

**Thermal and Environmental Stability of Polymeric Materials**  
**-New Generation, Novel Asymmetric Polyimides for Aerospace Materials-**

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For developing heat resistant and high performance polyimides, the relationships between the stereochemical imide structures and thermo-mechanical properties have been discussed. Addition type imide oligomers (TriA-PI) such as 2, 3, 3', 4'-biphenyltetracarboxylic dianhydride (a-BPDA), /oxydianiline (ODA)/4-phenylethynyl phthalic anhydride (PEPA) and/or other asymmetric monomers (fluorenylidene groups: BAFL, BAOFL) were synthesized and characterized. The cured oligoimides exhibited high thermal, mechanical properties in addition to the excellent melt fluidity and solubility, TriA-PI/carbon fiber composites were well consolidated for high temperature structural components. The heat sealable, thermoplastic thin films having high durability in space has been successfully developed by using asymmetric 2,3,3',4'-oxydiphthalic anhydride (a-ODPA) as well. Thin film of a-ODPA polyimide exhibited excellent high thermo-mechanical properties ( $T_g = 270^\circ\text{C}$ ) and heat sealing property with durability for irradiation of proton. It is shown that asymmetric aromatic imide structures without any weak linkages such as alkyl and methylene groups are powerful tools for a molecular design of high performance polymeric materials for solar sail membrane.

**Keywords:** Thermo plasticity, Asymmetric polyimide, Heat resistance, Solar sail, Primary structure

### 1, Introduction

Aromatic polyimides such as PMDA/ODA and BPDA/PDA have been widely used for aerospace applications due to their outstanding combinations of thermo-mechanical and space environmental stability [1-5]. However, these rigid and symmetric polyimides prefer to form order-structure because of geometrically planar, rod-like structures resulting in poor solubility and melt fluidity. Therefore, it is normally difficult to have thermo plasticity and to use as a molding or a matrix resin for carbon fiber reinforced composites [6]. Recently, the polyimides derived from asymmetric aromatic dianhydride such as BPDA and ODPA have been reported as novel high performance polymeric materials with unusual and attractive properties [7].

We have successfully reported at the Polycondensation 2004 in V.A. that the polyimides consisting of asymmetric BPDA dianhydrides (a-BPDA or I-BPDA) indicated not only high  $T_g$  but also amorphous processable polyimide resins due to bent and rotationally hindered structure of a,i-BPDA, resulting in high solubility in organic solvent and high melt fluidity [8]. A strong demand of improving high performance polymeric materials for spacecrafts is increases year after year [9-13]. So, this paper will describe a way of improving thermal, mechanical and space environmental properties by using asymmetric imide structures as follows: 1) Isomeric biphenyl (BPDA) polyimides. -Attractive characteristics of asymmetric aromatic polyimides-, 2) Novel heat resistant thermoset-polyimide resins (TriA-PI) and their graphite fiber composites, 3) Newly developed asymmetric thermoplastic polyimide films for solar sail membrane [14]

3/10/2008 Tsukuba

## Thermal and Environmental Stability of Polymeric Materials -New Generation, Novel Asymmetric Polyimides

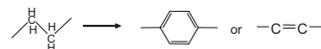
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### 1, Thermal Stability of Polymeric Materials

1) Physical view point: Max. service temperature :  $T_g$  ( $T_m$ )

Chemical structure : flexible to rigid



Disadvantages : Insoluble, difficultly on molding

2) Chemical view point: Polymer degradation : Bond dissociation (D)

C-C (83kcal/mol)  $\rightarrow$  C=C (145 kcal/mol)

C-H (99kcal/mol)  $\rightarrow$  C=C (123 kcal/mol)

3) Ablation and thermal insulation; evaporation of low molecules and carbonization---hetero-aromatic rings with ??

[5] Yokota R 1995 *Photosensitive Polyimides: Fundamentals and Applications* eds (Lancaster, PA: Technomic)

### Evaluation of thermal stability of polymers by TG

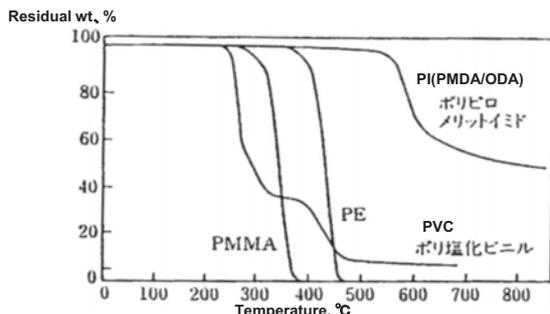


Figure 1. Thermal stabilities of various polymers in  $N_2$  flow by thermo-gravimetric measurement

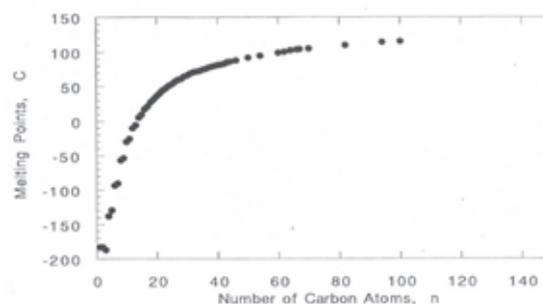


Figure 2 Melting temperature of normal alkanes vs  $-(CH_2)_n-$

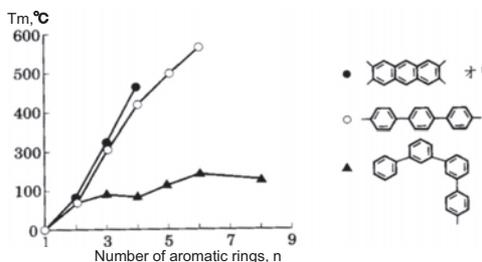


Figure 3 Melting temperature, vs number of aromatic rings, n

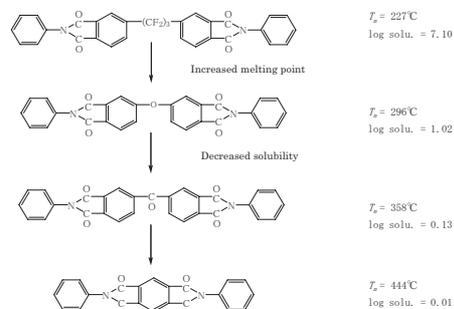


Figure 4. Relationships between chemical structure and  $T_m$ , solubility of aromatic imide model compounds (Dine hart et al)

