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Introduction

Polyimide insulated electrical wire has been widely used in the aerospace industry in commercial, military, and to a lesser degree, general aviation aircraft since the early 1970's. The insulation offers benefits in terms of compact physical size, very good high and low temperature characteristics, and good electrical properties. It was selected for wiring in the Space Shuttle systems primarily because of its high strength, low weight and low flammability.

Wiring failures linked to insulation damage have drawn much attention in the media and concerns have developed regarding the long term stability and safety of polyimide insulated electrical wire. The mechanical durability and chemical stability of polyimide insulated wire are affected by hydrolysis, notch propagation, wet and dry arc tracking, topcoat flaking and degradation due to high pH fluids.[1-3][a] Prolonged exposure to water or aqueous fluids can cause hydrolysis of polyimide insulation leading to degradation and subsequent loss of strength. Polyimide insulated electrical wire is routinely exposed to high humidity, alkaline cleaners, and paint removers while under mechanical stresses, due to the nature of the wiring and its installation in aircraft. These conditions, commonly encountered during aircraft maintenance and operation, can cause degradation of the polyimide insulation, and result in

electrical failure (short circuit), commonly referred to as carbon arc tracking. The heat from electrical current passing through the conductor in the degraded material can lead to more insulation degradation and can propagate the arc to additional wiring. The presence of moisture can also accelerate the arc (wet arc tracking). In some cases, carbon arc tracking and subsequent electrical fires have been reported.[4]b Although the cause is usually attributed to mechanical damage due to poor wiring installation or abuse, the actual phenomenon leading to the damage has not been satisfactorily explained.

In this study, several polyimides have been selected for evaluation for resistance to degradation by various aqueous alkaline solutions. The polyimides under evaluation include commercially available films such as KAPTON®, APICAL®, LaRC-TPI, and UPILEX®R and S, as well as a number of experimental films prepared at NASA Langley Research Center. Material properties under study include glass transition temperature (T_g), dielectric constant, viscosity, solubility, moisture absorption and mechanical properties before and after exposure to alkaline solutions. The films were exposed in unstressed configurations and stressed configuration data is still being collected. The effect of the exposure condition on the properties of the various polyimides is discussed herein.

[b] Campbell, Frank J., Naval Research Lab, Washington, D.C., 20375-5000, unpublished results.

Experimental

Commercially available films used in this study are listed below.

<u>Commercial Films</u>*

Material	Manufacturer
KAPTON® 200HN	DuPont, Centerville, OH
UPILEX®R	UBE Industries, LTD, Japan
UPILEX®S	UBE Industries, LTD, Japan
APICAL® 300AV	Allied Signal, Des Plaines, IL
LaRC-TPI	Mitsui Toatsu Chemicals, Tokyo, Japan

* Use of trade names or manufactures does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

The dianhydride and diamines used to make the experimental films for the study follow.

Starting Materials

Material	Acronym	Source	Purification
4,4'-Isophthaloyl diphthalic anhydride	IDPA*	NASA-LaRC[5]	Vacuum dried at 125°C
4,4'-Oxydiphthalic anhydride	ODPA	Occidental Chemical Corporation	Sublimed at 200-210°C
Hydroquinone diether anhydride	HQDEA	Occidental Chemical Corporation	Used as received
2,2-Bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride	6F	Hoechst Celanese (American Hoechst Corporation)	Used as received
Pyromellitic dianhydride	PMDA	Allco Chemical Corporation	Used as received
3,3',4,4'-Benzophenone tetracarboxylic dianhydride	BTDA	Allco Chemical Corporation	Sublimed at 200-210°C
3,3',4,4'-Biphenyl tetracarboxylic dianhydride	BPDA	Mitsubishi International Corporation	Used as received
1,3-Phenylenediamine	m-PDA	Fluka AG	Used as received
1,4-Phenylenediamine	p-PDA	Fluka AG	Recrystallized from ethanol and sublimed at 120°C
3,4'-Oxydianiline	ODA	Kennedy and Klim, Inc.	Used as received
4,4'-Oxydianiline	ODA	Kennedy and Klim, Inc.	Used as received
3,5-Diaminobenzotrifluoride	DABTF	NASA-LaRC[6]	
2,2-Bis[4-(4-aminophenoxy) phenyl]hexafluoropropane	BDAF	Tokyo Research Center	Recrystallized from dichloromethane and hexane
1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene	BABB	DayChem Laboratories, Inc.	Recrystallized from toluene

* Allco Chemical Corporation is presently developing a commercial procedure for the preparation of 4,4'-isophathaloyl-diphthalic acid to its anhydride, IDPA.

Polymer Synthesis

The polyamide acids were prepared at a concentration of 20% solids (wt/wt) by the slow addition of a stoichiometric amount of the dianhydride to a magnetically stirred solution of the diamine in N,N-dimethylacetamide (DMAc) at room temperature. Polymerized solutions were stirred overnight and inherent viscosities (η_{inh}) at 0.5% concentration in DMAc were subsequently determined at 25°C. The polyamide acid solutions were centrifuged, cast onto a soda-lime glass plate using a doctor blade set at 0.058 cm (23 mils) and dried to a tack-free form in a low humidity, dust free chamber. The films on glass were then thermally converted to the polyimide by heating in a forced air oven at 100°C, 200°C, and 350°C for 1 hr at each temperature. Cooled films were removed from the glass plates by immersion in warm water.

Characterization

Glass Transition Temperature (T_g)

Glass transition temperatures (T_g), determined by Differential Scanning Calorimetry (DSC) were obtained on a DuPont 990 Thermal Analyzer in conjunction with a Model 910 Differential Scanning Calorimeter. Polyimides were heated to 400°C at 20°C/minute, quenched, and rerun to obtain the T_g. The T_gs were obtained from the second heating at the midpoint of the ΔT versus temperature curve.

Dielectric Constant

Dielectric constants were obtained from various sources including literature values. Direct comparison should not be made since the instruments and methods by which the values were determined were not consistent for each polyimide.

Viscosity Measurements

A sample of polyimide film was cut into fine pieces using a Wiley Laboratory mill equipped with a 40 mesh stainless steel screen. The 0.0500g. sample was weighed directly into an Erlenmyer flask and 10ml of 98% sulfuric acid (H_2SO_4) was pipeted to give a concentration of 0.5 g/dL. Agitation was accomplished by a magnetic stir bar. The resulting solution was filtered through glass wool in a gravity funnel into a clean, dry Cannon viscometer. Viscosities were run at 25°C using a water bath.

Moisture Absorption

Moisture absorption was determined by weighing a clean, dry 7.62 x 12.7 cm (3 x 5 inch) piece of film and placing it in a drying oven overnight at 100°C. The film was removed, reweighed, and submersed in water for 31 days. After immersion, the film was blotted dry and weighed again. Moisture pick-up was determined by the amount of weight gained.

Tensile Properties of Thin Films

A Model 2000/2 table-top SINTECH load frame, equipped with a CompuAdd Model 286 computer and HP graphics plotter, was used for measuring tensile properties. Pneumatically actuated, one inch grips with steel faces were used for clamping the polyimide films. All mechanical properties measurements were performed at room temperature.

The tensile specimens were 0.508 cm ± 0.003 cm (0.200 in ± 0.001 in) wide and varied in length with a minimum of 10.16 cm ± 0.64 cm (4.00 in ± 0.25 in). At least 5.08 cm (2.00 in) beyond the gage length was required for clamping purposes. Each specimen thickness was determined to within 0.00013 cm (0.00005 in) with a Testing Machines, Inc. Model 549M electronic micrometer. Thickness measurements were made at every 2.54 cm (1.0 in) mark over the specimen length and the average was used for the calculations. Film thickness for experimental films was approximately

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0.005 cm (0.002 in) and commercial films of the same thickness were obtained where available.

Film strips were cut to 0.508 cm width using a machined device that holds a series of razor blades at 0.508 cm intervals and is pulled on top of guide rests over the polyimide film as shown in Figure 1. A minimum of five samples was used for each condition. A crosshead speed of 0.508 cm/min was used for determination of elastic modulus, tensile strength and elongation at break.

A baseline for unexposed films was established for each of the three configurations chosen. Normal configurations were placed in solvents, flat and horizontal to each other. Rolled configurations were around a constant diameter object and secured by a polyethylene paper clip. Figure 2 illustrates the normal and rolled configurations. Figure 3 displays the machined clamping device, fabricated from 300 series stainless steel, used for the twisted configuration. The number of twists imposed on each specimen was constant (4 twists/specimen).

Retention of mechanical properties for the rolled and twisted configurations are presently being determined and will be reported when the data is more complete. The tensile specimens used in this study were smaller in size than recommended in ASTM Standard D882 but this standard was used as a guide. The ratio of length to width was 10:1. A data base using 0.508 cm width of KAPTON® and ULTEM® compared to full sizes clearly indicated that for measurements of changes in tensile properties, that data for small specimens was acceptable.[7]

The following basic solutions were made for the chemical exposure portion of the study: 1M ammonium hydroxide (7% vol/vol, pH = 11), 1M sodium carbonate (11% wt/wt, pH = 12), 0.5M trisodium phosphate (19% wt/wt, pH = 13) and 1M sodium hydroxide (4% wt/wt, pH = 14).

Films were immersed for 48 hours. After exposure, the specimens were removed, washed with large quantities of tap water and rinsed with distilled water. They were blotted dry and placed in a desiccator overnight. There was a minimum of 16 hours and a maximum of seven days between removal from the basic solution and tensile property measurements.

Results and Discussion

To date, there is no final document that specifies performance requirements for wire insulation. Presently, much work is being done to write and review the aerospace standard AS 4372. The preliminary standard includes 18 requirements for the design engineer to include in the evaluation for new wire construction and more than 25 properties that require test values be measured and recorded but do not establish a minimum performance level.[8] This evaluation addresses some items listed in the preliminary standard and will be discussed herein. The intent of this evaluation is not to promote or denote any particular commercial or experimental polyimide but to compare some important points of technical interest.

Physical Properties

Shown in Figures 4a-4c are the structures of the polyimides used in this investigation. Inherent viscosities for the polyamide acid solutions ranged from 0.51 dL/g to 1.60 dL/g and are listed in Table I. Films of the polyimide varied in color from nearly transparent to light orange-brown after heating to 350°C, where films appeared to be fully imidized. All films were clear except LaRC-CPI, which was translucent and exhibited some degree of crystallinity.

Most of the polyimides (Table I) were amorphous with T_gs from 222°C to greater than 500°C. The introduction of flexible linkages, such as oxygen, into a macromolecule increases the number of degrees of freedom available and tends to lower the T_g of the polymer.[9] Two systems exhibiting low T_gs are the LaRC-CPI system, T_g 222°C, which contained oxygen and carbonyl linkages in the backbone and the HQDEA/4-BDAF system, T_g 227°C, which contained several oxygen linkages that reduced rigidity in the molecule.

Polyimides are used widely in electronic applications because they have low dielectric constants. Variations in the backbone structure, such as the introduction of fluorine atoms, tend to afford better insulative properties, substantially improve thermo-oxidative stability, minimize

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moisture pick-up, and lower chain-chain interactions.[10] Two systems that exhibited dielectric constants below 2.6 were 6F/3,5-DABTF and HQDEA/4-BDAF[6, 11] as illustrated in Table I. Both contained fluorine atoms in the backbone.

Viscosities and solubilities for the polyimide films are listed in Table II. The time for dissolution varied from six hours to polyimides insoluble after four days. KAPTON® dissolved in concentrated sulfuric acid in less than six hours. A correction factor must be added to the viscosity determination if the viscosity is not performed within six hours because degradation occurs after this time period.[12] KAPTON® was the only polyimide that dissolved in sulfuric acid in less than six hours. A few systems dissolved in less than 48 hours, ODPA/3,4'-ODA, 6F/3,5-DABTF, and PMDA/3,4'-ODA, but most systems were only slightly soluble or insoluble. Solubility aids in processability in many cases but resistance to solvents is also a quality often desired in a polyimide. LaRC-CPI is insoluble in DMAc, m-cresol, sulfuric acid, hydraulic fluid and jet fuel.[13]

Moisture Absorption

Figure 5 compares moisture absorption in the polyimide systems. Although there is no standard for moisture absorption in aromatic polyimides, less than 2% absorption is certainly desirable. Several systems that showed moisture absorption at approximately 1% or less include LaRC-CPI, LaRC-TPI, UPILEX®R, 6F/3,5-DABTF, and HQDEA/4-BDAF. Crystallinity or contiguity may contribute to low moisture absorption in LaRC-CPI and UPILEX®R while the 6F/3,5-DABTF and HQDEA/4-BDAF systems contain fluorine atoms in the backbone which tend to impart low moisture pick-up. The tendency for polyimides to absorb moisture impacts their electrical performance and processability.[14] Many PMDA/ODA polyimides including KAPTON® and APICAL® exhibited high moisture absorption.

