_2SO_4 at 30°C was conducted for all polyamic acids.

RESULTS AND DISCUSSION

During the synthesis of the poly(amic acid)s very unusual solution behavior was noted. Upon the addition of the dianhydride, all solutions took on a cottage cheese-like texture. However, with continued stirring for various times, 2—12 hours, this texture disappeared and clear solutions of various colors resulted. This was accompanied by increase in the molecular weight as seen by the increase in the viscosity of the solution. The solution composition that results in the highest molecular weight of the ODA-PMDA poly(amic acid), as seen in Figure 2, is the THF/MeOH 80/20 wt% (78/22 vol%) solution. Figure 2 also shows the lack of solubility of the reactant in the solutions with less than 50 wt% and more than 90 wt% THF. Consequently, all further polyamic acid synthesis was conducted using the 80/20 solution composition. Molecular weights of the various polyamic acids were determined from the inherent viscosity of the poly(amic acid) solutions. The inherent viscosities and solution appearance of the various poly(amic acid)s are listed in Table I. As can be seen by the relatively high inherent viscosities, the facile synthesis of the various polyimides of high molecular weight in the THF/MeOH solvent system was achieved.

Various diamines had varying solubilities in the 80/20 (THF/MeOH) solvent system. 3,3'-ODA had the lowest solubility (less than 3 wt%) with 6-FDA having the highest (greater than 8 wt%). The diamine must first be dissolved into the solvent because it is much less soluble than the dianhydrides and would not dissolve

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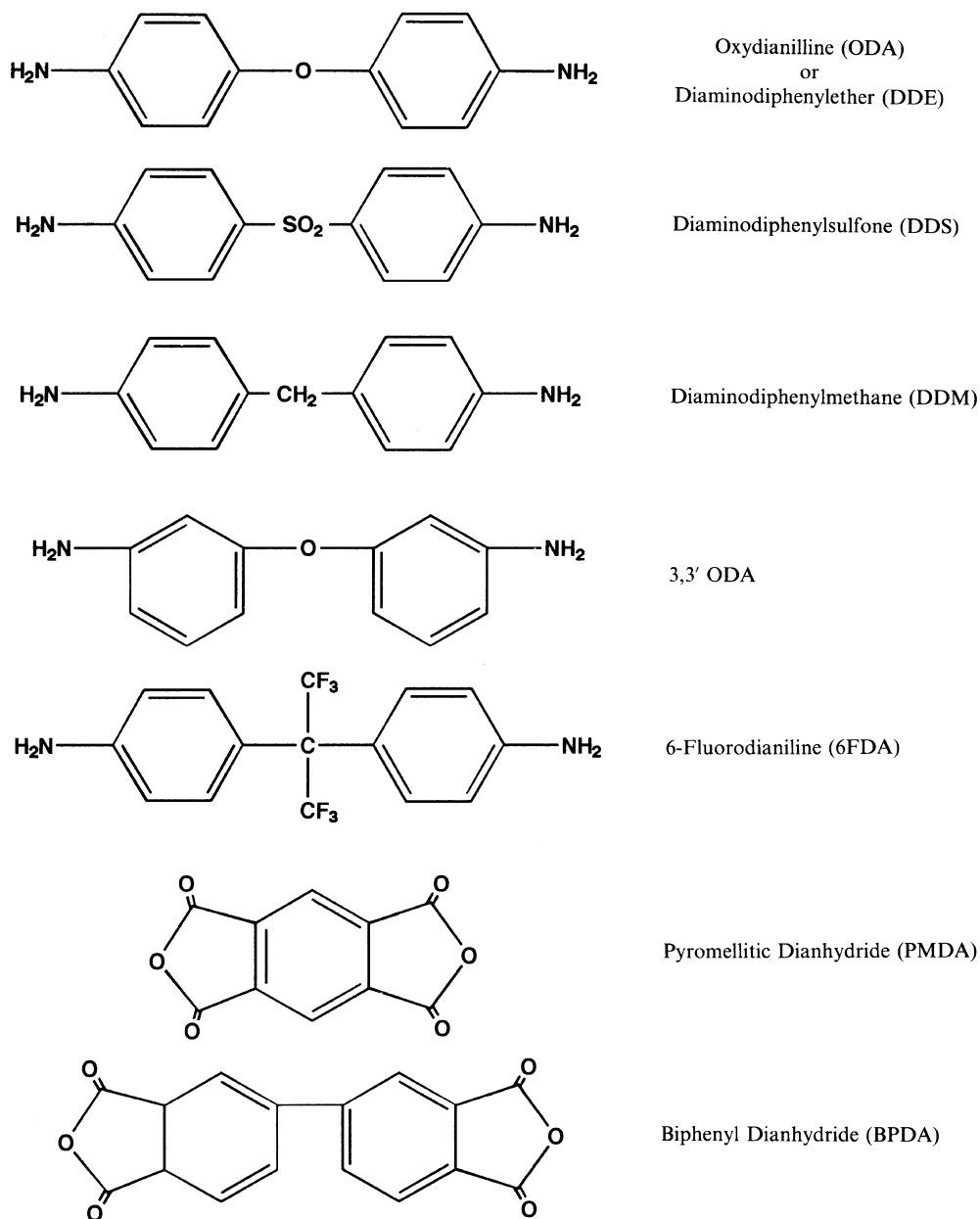


Figure 1. Structures and abbreviations of diamines and dianhydrides.

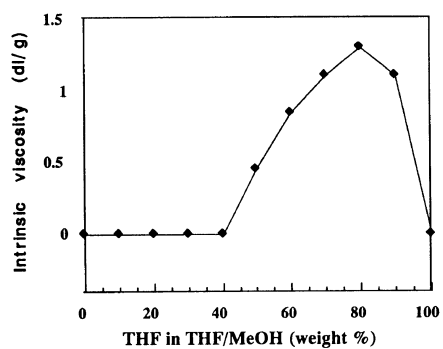


Figure 2. Inherent viscosity of ODA-PMDA polyamic acid versus THF content in THF/MeOH solution.

Table I. Reaction conditions and solution and polyamic acid precipitate appearance for various reactants

Diamine	Dianhydride	Reaction time/h	Inherent viscosity/ dL g ⁻¹	Solution/ppt. color
DDE	PMDA	6	1.41	Yellow/Yellow
DDM	PMDA	3	0.99	Gold/Golden
DDS	PMDA	6	1.10	Tan/Pale yellow
3,3'-ODA	PMDA	2	0.89	Gold/Yellow
6-FDA	PMDA	12	2.42	Clear/White
DDE	BPDA	6	0.94	Yellow/Yellow
DDS	BPDA	6	0.87	Pale brown/Tan
6-FDA	BPDA	3	1.46	Clear/White

in a solution containing dissolved dianhydride. The polymerization reaction could not be made to go forward in experiments wherein the order of addition of the components to the solution was dianhydride, diamine.

CONCLUSIONS

The use of THF/MeOH solutions for the synthesis of polyimides is feasible and makes it possible to obtain polyamic species of high molecular weight. The 80/20 wt% THF/MeOH solutions resulted in the production of high molecular weight polyamic acids. The polyimides formed from polyamic acids seemed identical to those obtained with more conventional aprotic solvents such as dimethylacetamide (DMAc) and *N*-methylpyrrolidone

(NMP).

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