Table 1 Commercially available polyimide and heteroaromatic polymers

Name	Structure	Film (μm)	Tg (°C)	Modulus (GPa)	Elong. (%)	Stability UV	Stability Red	Plasticity
APIOL AH (KAPTON)		~7.5	420	3.0	~50	○	○	X
UPILEX-S		~7.5	380	9.0	30	○	○	X
UPILEX-R		12.5	300	3.0	100	○	○	Δ
AURAM		25	250 (Tm: 380)	3.0	90	○	○	○
ULTEM		12.5	218	3.0	80			Δ ○
ZYLON (PBO)		Δ	?	(10.0)		Δ	○	X
ARAMIDA (ARAMID)		2.5	?	15.0	20	Δ	Δ	X

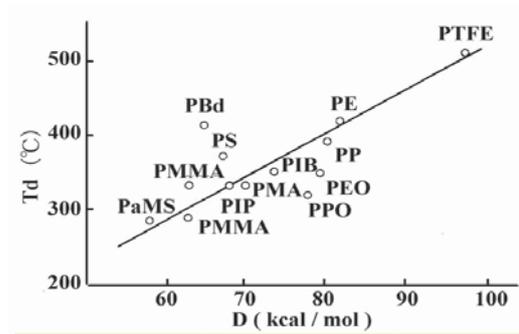


Figure 5. Thermal stability at 50% wt loss temperature vs the lowest bond dissociation energy, D in the polymers

Table 2. Important bond strength

Bond	Bond Strength (eV)
C-N	3.16
C-C	3.58 (82.7kcal mol <sup>-1</sup> )
C-O	3.70
C-H	4.24
C-F	5.02 (132.3kcal mol <sup>-1</sup> )
Al-O	5.30
P=O	5.63
C=C	6.24 (144.1kcal mol <sup>-1</sup> )
N=O	6.28
Zr-O	8.10
C=O	8.27
Si-O	8.30

Photon of λ = 200 nm corresponds to 143 kcal mol<sup>-1</sup> (λ = 500 nm : 57 kcal mol<sup>-1</sup> (1 eV = 23.1kcal))

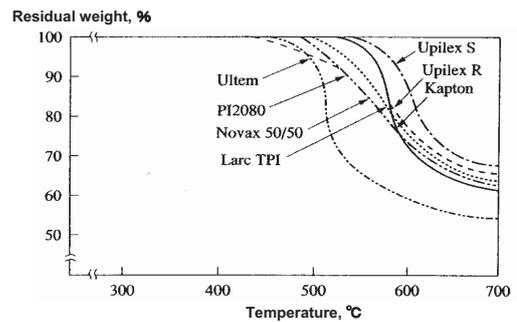


Figure 6. Thermal stability for commercially available aromatic polyimides in N<sub>2</sub> flow, ΔT = 5°C/min

Table 3. Chemical structures and Tgs of polyimides

Kapton		428
Novax		407
Upilex R		303
Upilex S		359
Larc TPI		256
PI2080		310
Aurum		250
Ultem		215

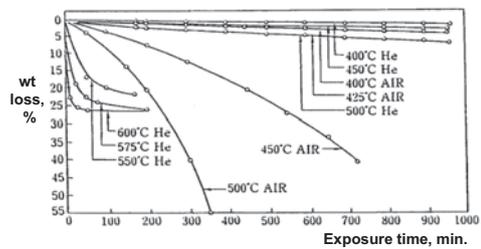


Figure 7. Isothermal thermal stability of KAPTON H  
C.E.Sroog et al, J.Polym.Part A,vol3. 1373(1965).Sci.,

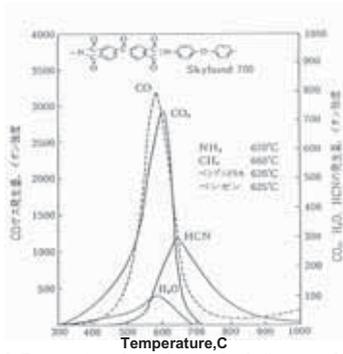
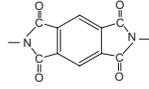


Figure 8. Temperature dependence of volatile gases for Skybond 700 polyimide

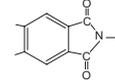
### Symmetric type Aromatic Polyimide

pyromellitimide



rigid and planar structure  
strong intermolecular interaction  
charge transfer complex,  
high-order structure

phthalimide



excellent thermal stability,  
low C.T.E  
Outstanding Environmental Stability  
Difficulty on Molding: need a flexible structure into diamine part  
Decrease Max. Service Temperature