Resistance to Aqueous Alkaline Solutions

An important performance standard for polyimides used as wire and cable insulation is resistance to chemicals. Several reports have been published stating concerns that certain polyimides are known to deteriorate because of hydrolytic action. [1-3, 15-16]acd The high pH of aircraft cleaning solutions accelerates the hydrolysis. The polyimides in this evaluation were subjected to various high pH solutions and their retention of mechanical properties, tensile strength, elongation and tensile modulus are listed in Tables III-VII. The chemical structure of the dianhydride and diamine, strength of the imide links, incomplete imidization after curing, morphology, and water absorption are several factors that can affect hydrolysis.[e]

Caustic solutions were selected because they accelerate hydrolysis, are found in cleaning agents used to maintain aircraft and they varied in basicity (pH ranges from 11-14). Nominal changes in thickness before and after exposure were recorded to identify those polyimides that swelled during exposure. The thickness of the PMDA/4,4'-ODA system increased in all solutions. A 56% increase was caused by exposure to sodium hydroxide and a smaller increase in the other less basic aqueous solutions. A 40% increase was seen in the ODPA/p-PDA system for all solvents. Other systems showed only a small increase.

Figures 6-8 compare tensile strength, tensile modulus and elongation for unexposed films. Figure 6 shows several systems exhibiting outstanding tensile strength values, ODPA/p-PDA at 38,372 psi and both grades of commercial UPILEX® over 40,000 psi. The laboratory film

[c]   Campbell, F. J., United States Government Memorandum, Naval Research Laboratory, unpublished results.

[d]   "Airframe Wire Evaluation - Resistance to Heat and Aircraft Surface Cleaners," Naval Air Development Center Report (1978), unpublished results.

[e]   Kreuz, J. A., E. I. DuPont de Nemours and Company, Electronics Department, Circleville, Ohio, unpublished results.

PMDA/4,4'-ODA and its manufactured versions, KAPTON® and APICAL®, had excellent tensile strengths greater than 28,000 psi. In the tensile modulus comparison, the ODPA/p-PDA and UPILEX®S systems exhibited higher modulus than the other polyimides tested (Figure 7). UPILEX®S has experienced some level of orientation during manufacture; the ODPA/p-PDA has not. Those systems having elongation greater than 50% include HQDEA/4-BDAF, PMDA/4,4'-ODA, KAPTON®, APICAL® and UPILEX®R as illustrated in Figure 8.

Three systems, LaRC-ITPI, LaRC-TPI and LaRC-CPI, are compared in Figure 9 and Table III. LaRC-CPI, a semi-crystalline material, retained greater than 90% of its initial mechanical properties in all cases but one. The crystalline regions in LaRC-CPI polyimide apparently protect the polymer from chemical and solvent attack.[13] Decrease in elongation generally indicates a measure of chain degradation. These three systems retained 100% of their original elongation in all cases but one; the LaRC-ITPI in ammonium hydroxide (80% retention).

The systems containing fluorine in the backbone are listed in Table IV. Retention of mechanical properties ranged from 64-100%. Each system showed similar losses of properties. A graphic comparison of these systems is shown in Figure 10.

Table V compares resistance of the ODPA and PMDA based polyimides. Figures 11-13 compare the ODPA/3,4'-ODA, PMDA/3,4'-ODA, and ODPA/p-PDA systems. ODPA/3,4'-ODA showed good retention of all properties while the PMDA/3,4'-ODA system exhibited a substantial decrease in properties especially after exposure to ammonium hydroxide and sodium hydroxide. ODPA/p-PDA retained an average of 75% of its mechanical properties after various exposures. Work done by Mundhenke[17] et al. showed ODPA based polyimides have excellent dielectric properties, low moisture regain, good resistance to acid, bases, organic solvents, boiling water, thermal durability and excellent mechanical properties. Figure 13 shows the higher tensile strength values exhibited by the ODPA system using p-PDA as opposed to 3,4'-ODA. Figure 14 compares IDPA/m-PDA (LaRC-ITPI) with ODPA/p-PDA.

Table VI lists compounds nearly identical in structure but with differences in manufacturing. PMDA/4,4'-ODA is a laboratory version of KAPTON® and APICAL®. APICAL® is believed to be of the same

chemical structure as DuPont's KAPTON®. All systems exhibited similar degradation in aqueous ammonium hydroxide and sodium hydroxide. Degradation is evidently connected with hydrolysis of the imide moiety. Therfore, resistance to hydrolysis seems to depend strongly on the chemical structure of the dianhydride component of the polymer. PMDA based polymers appear to be least resistant to hydrolysis of polyimides.[18] The comparison of the ODPA and PMDA based polyimides in Figure 13 seems to verify this hypothesis. Graphic comparison of the three PMDA systems is shown in Figure 15.

UPILEX®R and S showed outstanding properties before and after exposure. UPILEX®R had a tensile strength of 30,404 psi, modulus of 583,074 psi, and elongation of 70% after immersion in aqueous sodium hydroxide for 48 hours. Although UPILEX®R retained approximately 75% of its properties after exposure to the most basic solution, it still maintained excellent mechanical properties, see Table VII. UPILEX®S maintained greater than 80% of its properties after exposure, with its lowest tensile strength at 51,581 psi, modulus of 1,240,825 psi and elongation of 17%. In Figure 16, the y-axis is the same as the other figures previously listed to graphically demonstrate the magnitude of the tensile strengths of UPILEX®R and S. Figure 17 shows the actual values of the films.

Conclusions

In this study, several polyimides were selected for evaluation for resistance to degradation by various aqueous alkaline solutions. Material properties studied included glass transition temperature (T_g), dielectric constant, viscosity, solubility, moisture absorption and mechanical properties before and after exposure to alkaline solutions.

Several polyimides exhibited attractive properties. The HQDEA/4-BDAF system had low moisture absorption, a low dielectric constant, and elongation greater than 50%. The LaRC-CPI system had low moisture absorption, good mechanical properties and excellent resistance to

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solvents and basic solutions. The 6F/3,5-DABTF system exhibited low moisture absorption and a low dielectric constant. The ODPA/p-PDA, UPILEX®R and S systems possessed high tensile strength and modulus prior to exposure and maintained high values after exposure to strong bases. The ODPA/3,4'-ODA and BPDA/3,5-DABTF systems exhibited excellent resistance to strong bases. All of the PMDA-based polyimides, which includes KAPTON® and APICAL®, exhibited relatively poor resistance to alkaline solutions.

Acknowledgements

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Table I - Physical Properties of Polyimides

Polyimide Film	Polyamide acid Inherent Viscosity, dL/g	Tg, °C		Dielectric Constant
LaRC-ITPI	0.51	259		3.29*
LaRC-CPI	1.38	222	(Tm = 350)	3.10
LaRC-TPI (comm.)	--	250		3.30
6F/3,5-DABTF	0.58	297		2.58
BPDA/3,5-DABTF	0.96	329		3.02
HQDEA/4-BDAF	0.68	227		2.56
ODPA/3,4'-ODA	1.60	245		3.06
PMDA/3,4'-ODA	0.70	>325		3.18
ODPA/p-PDA	0.81	none	(crystalline)	--
PMDA/4,4'-ODA	0.86	297		--
KAPTON®	--	(400)		3.20
APICAL®	--	(400)		3.00
UPILEX R®	--	285		3.50
UPILEX S®	--	>500		3.50

* Calculated value of dielectric constant provided by J. R. Pratt, Amoco, Atlanta, GA.

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Table II - Viscosity and Solubility of Polyimide Film in Concentrated Sulfuric Acid

Polyimide Film	Viscosity	Dissolution Time, hr	Solubility*
LaRC-ITPI	- -	80	S S
LaRC-CPI	- -	120	I
LaRC-TPI (comm.)	- -	64	S S
6F/3,5-DABTF	0.23	24	S
BPDA/3,5-DABTF	- -	64	S
HQDEA/4-BDAF	- -	88	I
ODPA/3,4'-ODA	0.15	48	S
PMDA/3,4'-ODA	0.16	48	S
ODPA/p-PDA	- -	88	S S
PMDA/4,4'-ODA	- -	80	S S
KAPTON®	1.15	6	S
APICAL®	- -	- -	- -
UPILEX R®	- -	64	S
UPILEX S®	- -	64	I

*S = Soluble

SS = Slightly Soluble

I = Insoluble

Table III - Resistance of LaRC-ITPI, LaRC-CPI and LaRC-TPI to Aqueous Alkaline Solutions

Normal Configuration

2 Day Immersion at Room Temperature

Polyimide Alkaline Solution	% Tensile Strength Retained	% Elongation Retained	% Tensile Modulus Retained
LaRC-ITPI			
7% NH$_4$OH (1M)	80	88	77
11% Na$_2$CO$_3$ (1M)	100	100	92
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	93	100	88
4% NaOH (1M)	89	100	90
LaRC-CPI			
7% NH$_4$OH (1M)	91	100	94
11% Na$_2$CO$_3$ (1M)	100	100	100
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	95	100	88
4% NaOH (1M)	100	100	100
LaRC-TPI			
7% NH$_4$OH (1M)	80	100	84
11% Na$_2$CO$_3$ (1M)	97	100	90
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	78	100	82
4% NaOH (1M)	80	100	85

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Table IV - Resistance of Polyimides Containing Fluorine Atoms to Aqueous Alkaline Solutions

Normal Configuration

2 Day Immersion at Room Temperature

Polyimide Alkaline Solution	% Tensile Strength Retained	% Elongation Retained	% Tensile Modulus Retained
6F/3,5-DABTF			
7% NH_4OH (1M)	82	72	100
11% Na_2CO_3 (1M)	100	100	100
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	80	71	98
4% NaOH (1M)	86	85	98
BPDA/3,5-DABTF			
7% NH_4OH (1M)	99	64	100
11% Na_2CO_3 (1M)	100	85	100
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	93	100	100
4% NaOH (1M)	86	85	98
HQDEA/4-BDAF			
7% NH_4OH (1M)	80	91	87
11% Na_2CO_3 (1M)	87	91	93
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	70	64	77
4% NaOH (1M)	66	87	74

Table V - Resistance of ODPA and PMDA Based Polyimides to Aqueous Alkaline Solutions

Normal Configuration

2 Day Immersion at Room Temperature

Polyimide Alkaline Solution	% Tensile Strength Retained	% Elongation Retained	% Tensile Modulus Retained
ODPA/3,4'-ODA			
7% NH$_4$OH (1M)	100	100	98
11% Na$_2$CO$_3$ (1M)	92	53	94
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	95	95	94
4% NaOH (1M)	95	93	97
PMDA/3,4'-ODA			
7% NH$_4$OH (1M)	51	8	100
11% Na$_2$CO$_3$ (1M)	100	90	95
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	95	60	95
4% NaOH (1M)	48	15	83
ODPA/p-PDA			
7% NH$_4$OH (1M)	70	74	74
11% Na$_2$CO$_3$ (1M)	80	81	81
19% Na$_3$PO$_4$ · 12H$_2$O (0.5M)	69	66	73
4% NaOH (1M)	74	100	75

Table VI - Resistance of PMDA/4,4'-ODA Polyimides to Aqueous Alkaline Solutions

Normal Configuration

2 Day Immersion at Room Temperature

Polyimide Alkaline Solution	% Tensile Strength Retained	% Elongation Retained	% Tensile Modulus Retained
PMDA/4,4'-ODA			
7% NH_4OH (1M)	55	20	100
11% Na_2CO_3 (1M)	71	62	100
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	72	71	96
4% NaOH (1M)	49	58	56
KAPTON® (200 HN)			
7% NH_4OH (1M)	61	13	100
11% Na_2CO_3 (1M)	98	90	100
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	61	16	100
4% NaOH (1M)	(D)*	(D)*	(D)*
APICAL® (300 AV)			
7% NH_4OH (1M)	50	6	100
11% Na_2CO_3 (1M)	90	83	100
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	52	10	100
4% NaOH (1M)	(D)*	(D)*	(D)*

*(D) = Decomposed

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Table VII - Resistance of UPILEX® Polyimides to Aqueous Alkaline Solutions

Normal Configuration

2 Day Immersion at Room Temperature

Polyimide Alkaline Solution	% Tensile Strength Retained	% Elongation Retained	% Tensile Modulus Retained
UPILEX R®			
7% NH_4OH (1M)	100	100	96
11% Na_2CO_3 (1M)	100	100	89
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	88	97	91
4% NaOH (1M)	72	73	96
UPILEX S®			
7% NH_4OH (1M)	83	100	84
11% Na_2CO_3 (1M)	81	100	82
19% $Na_3PO_4 \cdot 12H_2O$ (0.5M)	87	100	86
4% NaOH (1M)	80	89	84

