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Improved Thermal Performance of Polyimides by Incorporation of Cardo and Trifluoromethyl Moieties

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Background

Advances in the modern technologies are focused on reducing the cost of demanding industrial processes by replacing metals/ceramics with plastics. In this respect, polyimides are the materials of interest, attributed to several beneficial properties like outstanding thermal stability, excellent mechanical strength, chemical/radiation resistance and low dielectric constant. They have broad spectrum of applications in aerospace, electronics and various other industries as matrices, foams and gas separation membranes [1-3]. Their properties are dependent upon the backbone structure, hence can be tailored/attuned to desired ones by modifying the structures of monomers used.

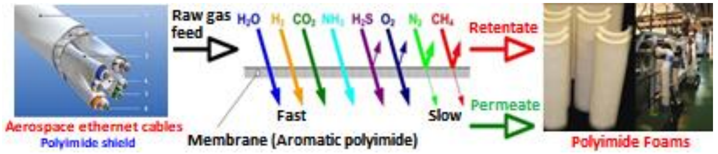


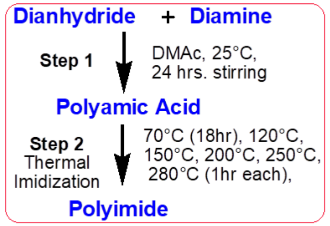
Figure 1: Applications of polyimides: aerospace, gas separation membranes, polyimide foams (NASA's commercial invention of 2007).

Objectives

The presented research describes the structure/property relationship of polyimides. The goal of the study was to monitor the effect of 9-fluorenylidene unit (cardo moiety) and trifluoromethyl (-CF_3) groups on the thermal performance of polyimides. It involves the thermal measurements (TGA, DMTA) to evaluate and compare distinct conditions relevant to application of polyimides with high thermal stability.

Experimental

Three different polyimides (BMDA, BHFA, B9FA) were synthesized from structurally related diamines (Figure 2) according to synthetic scheme shown below [4].



Scheme: Synthesis of Polyimides.

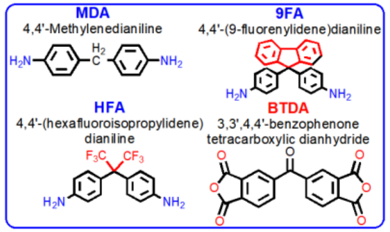


Figure 2: Structures of diamines & dianhydride.

Results and Discussion

The dynamic temperature scan of polyimides revealed that substitution of methylene hydrogens with 9-fluorenylidene unit (cardo moiety, B9FA) enhanced the temperature resistance of the resulting polyimide (Figure 3) as T_5 was increased from 540 to 565 °C (Table 1). The onset of thermal degradation was delayed by substitution of methylene hydrogen atoms with trifluoromethyl (-CF_3) groups. Isothermal TGA supported the findings of dynamic TGA since W_{35} was higher for BMDA in comparison with B9FA and BHFA (Figure 4). Both the groups increased the T_g of polyimides (Table 1).

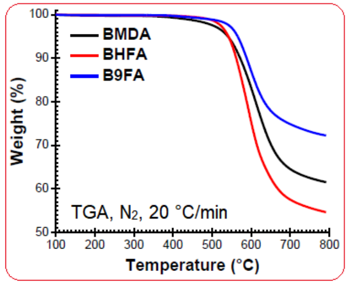


Figure 3: Dynamic TGA curves of polyimides.

Table 1: TGA and DMTA data of polyimides.

Polyimide	T_5 (°C)	T_{10} (°C)	R_{800} (%)	W_{35} (400 °C) (%)	W_{35} (450 °C) (%)	T_g (°C)
BMDA	540	572	62	2.56	4.93	293
BHFA	541	561	55	2.01	-	320
B9FA	565	588	72	3.06	4.09	395

T_5 = Temperature at 5% weight loss T_{10} = Temperature at 10% weight loss
R_{800} = Residual weight (%) at 800 °C W_{35} = Weight loss (%) after 35 minutes of experiment

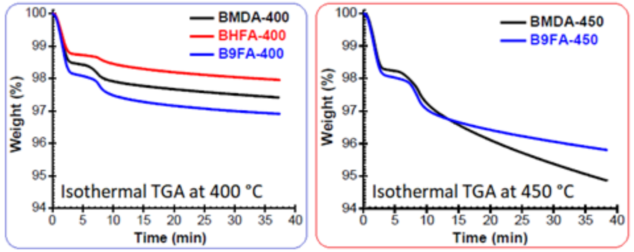


Figure 4: Isothermal TGA plots illustrating the effect of 9-fluorenylidene (B9FA) and trifluoromethyl (BHFA) moieties on the thermal endurance of polyimides.

Conclusions:

The synthesized polyimides displayed significant thermal stability as their degradation started after 400 °C. The thermal stability/endurance and glass transition temperatures of polyimides were considerably improved by incorporation of cardo and trifluoromethyl moieties as pendant groups within the polyimide chain. The developed polyimides have the potential for applications involving extended exposure at elevated temperatures (≈ 400 °C).

References:

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