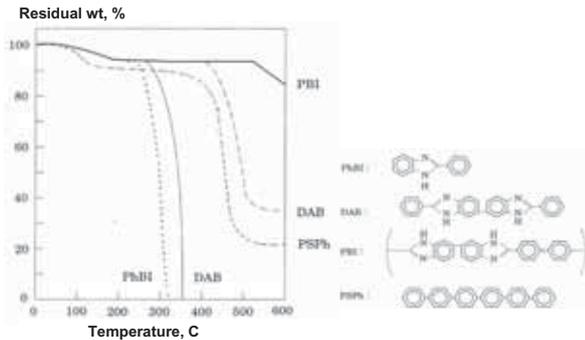


Figure 9. Tg curves of aromatic polybenzimidazole and their model compounds: — in vac, ---- in N<sub>2</sub> flow



1-2 Space Environmental Stabilities of Polymeric Materials

Table 4. Space environments-pressure, gases and radiation

Altitude (km)	Pressure (torr)	Thermo-dynamic temperature (K)	Gas concentration (No. of particle)	Composition	Ultraviolet radiation	Particle radiation (particles cm <sup>-2</sup> s <sup>-1</sup> )
Sea level	760	~300	2.6 × 10 <sup>19</sup>	78%N <sub>2</sub> , 21%O <sub>2</sub> , 1%Ar	Section of solar spectrum λ	—
80	10 <sup>-6</sup>	—	4 × 10 <sup>17</sup>	N <sub>2</sub> , O <sub>2</sub> , Ar	—	—
200	10 <sup>-8</sup>	~1200	10 <sup>16</sup>	N <sub>2</sub> , O <sub>2</sub> , O <sup>+</sup>	—	—
800	10 <sup>-9</sup>	~1300	10 <sup>8</sup>	O, He, O <sup>+</sup> , H	>0.3	10 <sup>10</sup> protons>85MeV
6,500	10 <sup>-12</sup>	—	10 <sup>5</sup>	H <sup>+</sup> , H, He <sup>+</sup>	Absorption zone	10 <sup>10</sup> electrons>40KeV
23,000	<10 <sup>-14</sup>	—	10 <sup>-10</sup>	86%H <sup>+</sup> , 14%He <sup>+</sup>	Full solar spectrum	10 <sup>10</sup> protons>5MeV
					Full solar spectrum	10 <sup>10</sup> electrons>40KeV
						10 <sup>10</sup> electrons>1.6MeV

Table 5. Variation of space environment with altitude

Categories	Distance from earth	Constituents
Low Earth Orbit (LEO)	up to 1,000 km	Atomic Oxygen, Meteoroids, Debris, Ultraviolet, Thermal Cycling
Mid Earth Orbit (MEO)	1,000-35,000 km	Van Allen Radiation, Meteoroids, Debris, Ultraviolet, Thermal Cycling
Geosynchronous Orbit (GEO)	> 35,000 km	Solar Flare Protons, Spacecraft Charging, Ultraviolet Thermal Cycling

Table 6. Space environments and the durability of polymeric materials

Space environment	Effects and factors	Changes of materials	Items
High vacuum	Vaporization of the additives and degradation volatiles	Contamination to the surfaces, decreasing transparency	Rubber and lubricant, grease
Micro-gravity	Diffusion and condensation	Contamination to the surfaces	
Thermal cycle	Thermal stress and C.T.E mismatching	Delamination and crack	Composites, adhesives
High and low temperatures	Thermal degradation	Brittleness	Films, adhesives and composites
Visible. & UV exposure	Absorption and degradation	Decreasing Mw and increasing coloration, Brittleness	Films, TML
Space radiations	Degradation	Decreasing Mw, crosslink and coloration, Brittleness	Films, TML, Solar cell
Atomic Oxygen	Oxidation and erosion	Decreasing thickness and coloration	All organic materials
Electrification	Static electricity	Electric discharge	Solar array, cables and spacecrafts

1.3 Photochemical reactions

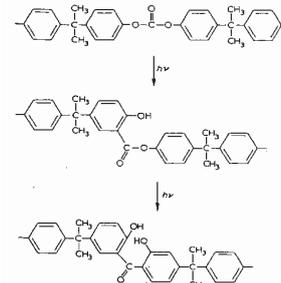
Most photochemical processes studied so far in polymers involve excited singlet or triplet states. In general, the distinction must be made between primary and secondary photochemical processes. In a primary process, the excited molecule dissociates into free radical fragments.



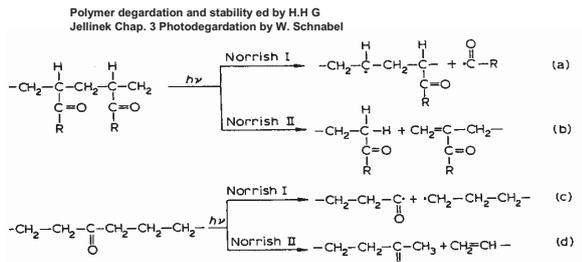
This will always happen if the excitation level reached is greater than the bond dissociation energy corresponding to this level or if the excited state is a repulsive one. Reaction (6) is supposed to occur very rapidly. A primary process according to reaction (6) was suggested to be responsible for the fragmentation of ketones during the Norrish type I process



Polymer degradation and stability, ed by H.H G Jellinek  
Chap. 3 Photodegradation by W. Schnabel

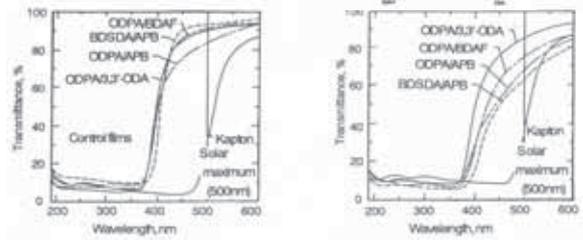


Scheme 4. Photo-Fries rearrangement of polycarbonate. Polymer degradation and stability ed by H.H G Jellinek Chap. 3 Photodegradation by W. Schnabel