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Figure 1: Film Cutter

23
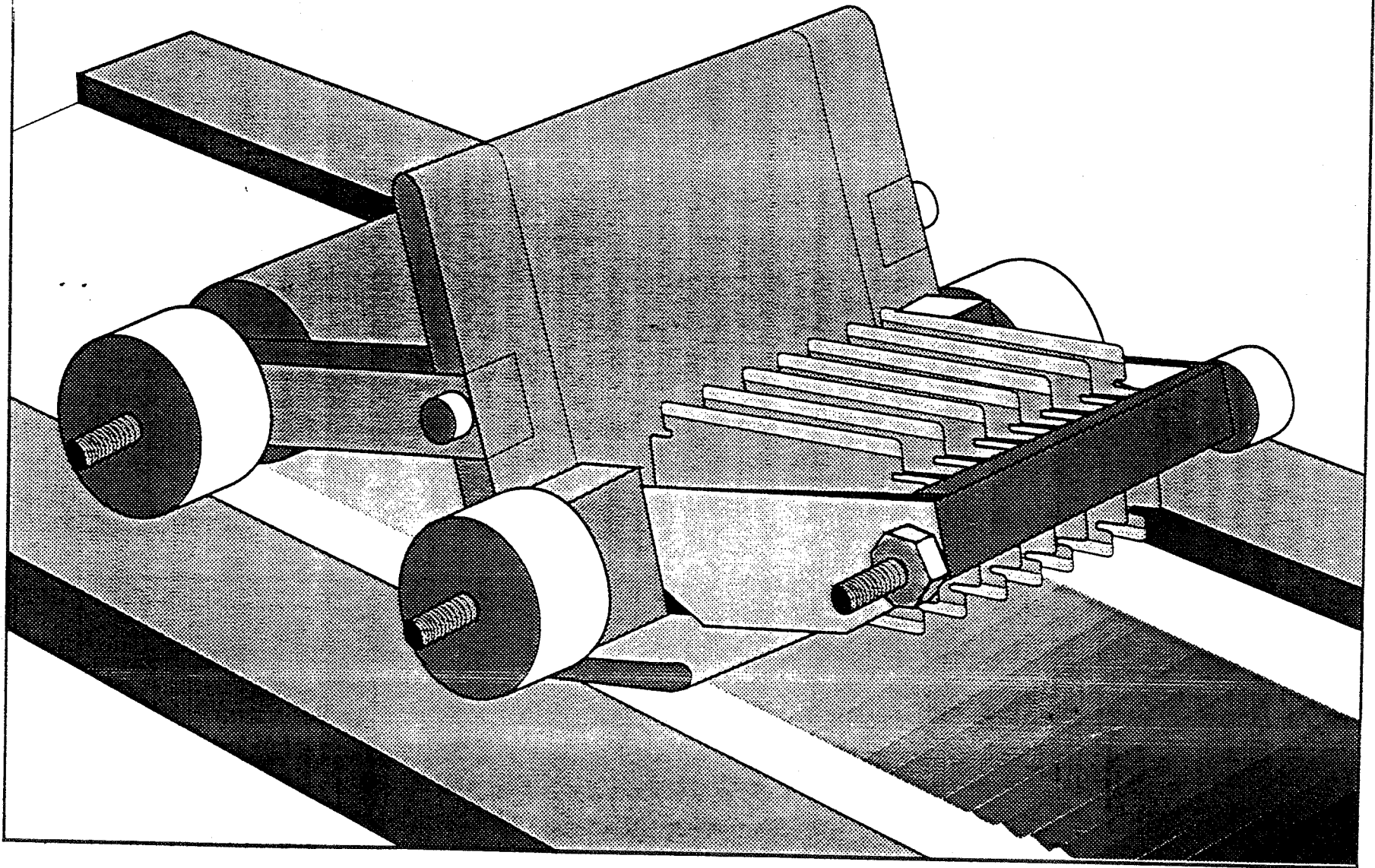
Figure 2: Configurations for Chemical Exposure of Polyimide Films

4.00"
Min.

0.20"
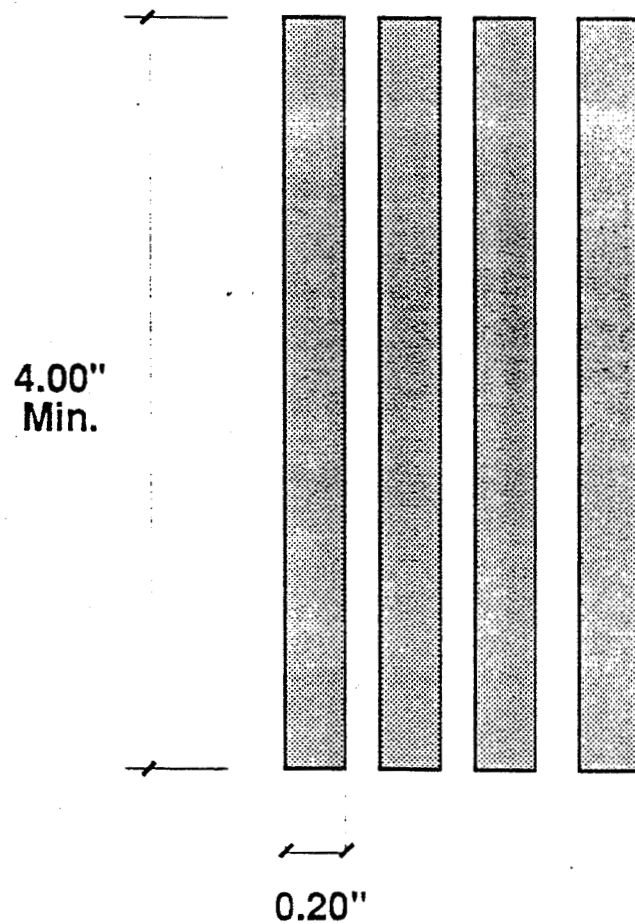
Normal Width = 0.20 Inches
Gage Length = 2.00 Inches
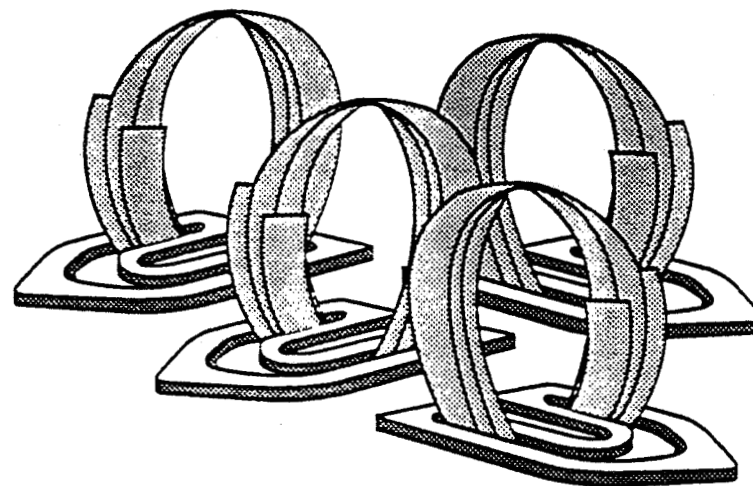
Rolled

Figure 3: Configuration for Chemical Exposure of Polyimide Films
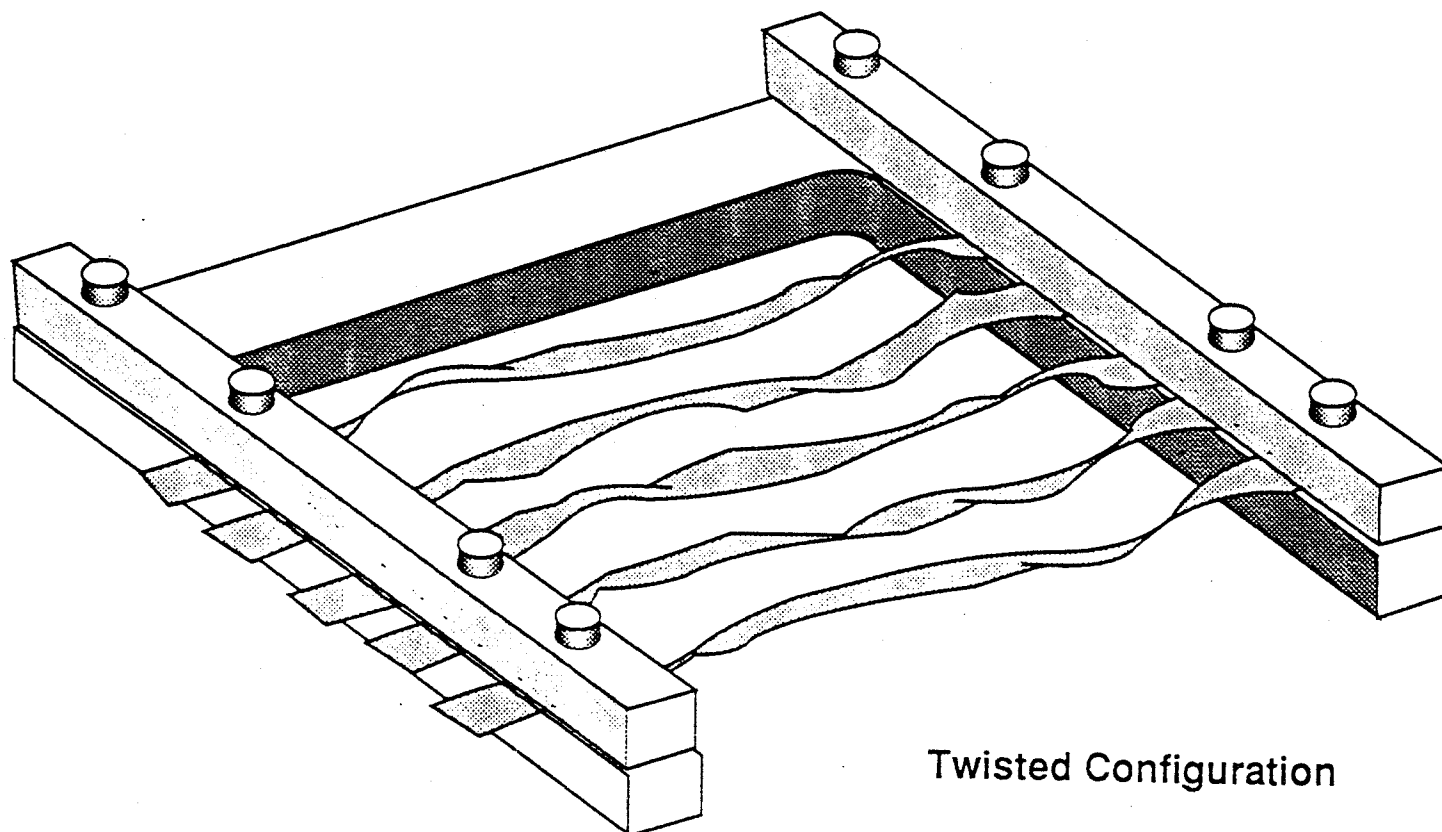
Twisted Configuration