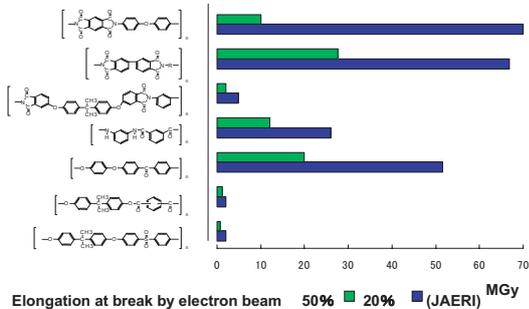
Scheme 2. Chemical reactions induced by light absorption of ketochron

Figure 10. UV - Vis spectra of polyimides :controlled and exposed (300 esh)



T.StClair et al, Sampe J, July/Aug, p28 1985

Figure 11. Space environmental stability of aromatic polymers



A STUDY ON POLYIMIDE MLJ OF THE TEN MONTHS FLOW SPACE FLYER UNIT

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Figure 12 Illustrated SFU





Figure 13 Discolored polyimide MLI surface of EPEX on SFU [5]

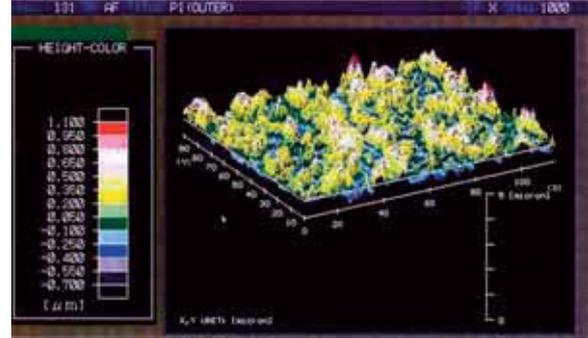


Figure 14. 3D SEM of retrieved polyimide MLI surface of EPEX on SFU

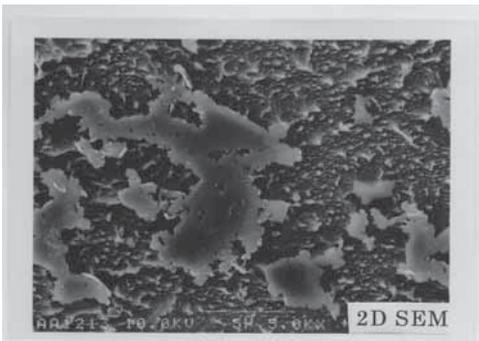
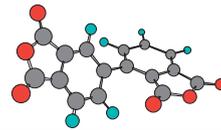
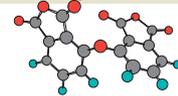


Figure 15. 2D SEM for the contaminated EPEX MLI surface retrieved



### 2-1) Asymmetric aromatic polyimides

We have reported at the Polycondensation 2004 in V.A. that the polyimides using asymmetric BPDA dianhydrides (a-BPDA or i-BPDA) are very attractive monomers for heat resistant polymeric materials. This is because asymmetric BPDA gives not only high T<sub>g</sub> but also amorphous PIs due to bent and rotationally hindered structure of a,i-BPDA, resulting in high melt fluidity.



### Why is polyimide almost the only heat resistant polymer films in industry ?

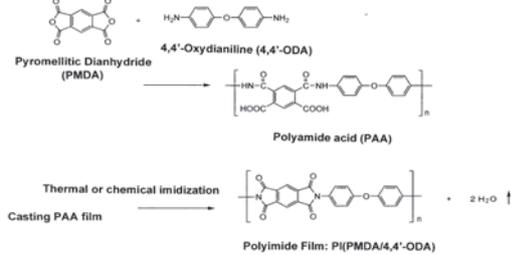
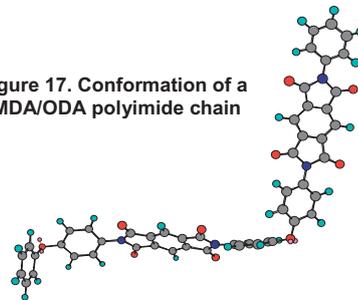


Figure 16 Process of Polyimide Film

PMDA/4,4'-ODA polyimide has been prepared by two step method through thermal imidization process of precursor PAA film

Figure 17. Conformation of a PMDA/ODA polyimide chain



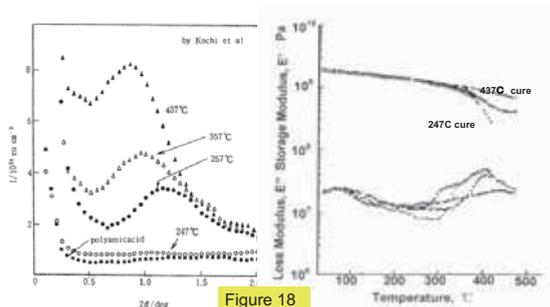
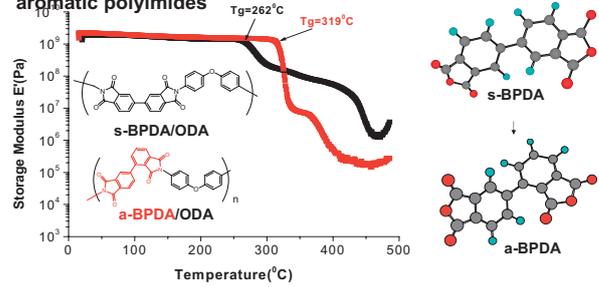


Figure 18

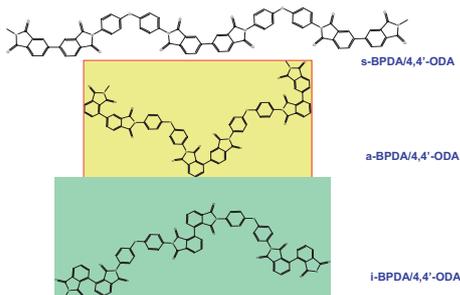
Ordered structures of PMDA/ODA are developed and thermal, mechanical properties of the films are extremely improved. [6]

Figure 19. Attractive characteristics of asymmetric aromatic polyimides



Highly bend a-BPDA/ODA, the Tg shifts to high temperature, and a large drop in E' at Tg indicates the possibility of processable polyimide with high Tg [8].

Figure 20. Conformation of Isomeric BPDA/4,4'-ODA polyimides



i-BPDA/4,4'-ODA needs the largest space for the segmental motion to a relaxation process, while s-BPDA needs the smallest space

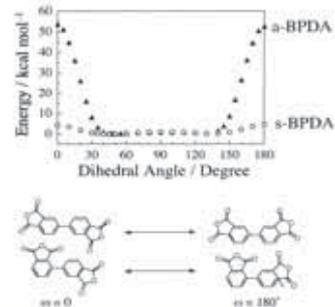


Figure 21. Rotational barrier estimated by semi-empirical M.O of s- & a-BPDA s-BPDA is very low rotational barrier, while free rotation in a-BPDA practically is inhibited due to steric hindrance between ortho-H & carbonyl group

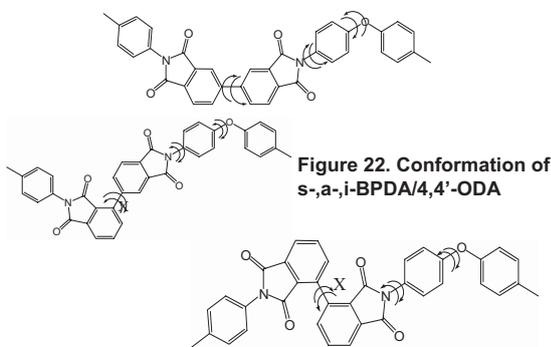


Figure 22. Conformation of s-, a-, i-BPDA/4,4'-ODA

The local rotation of the rigid segment composed of BPDA group and an adjacent diamine group were hindered

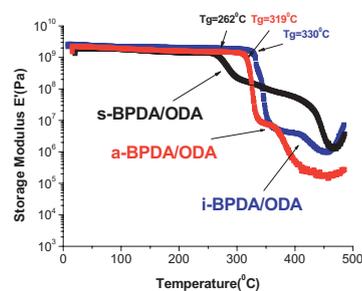


Figure 23. DMA curves of isomeric BPDA polyimides with 4,4'-ODA Tg moves towards high temperature with highly bend BPDA, suggesting the largest space for the segmental motion. The large drop in E' at Tg for a-, i-BPDA PIs provides much larger space in comparison with that of s-BPDA PI

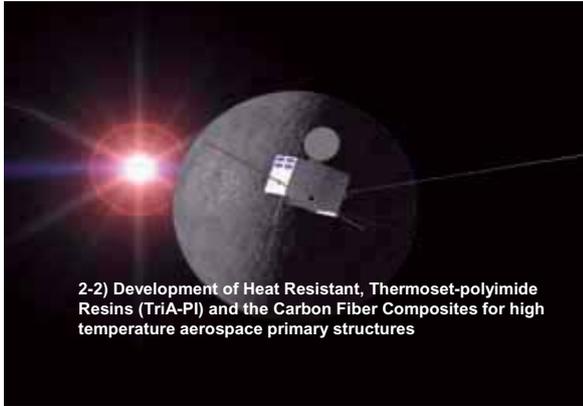
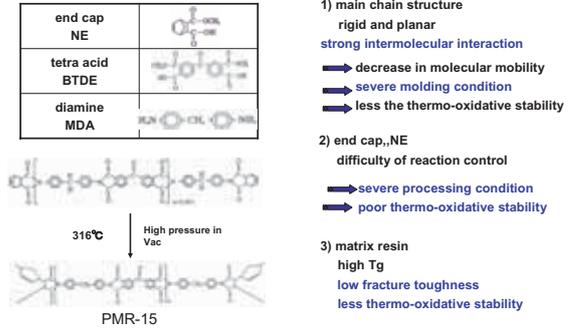


Figure 24. 1<sup>st</sup> Generation addition type polyimide resin:PMR-15 for heat resistant composites [9]



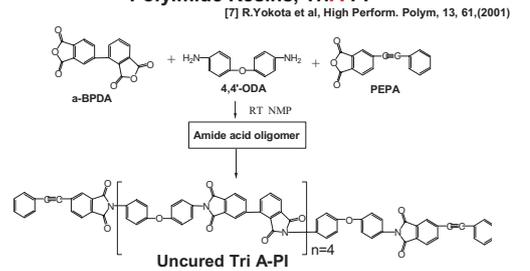
**Figure 25. 2<sup>nd</sup> Generation Polyimide Resin: PETI-5**  
NASA Langley Research Center  
P.M.Hergenrother et al. Polymer, 34, 630(1993)

PEPA s-BPDA/Ar PETI-5 85%:15%

Molecular weight (calc.), Mn	5000
Monomers	s-BPDA (3,3',4,4'- Biphenyl tetracarboxylic dianhydride) 3,4'- ODA (oxydiamiline) 1,3- APB (bis 3-aminophenoxy benzene) 4- PEPA (Phenylethynylphthalic anhydride)

Medium high temperature addition polyimide: Tg=270C(cured),  
Good processability, High fracture toughness,  
High oxidative stability(PEPA)

Figure 26. Asymmetric Aromatic Addition-type Polyimide Resins, TriA-PI



Cured TriA has high fracture toughness and good processability in addition to high Tg and high oxidation stability. We are developing the heat resistant fiber reinforced composites.