Figure 4a - Polyimide Film Structures

LaRC-ITPI

LaRC-TPI

LaRC-CPI

UPILEX R®

UPILEX S®
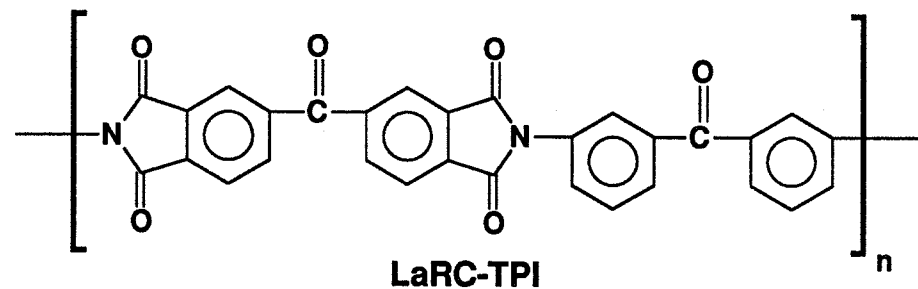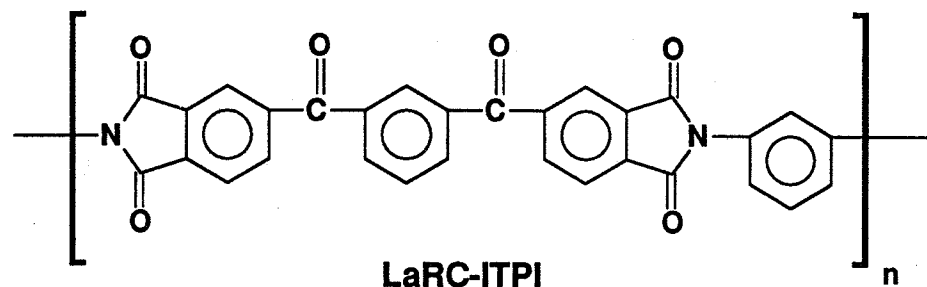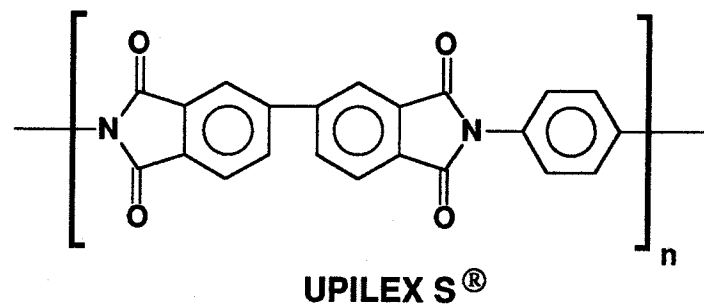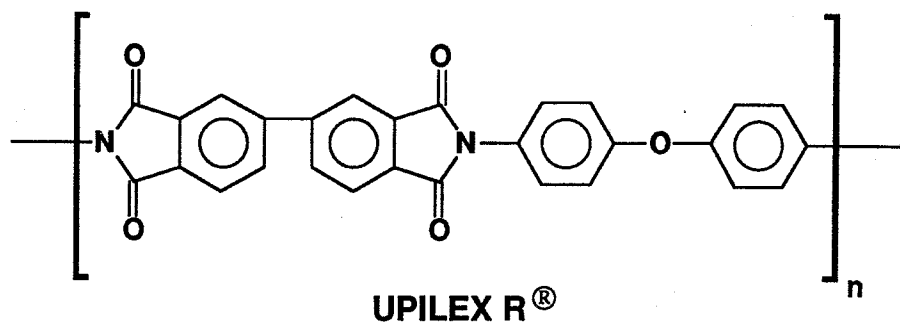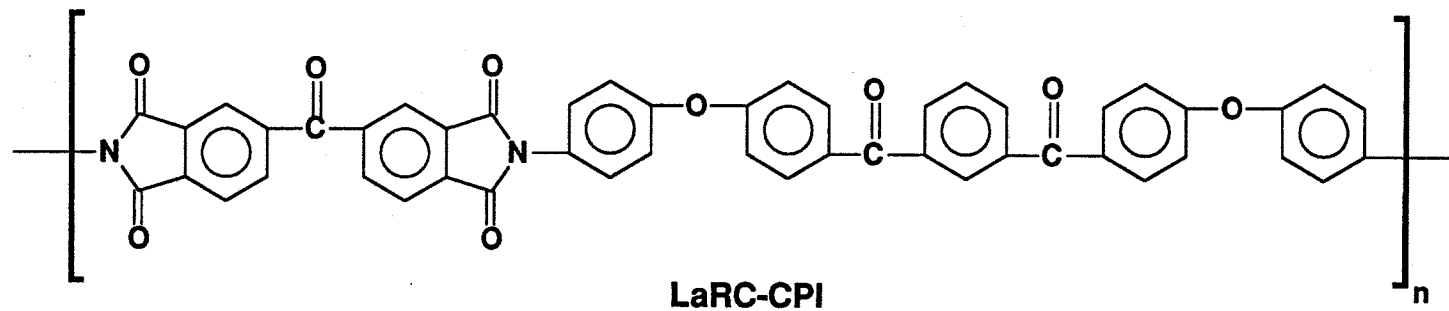
Figure 4b - Polyimide Film Structures (Continued)
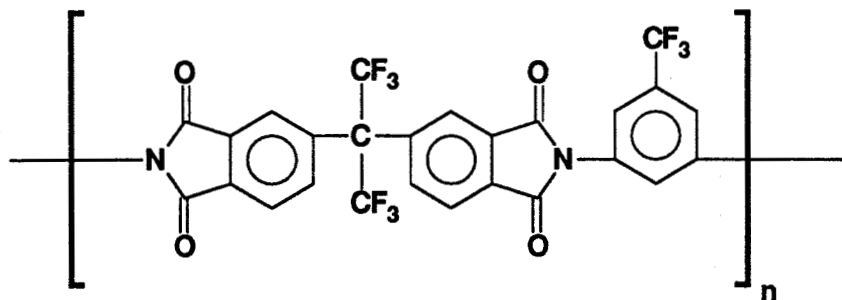
6F/3,5-DABTF
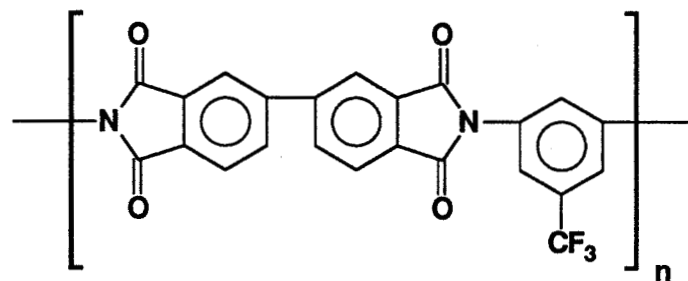
BPDA/3,5-DABTF
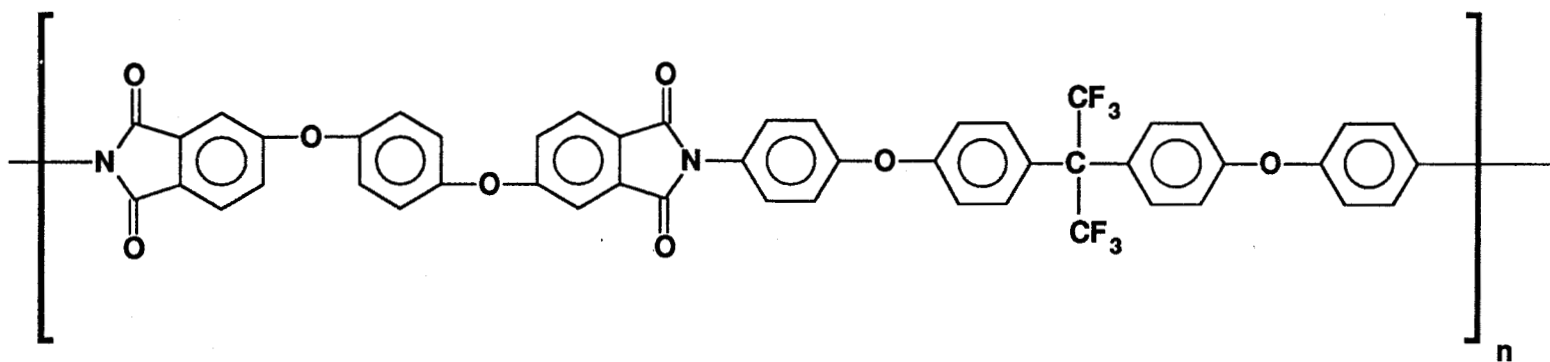
HQDEA/4-BDAF

Figure 4c - Polyimide Film Structures (Concluded)
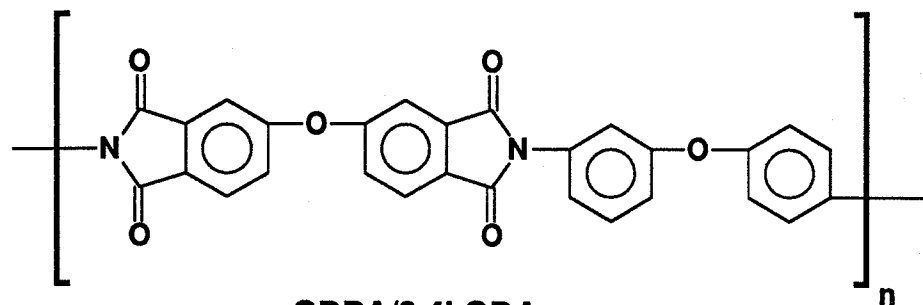
ODPA/3,4'-ODA
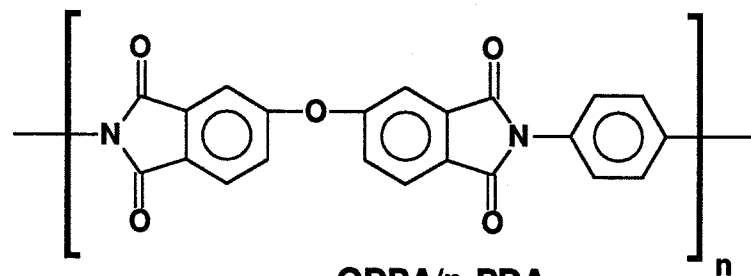
ODPA/p-PDA
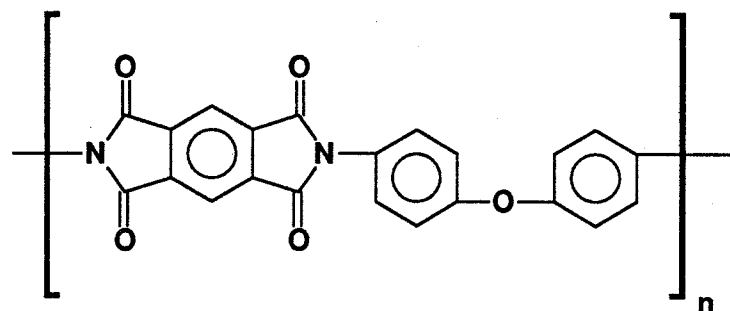
PMDA/4,4'-ODA
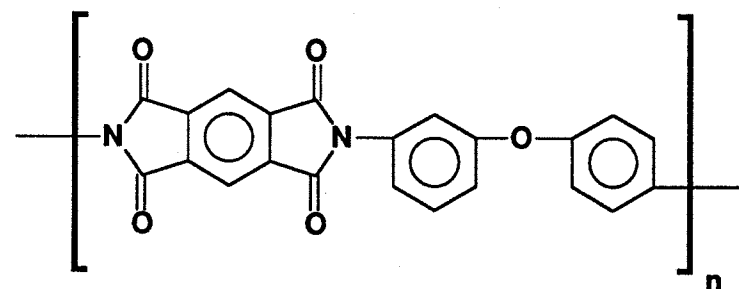
PMDA/3,4'-ODA

KAPTON ®

APICAL®

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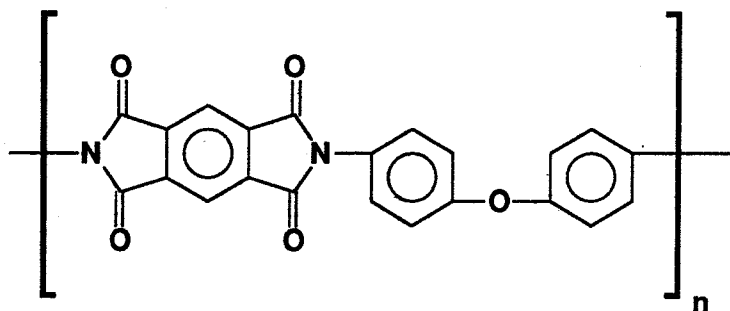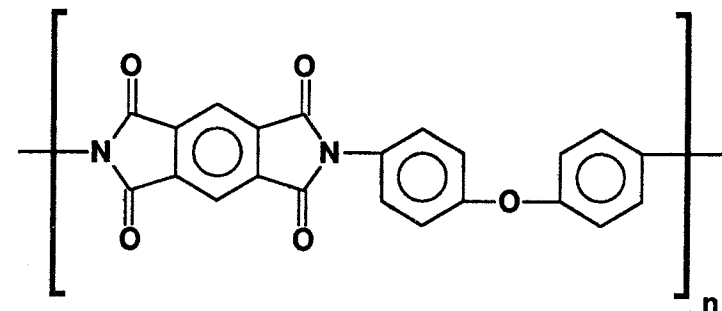
Figure 5 - Moisture Absorption of Polyimides
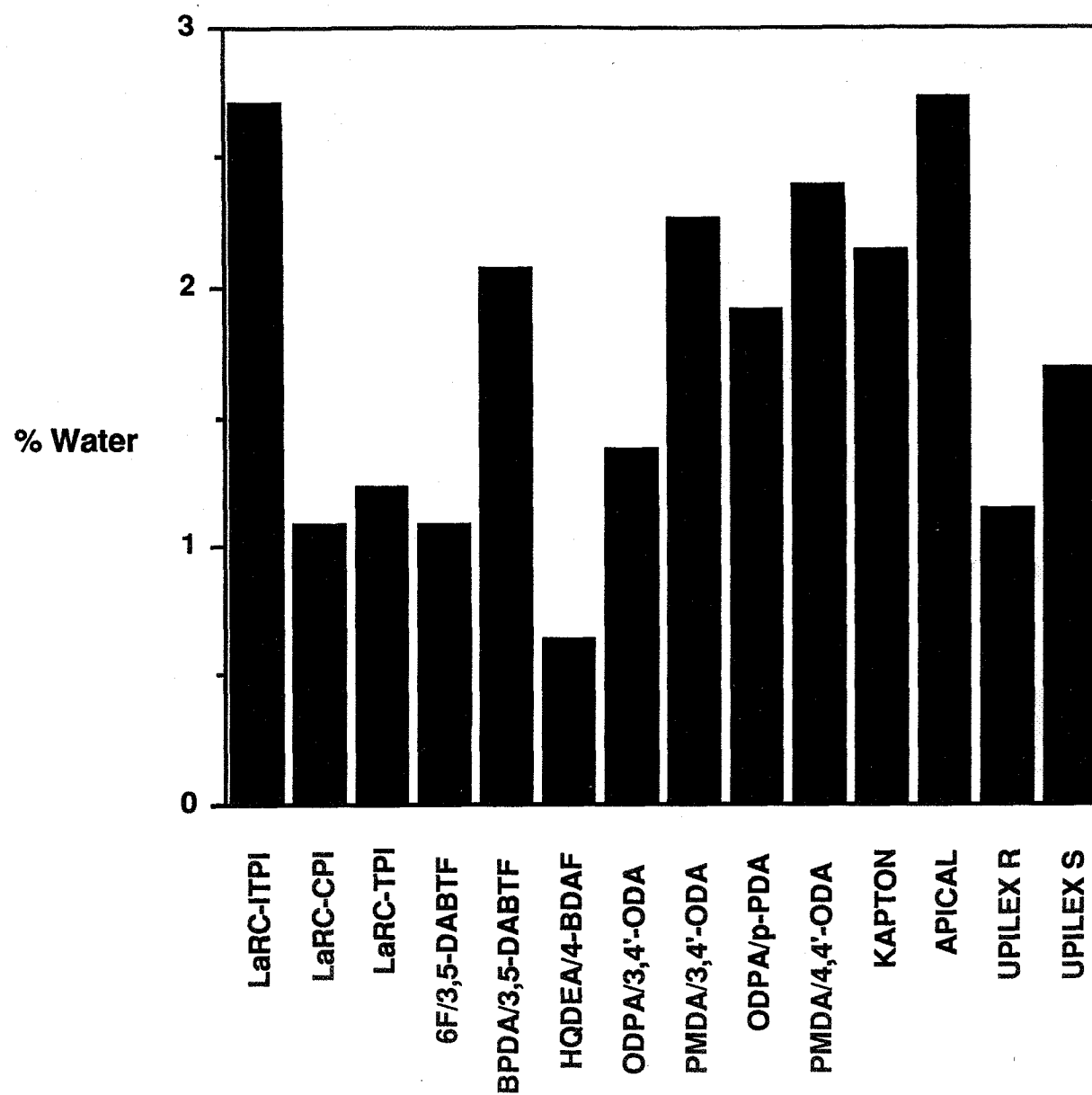
Figure 6 - Tensile Strength of Unexposed Polyimides