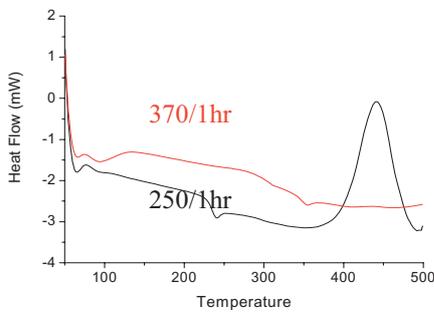
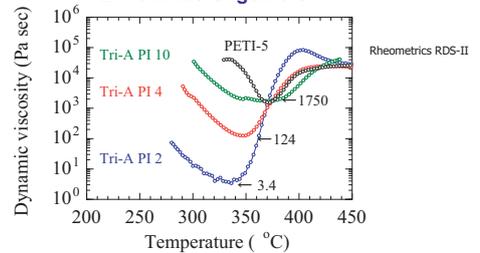


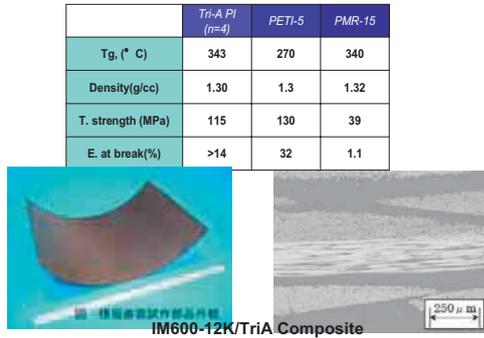
Figure 27. DSC curves of TriA-PI(n=4) resins with and without cured

Figure 28. Dynamic Melt Viscosities of the Tri-A PI and PETI-5 Imide Oligomers

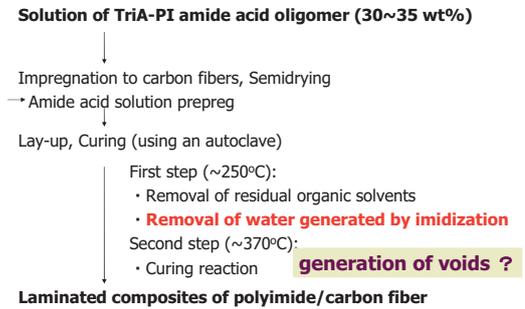


- The minimum viscosities were 3.4, 124, and 1750 Pa sec for Tri-A PI 2 (Mw~1600), Tri-A PI 4 (Mw~2500), and Tri-A PI 10 (Mw~5250), respectively
- This corresponded to the viscosities reported for PETI-5 (5.0, 90, and 1000 Pa sec for Mw~1250, ~2500, and ~5000).

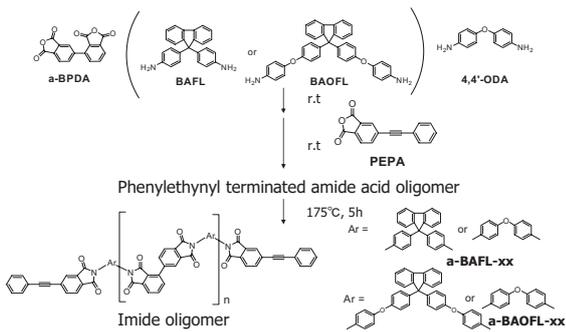
**Figure 29. Physical and mechanical properties of TriA-PI, PETI-5 and PMR-5 cured and the carbon fiber composite**



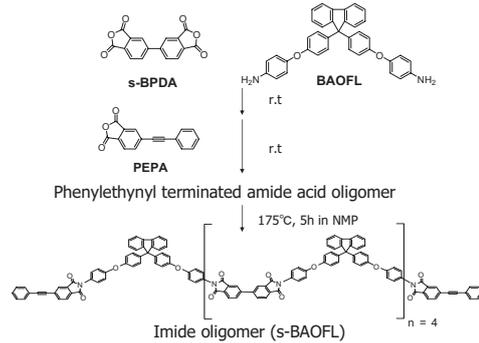
**Figure 30. Fabrication of TriA-PI/CF composites by routing from amide acid solution prepreg**



**Figure 31. Incorporation of additive fluorenylidene groups into TriA for improving solubility of the oligomers** (Y.Ishida, R.Yokota, T.Ogasawara, 7<sup>th</sup> China-Japan seminar on polyimides 2006, 9 in Tokyo)



**Figure 32. Synthesis of an additive imide oligomer with fluorenylidene groups: s-BPDA/BAOFL/PEPA**



**Figure 33. Properties of the imide oligomer and cured resins**

	Monomer			Solubility in NMP (wt %)	Processability	Min. melt viscosity <sup>a)</sup> (Pa s)
	s-BPDA (mmol)	BAOFL (mmol)	PEPA (mmol)			
s-BAOFL	4	5	2	33	good	326

a) Measured by a rheometer.

- Imide solution prepregs can be prepared
- Low minimum melt viscosity, good processability

**Properties of the cured resin film based on s-BPDA and BAOFL**<sup>a)</sup>

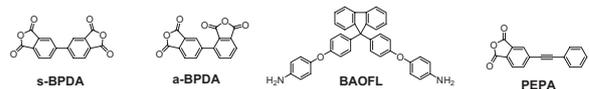
	T <sub>g</sub> (°C) <sup>b)</sup>	T <sub>5%</sub> (°C) <sup>c)</sup>	E (GPa) <sup>d)</sup>	σ <sub>b</sub> (MPa) <sup>e)</sup>	ε <sub>b</sub> (%) <sup>f)</sup>
s-BAOFL	321	551	2.79	110	10.2

a) Cured at 370°C for 1h. b) Determined by DSC at a heating rate of 10°C/min under argon. c) Determined by TGA at a heating rate of 10°C/min under argon. d) E: tensile modulus e) σ<sub>b</sub>: tensile strength f) ε<sub>b</sub>: elongation at break

**High thermal resistance, good mechanical properties**

**T<sub>g</sub> was 50 °C higher than that of PETI-5 (based on s-BPDA, T<sub>g</sub>=270 °C)**

**Figure 34. Comparison between dianhydride isomers : properties of imide oligomers**

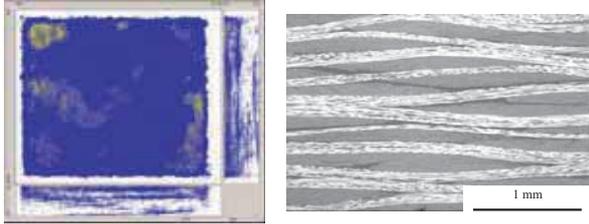


**Table. Properties of the imide oligomers containing fluorenylidene groups**

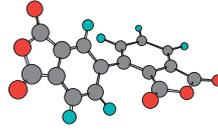
	Dianhydrides	Diamines BAOFL/4,4'-ODA	Solubility in NMP (wt %)	Processability	Min. melt viscosity <sup>a)</sup> (Pa s)
s-BAOFL-50	s-BPDA	50 / 50	partially soluble	good	1084
s-BAOFL-100	s-BPDA	100 / 0	33	good	326
a-BAOFL-50	a-BPDA	50 / 50	40	good	120
a-BAOFL-100	a-BPDA	100 / 0	40	good	167

a) Measured by a rheometer.

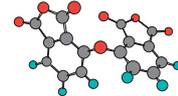
Figure 35. Evaluation of the polyimide/CF composite by ultrasonic inspection and optical micrograph



Good quality  
No voids and no clacks  
100 mm x 100 mm, plain woven fabric 12 ply



**Conclusions**  
Monomers of highly bent, asymmetric structures such as BPDAs, ODPAs, BOAFL etc are demonstrated as the key materials for new generation, high temperature composites with good processability and high temperature mechanical properties

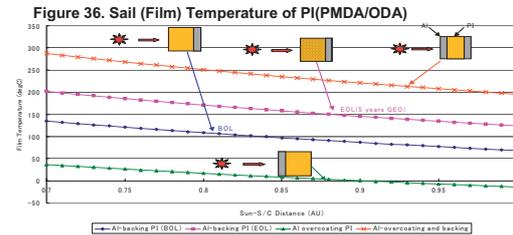


**What is a solar sail spacecraft ?**

Fridrikh Tsander proposed the concept of solar sail spacecraft obtained by reflecting sunlight off of a large, a very thin, metalized polymer film.

**What kinds of polymeric films can be used ?**

The key technologies for solar sail spacecraft are the sealing, fabricating, packaging, and deployment in addition to the development of thermally and space environmentally stable polymer film



**How can you fabricate a large solar sail**

Figure 37. Feasibility on various sealing methods of thin films for solar sail

Case 1. A high Tg polyimide film with a low Tg polymer on the surface layer for heat sealing  
Requirement : 1) Development of the coating technology and of the sealing machine for polyimide film. 2) Environmental stability (heat, radiation and UV)

Case 2. Thermo-plastic polyimide with relatively low Tg  
Requirement : 1) Evaluation of space environmental stability. 2) Sealing conditions such as temperature, pressure, time, etc.

Case 3. Sealing by using an adhesive tape  
Requirement : 1) Creep deformation of the adhesive layer, out gases, 2) Evaluation of space environmental stability



**Polyimide Solar Sail Deployment in Space by S-310-34 rocket 2004.8**  
Sail material and fabrication  
1. Sail film: Aluminized Apical AH polyimide 7.5 μ m, width 109cm  
2. Fabrication: PET based acrylic adhesive tape



Figure 38. S-310-34 sounding rocket at 2004.8

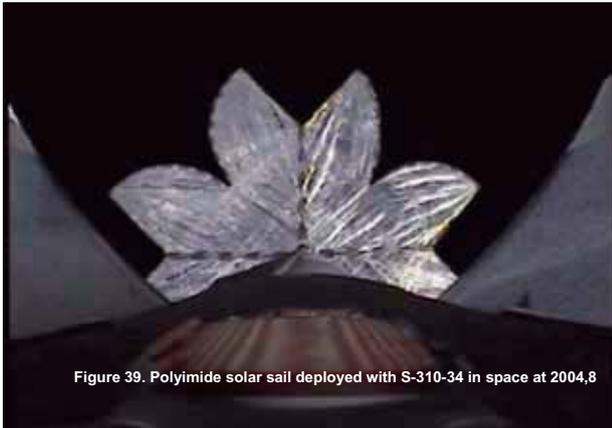
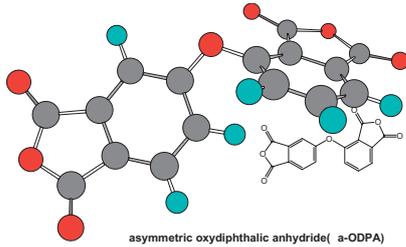