30
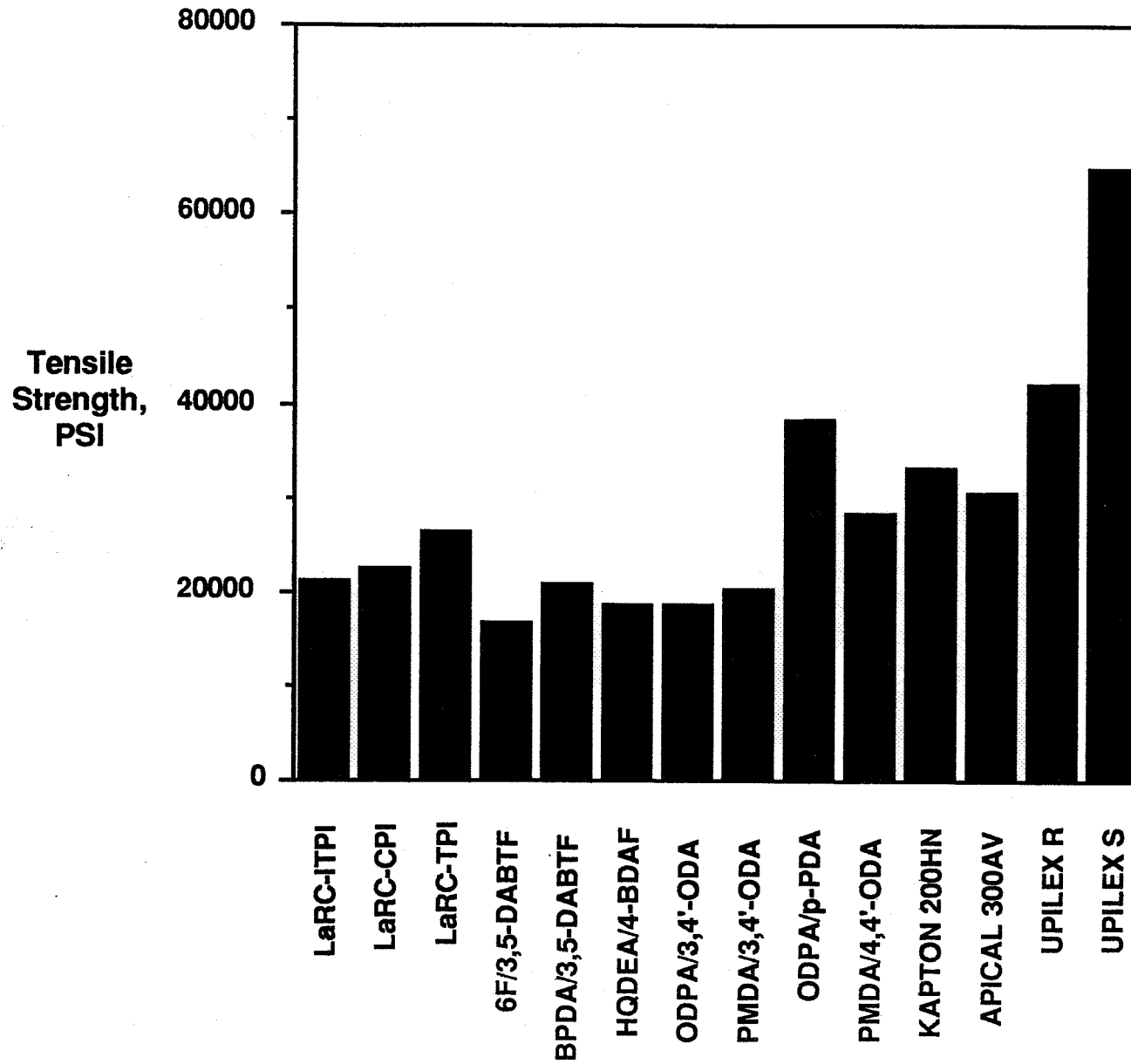
Figure 7 - Tensile Modulus of
Unexposed Polyimides
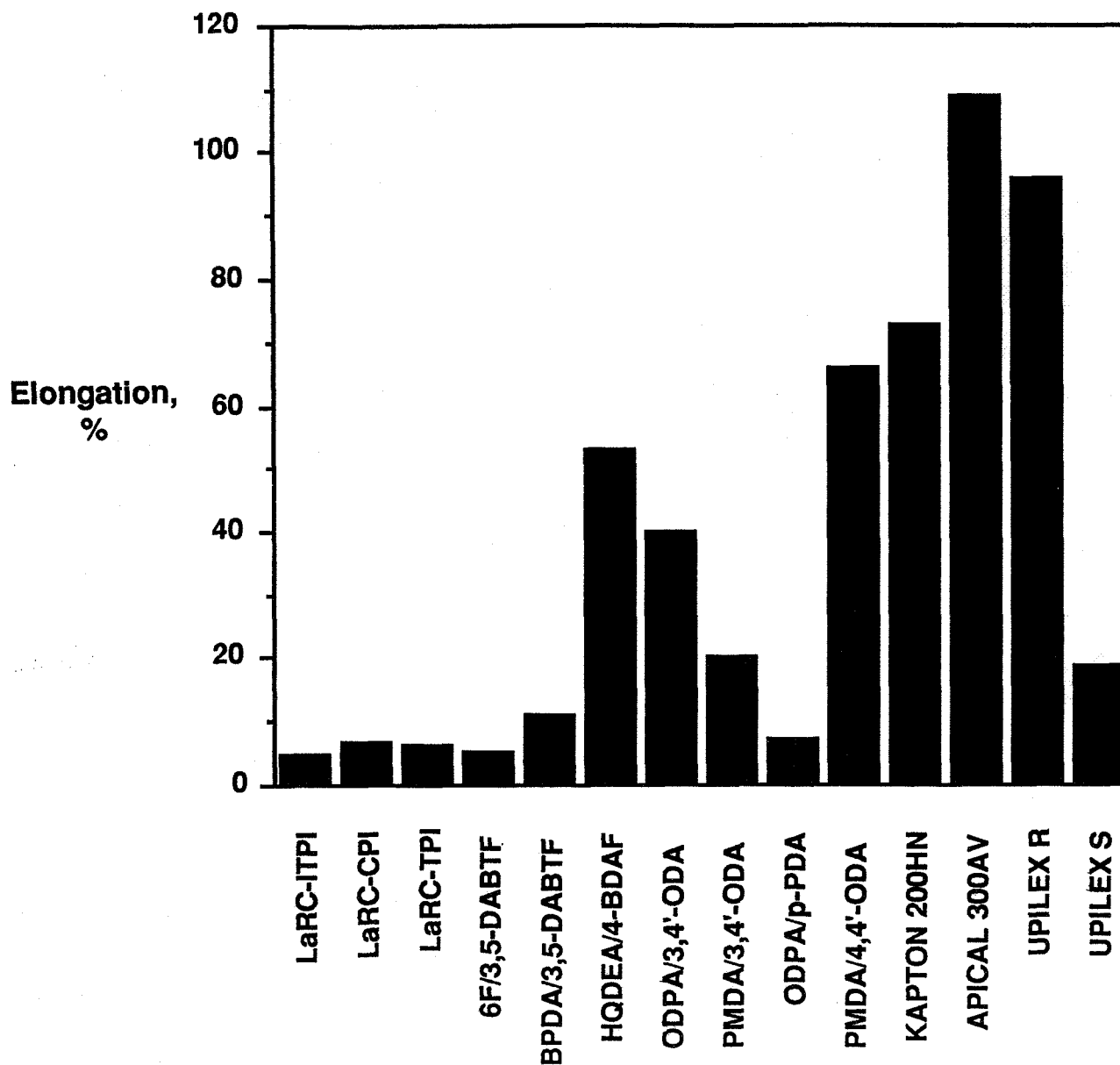

31
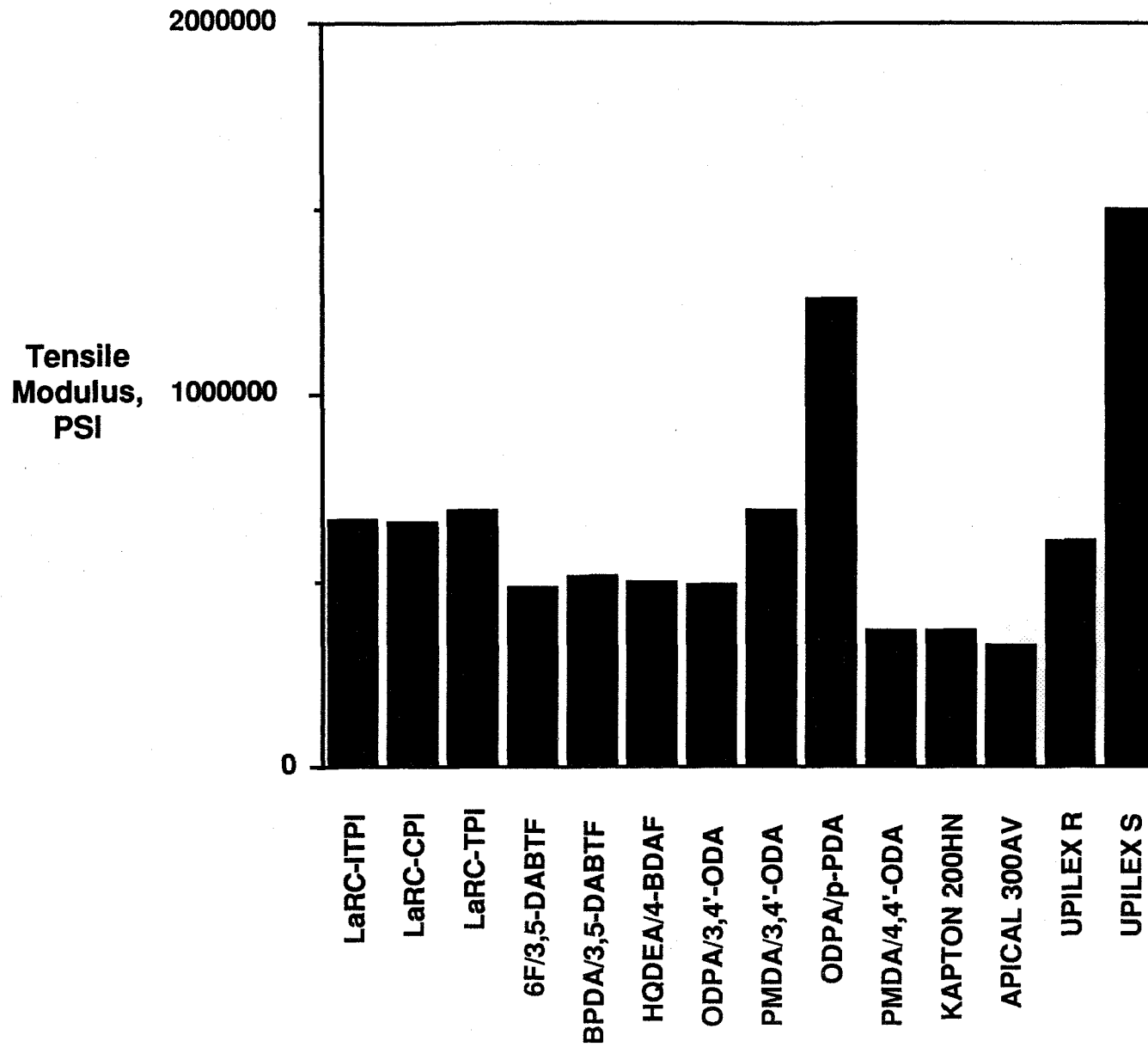
Figure 8 - Elongation of Unexposed Polyimides