Figure 39. Polyimide solar sail deployed with S-310-34 in space at 2004,8

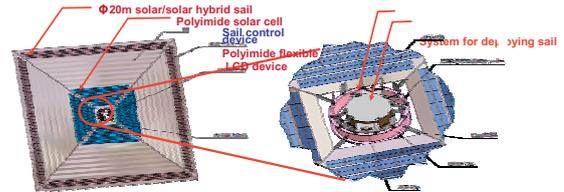


Figure 40. Polyimide solar sail deployed in space by S-310-34

**2-3) Newly developed asymmetric aromatic thermoplastic polyimide films for solar/solar cell hybrid sail spacecraft**



**Figure 41. Configuration of Solar/solar cell hybrid sail**



**Sail membrane and devices of hybrid sail**

- 1, Solar sail : ISAS/JAXA developed a-ODPA/ODA film (7 μ m) or Kaneka APICAL- AH 7.5 μ m
- 2, Polyimide thin solar cell film : Fuji FWAVE polyimide solar cell or ITFT(U.S.A) 25 μ m, 30cm(w)
- 3, Sail control device Polyimide flexible LCD device (Nihon Itagarasu )
- 4, Space debris counter PVDF film (Kureha)
- 5, Silicon adhesives : Toray/Dow (Silicone RTV4086)

**Developments of thermoplastic polyimide sail membrane**

- Goal
1. Heat sealing: 320 - 350 °C, 1min
  2. Solubility in DMAc or NMP 30 % <
  3. Space environment; proton 10kGy (1 year) radiation: 10~20MGy
  4. Thermal stability: Tg = 280 °C
  5. Film ( t ) 5~7 μ m, ( w ) 100cm width
  6. Mechanical properties σ b 100~200MPa modulus (E) 1~3GPa elongation at break, 50-80%

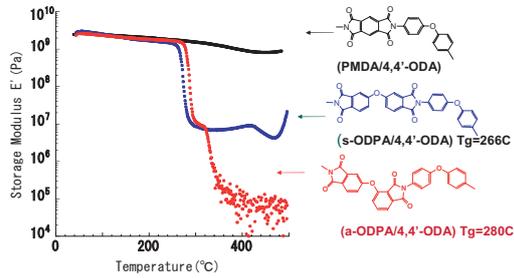
**Figure 42, Chemical structure of X linkage vs Tg for PMDA and BPDA**

略号	ポリイミド単位構造	Xの化学構造とTg (°C)				
		-C-	-CF-	-CH-	-S-	-S-
PMDA		271	248	247	233	217
BPDA		242	230	220	210	206

**Figure 43, Commercially available thermoplastic polyimides**

Larc TPI		256
PI2080		310
Aurum		250
Ultem		215

Figure 44, Chemical structure/molecular mobility relationship



Asymmetric PI(a-ODPA/4,4'-ODA) polyimide exhibits an high Tg and very large drop in E' at Tg, indicating amorphous and low melt viscosity (thermo-plasticity).

Figure 45, Space environmental stability of aromatic polymers

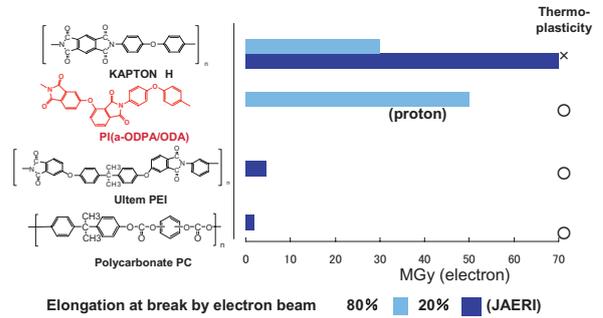


Figure 46, Summary of physical properties of ISAS Polyimides

Polyimide	[η]	Tg	Elongation at break	Solubility in NMP	Heat sealing
	(dl/g)	(°C)	(%)	(%)	
PI(a-ODPA/1,3,4-APB)	1.0	214	60	>20	Good
PI(a-ODPA/4,4'-ODA) (ISAS laboratory)	0.84	264	28	>20	Good
PI(a-ODPA/4,4'-ODA) (Fujimori Co.)	0.62	265	75	>20	Good

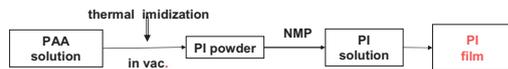


Figure 47, Development of Asymmetric ODPA thermoplastic polyimide sail membrane in ISAS

- Results (March 10, 2008)
- Heat sealing: 320 - 350 °C, 1min
  - Solubility in DMAc or NMP 30 % <
  - Space environment; proton 50MGy
  - Thermal stability: Tg = 280 °C
  - Film fabrication (t) 5~7 μm, (w) 100cm width
  - Mechanical properties σ b 100~200MPa  
modulus (E) 1~3GPa  
elongation at break, 50-80%

## Conclusion

Monomers of the highly bent, asymmetric structures such as BPDAs, ODPAs, BOAFL etc were demonstrated as the powerful tools for improving new generation, high temperature composites with good processability, thermo-mechanical properties, and high aerospace environmental durability. The heat sealable, thermoplastic thin films having high durability in space has been successfully developed by using asymmetric aromatic a-ODPA imide structures as a solar sail membrane. It is concluded that asymmetric aromatic imide structures without any weak linkages such as alkyl and methylene groups are very powerful tools for molecular design of high performance polyimides. The excellent properties exhibited of the asymmetric polyimides demonstrated a high potential for future aerospace applications.

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