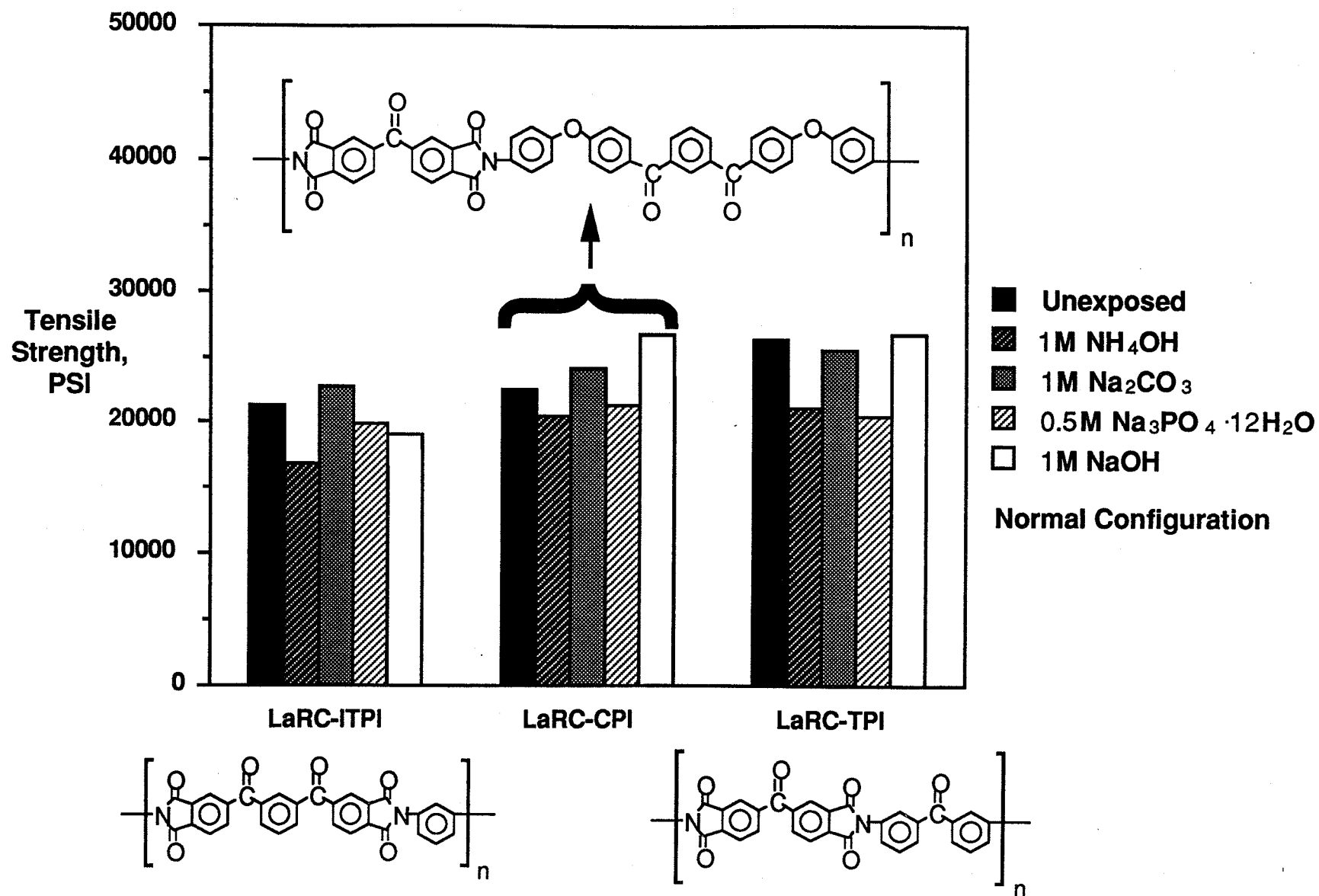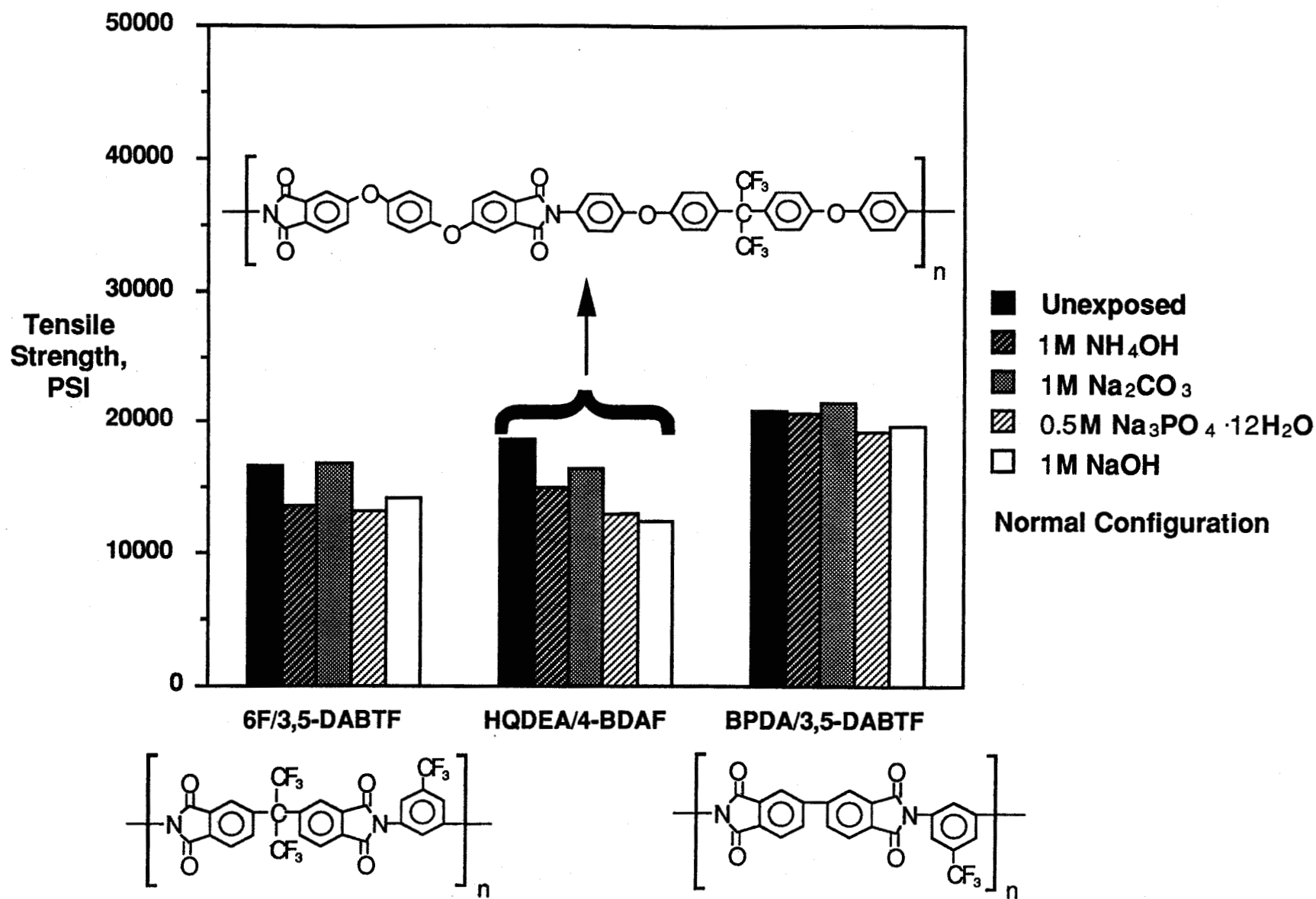# Figure 9 - Chemical Exposure Effects on Tensile Strength of LaRC-ITPI, LaRC-CPI and LaRC-TPI

Tensile Strength, PSI

■ Unexposed
▨ 1M NH$_4$OH
▨ 1M Na$_2$CO$_3$
▨ 0.5M Na$_3$PO$_4$ ·12H$_2$O
□ 1M NaOH

Normal Configuration

LaRC-ITPI   LaRC-CPI   LaRC-TPI

Figure 10 - Chemical Exposure Effects on Tensile Strength of Polyimides Containing Fluorine Atoms

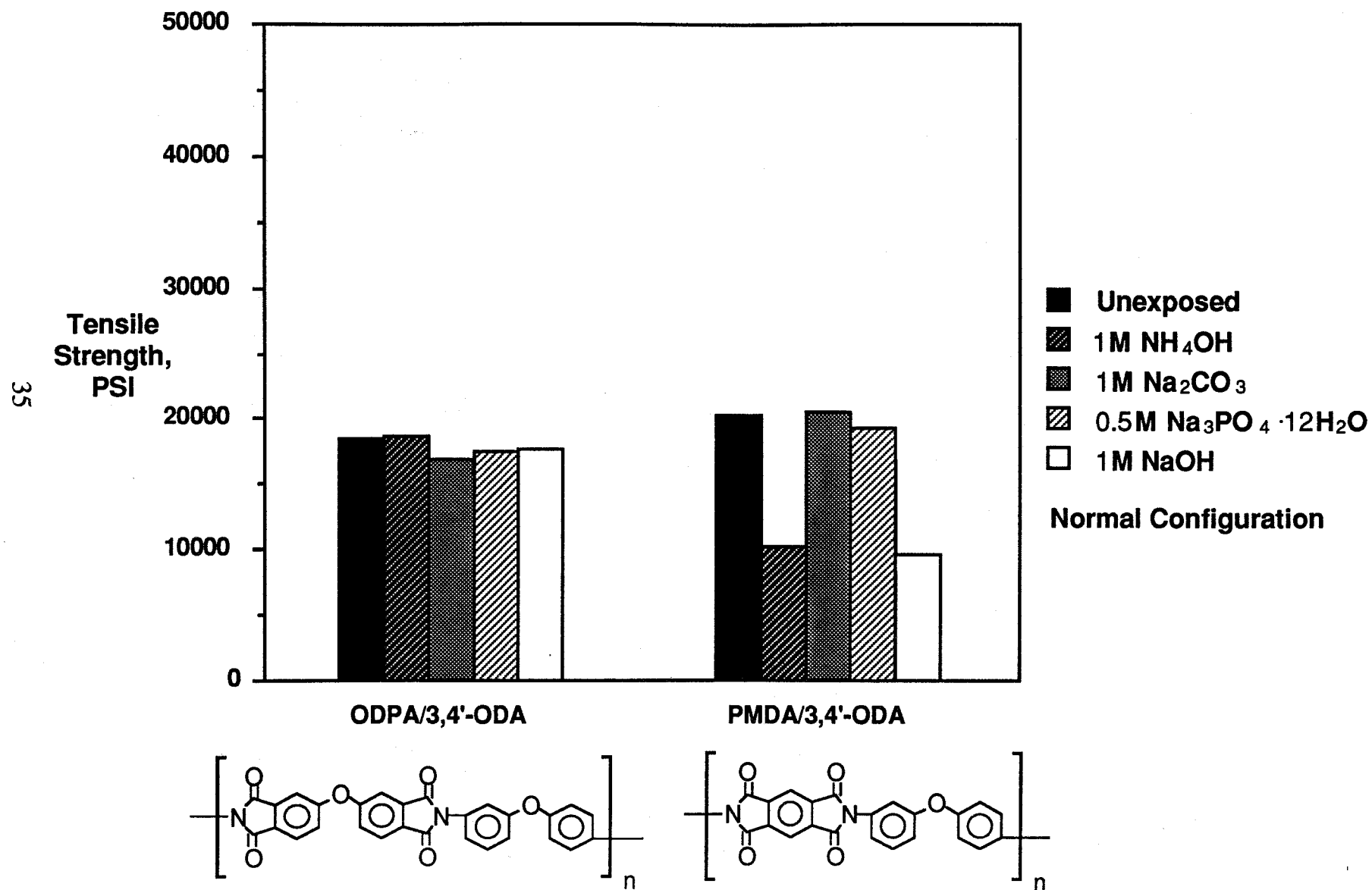# Figure 11 - Chemical Exposure Effects on Tensile Strength of Polyimides with 3,4'-ODA

Tensile Strength, PSI

50000

40000

30000

20000

10000

0

ODPA/3,4'-ODA   PMDA/3,4'-ODA

■ Unexposed
▨ 1M NH$_4$OH
▨ 1M Na$_2$CO$_3$
▨ 0.5M Na$_3$PO$_4$·12H$_2$O
□ 1M NaOH

Normal Configuration

Figure 12 - Chemical Exposure Effects on Tensile Strength of PMDA Based Polyimides
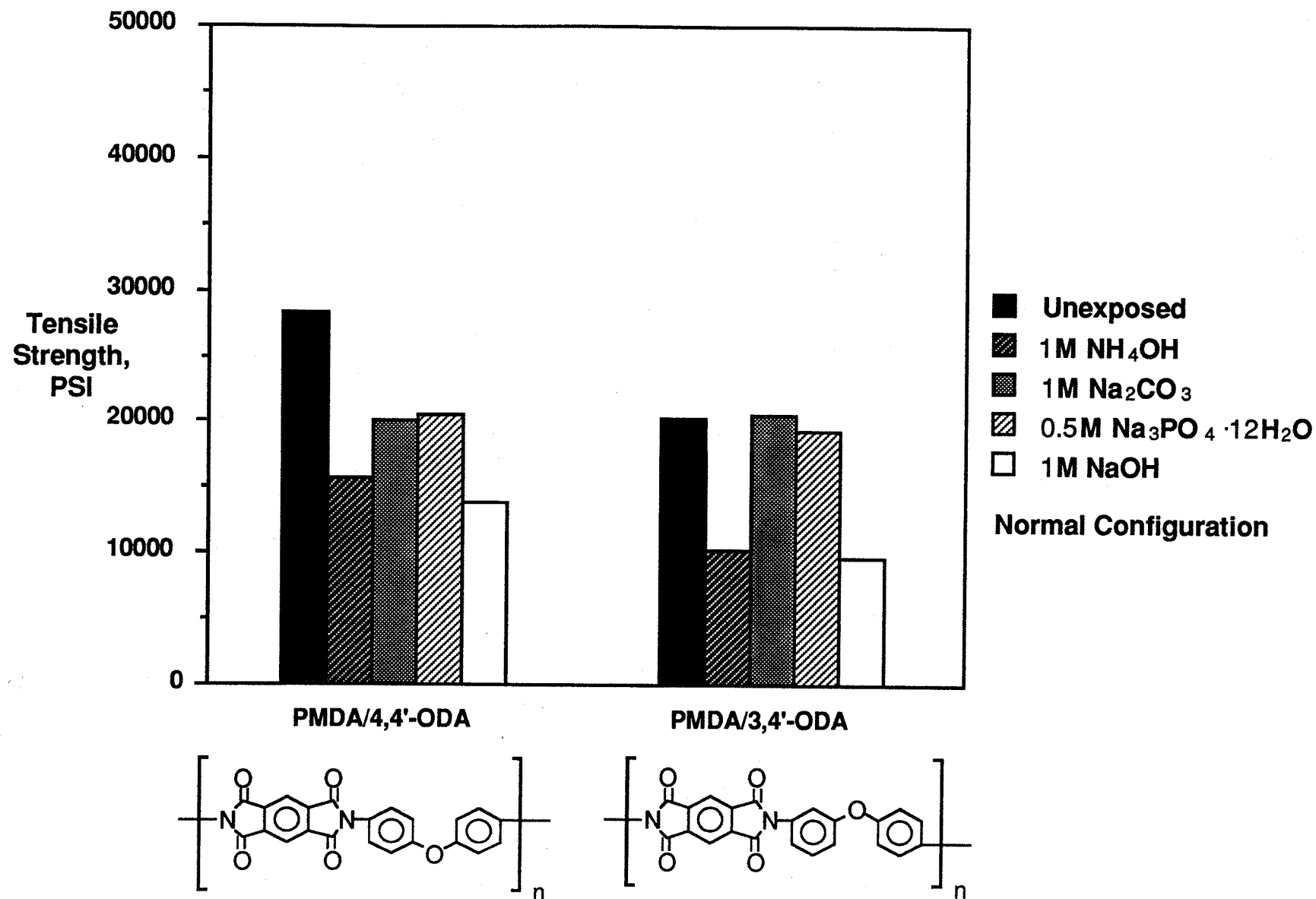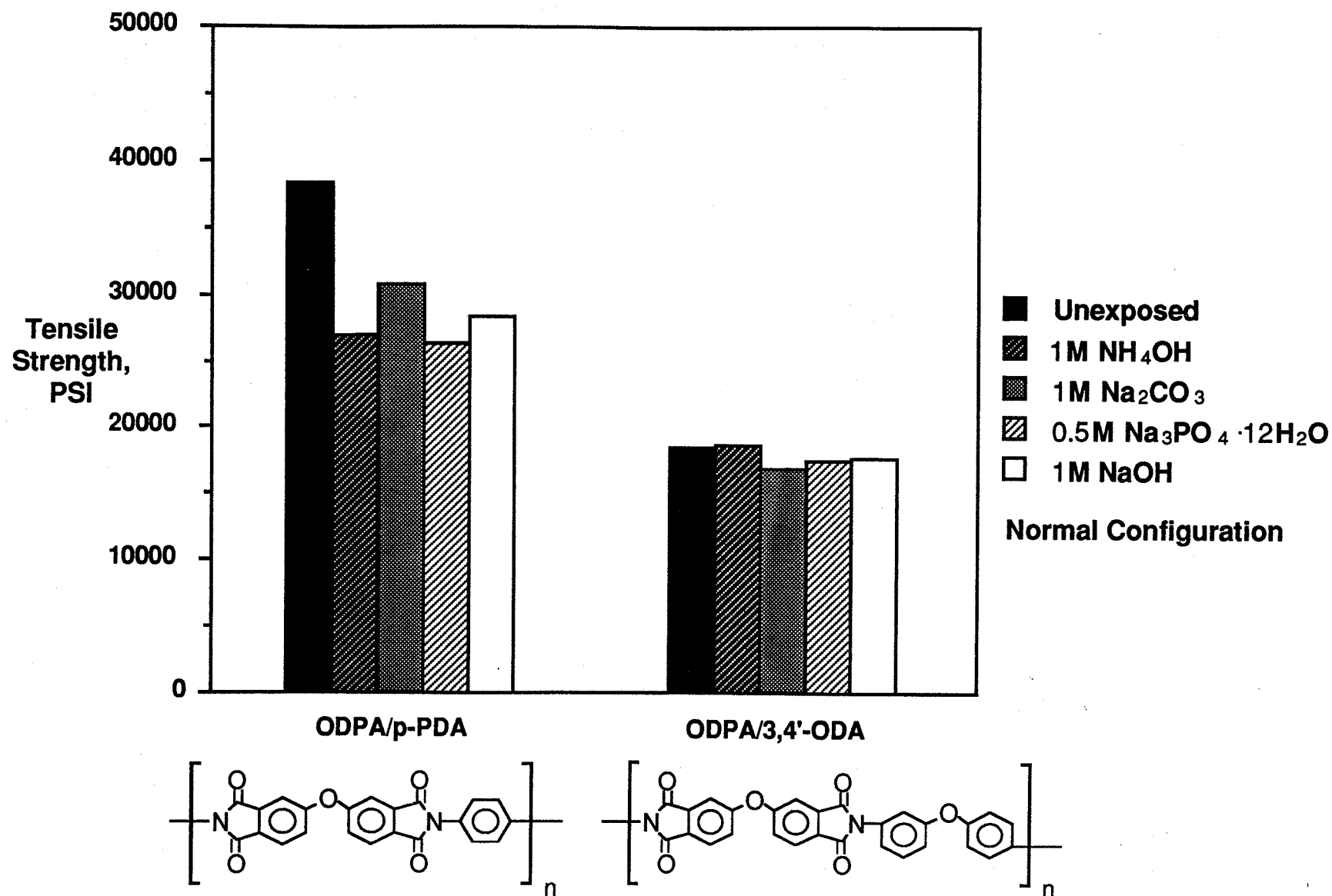
Figure 13 - Chemical Exposure Effects on Tensile Strength of ODPA Based Polyimides

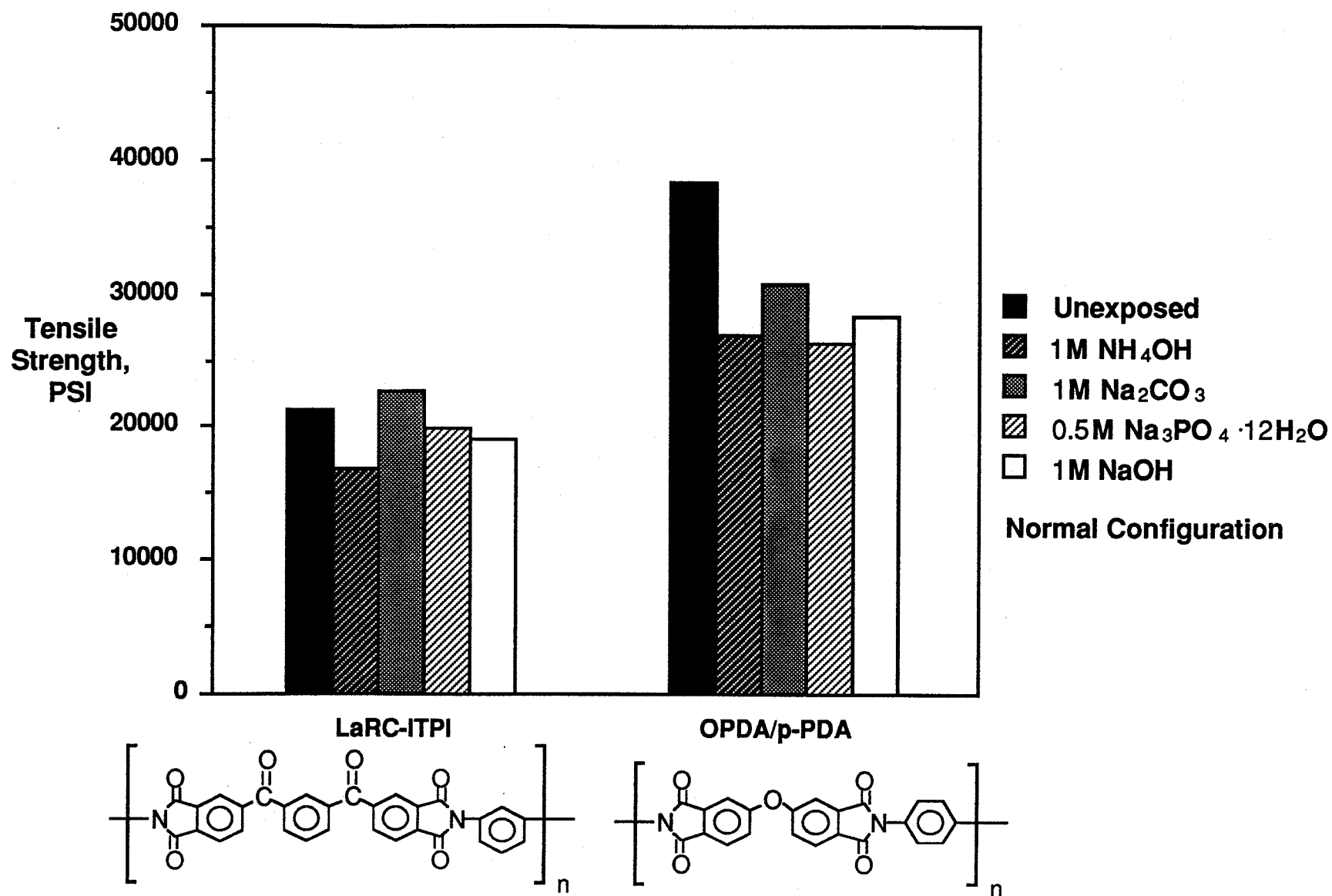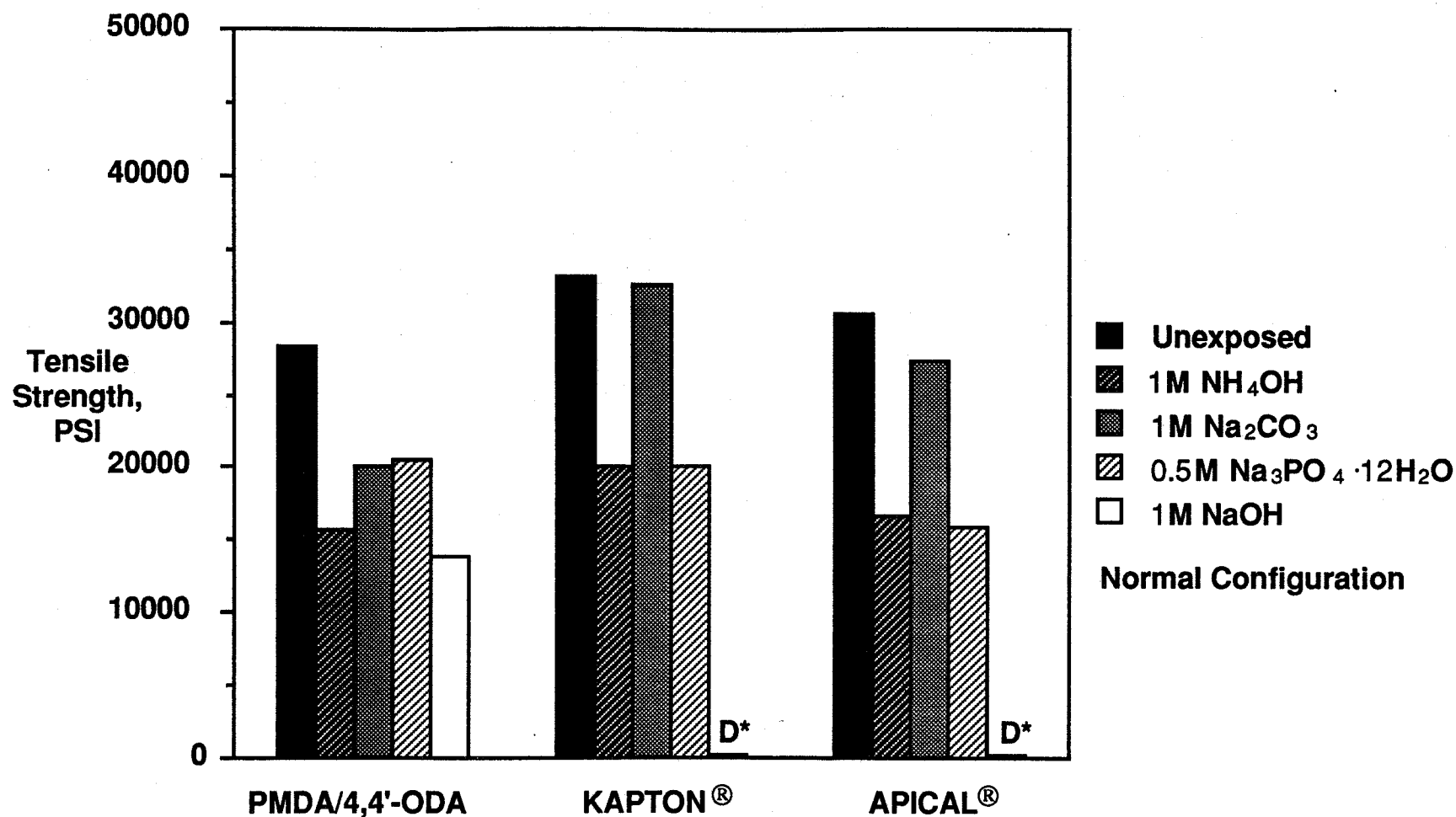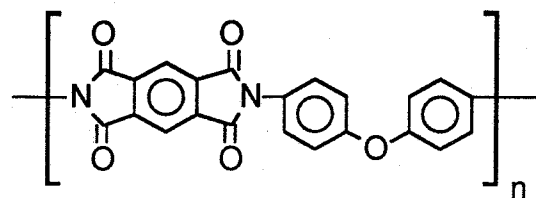# Figure 14 - Chemical Exposure Effects on Tensile Strength of LaRC-ITPI and ODPA/p-PDA

Figure 15 - Chemical Exposure Effects on Tensile
Strength of PMDA/4,4'-ODA Polyimides

*D = Dissolved

Figure 16 - Chemical Exposure Effects on Tensile Strength of UPILEX®R and S

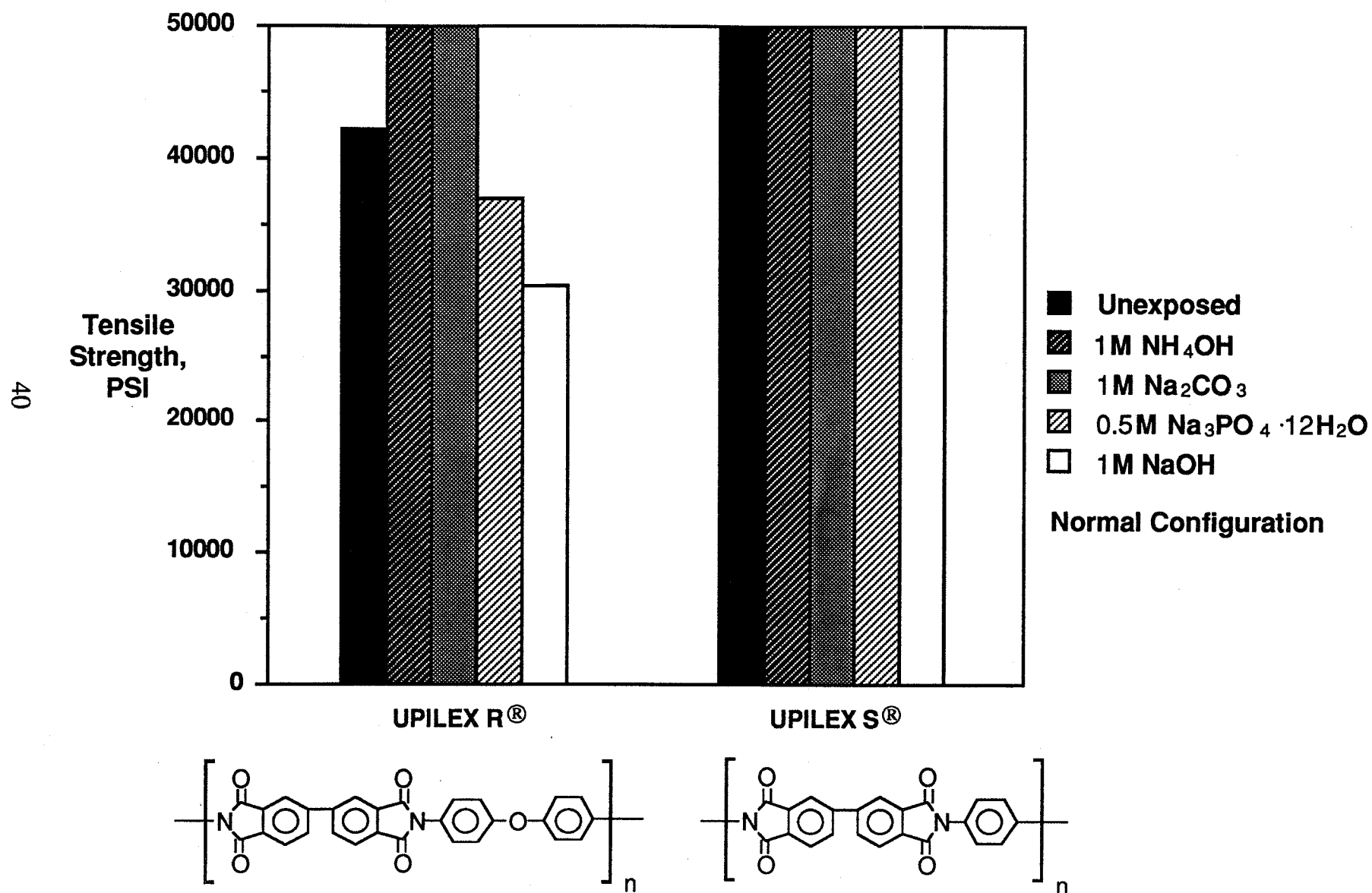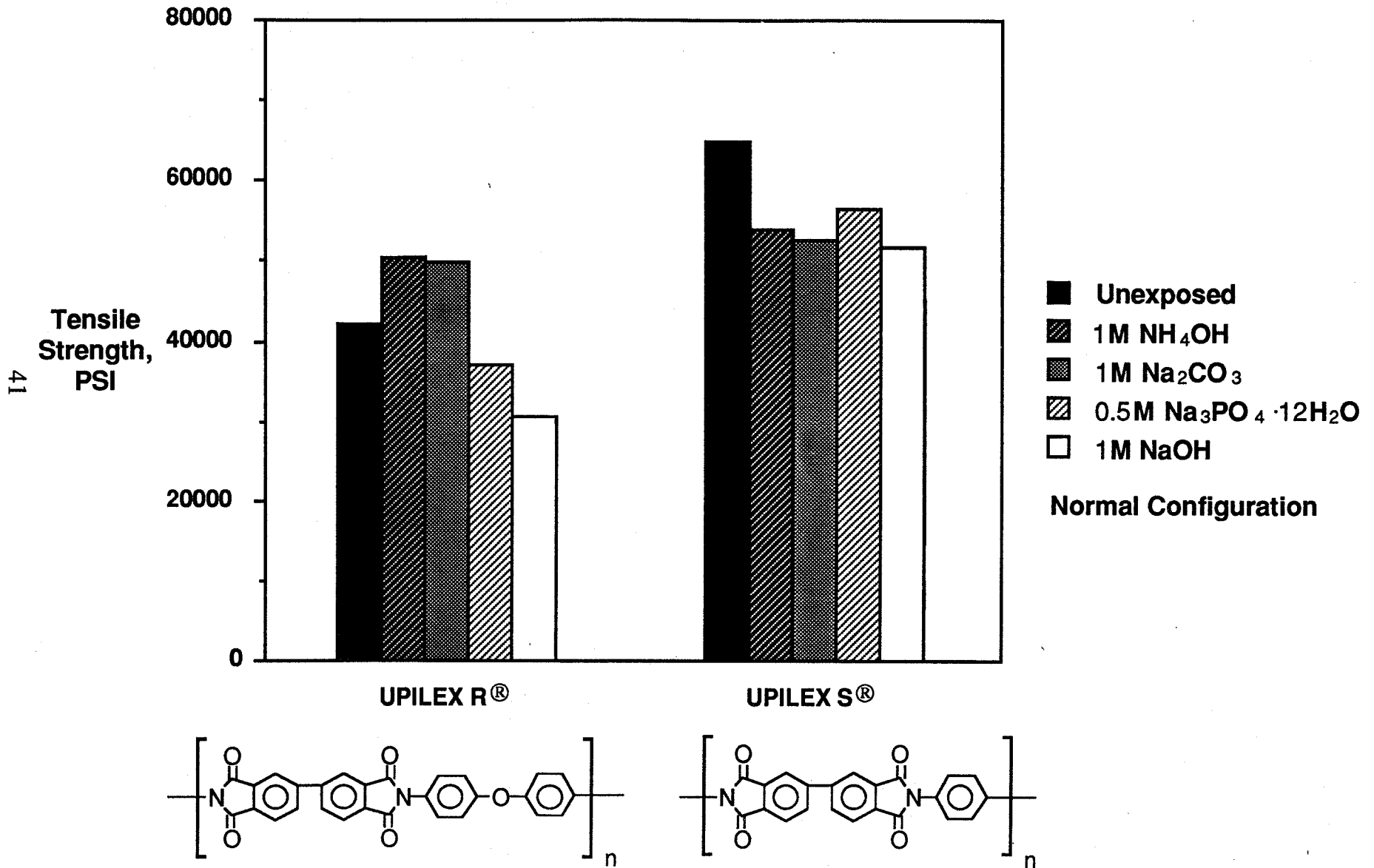Legend:
- Unexposed
- 1M NH_4OH
- 1M Na_2CO_3
- 0.5M $Na_3PO_4 \cdot 12H_2O$
- 1M NaOH

Normal Configuration

UPILEX R®   UPILEX S®

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Figure 17 - Chemical Exposure Effects on Tensile Strength of UPILEX®R and S

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16. Abstract

Polyimide insulated electrical wire has been widely used in the aerospace industry in commercial, military, and to a lesser degree, general aviation aircraft since the early 1970s. Wiring failures linked to insulation damage have drawn much attention in the media and concerns have developed regarding the long term stability and safety of polyimide insulated electrical wire. The mechanical durability and chemical stability of polyimide insulated wire are affected by hydrolysis, notch propagation, wet and dry arc tracking, topcoat flaking, and degradation due to high pH fluids.

In this study, several polyimides have been selected for evaluation for resistance to degradation by various aqueous alkaline solutions. The polyimides under evaluation include commercially available films such as KAPTON®, APICAL®, LARC-TPI, and UPILEX® R and S, as well as a number of experimental films prepared at NASA Langley Research Center. Material properties investigated include viscosity, solubility, moisture absorption, glass transition temperature (T_g), dielectric constant, and mechanical properties before and after exposure to various conditions.

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