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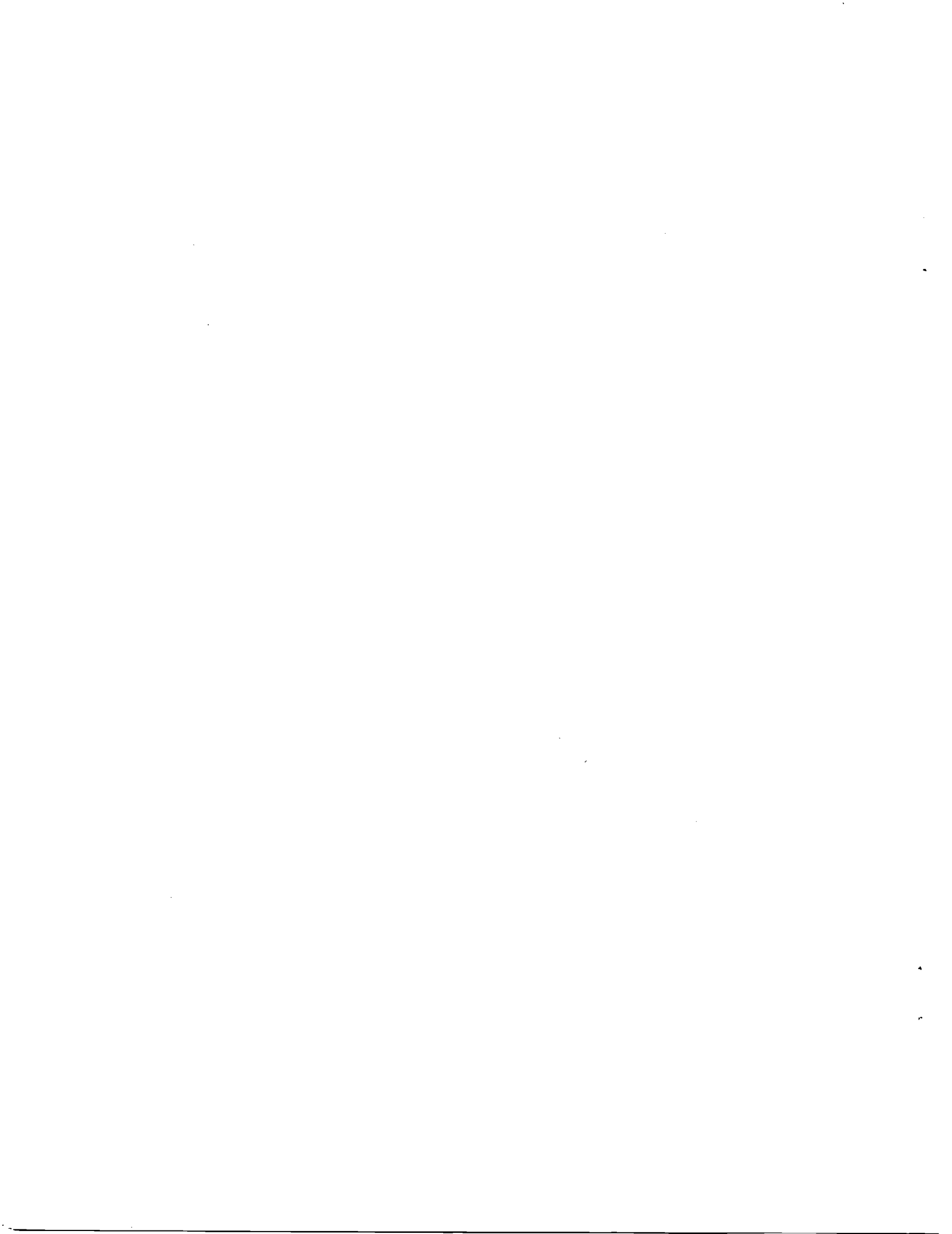
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EVALUATION OF COLORLESS POLYIMIDE FILM FOR THERMAL CONTROL
COATING APPLICATIONS

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A series of essentially colorless aromatic polyimide films has been synthesized and characterized with the objective of obtaining maximum optical transparency for applications in space. Optical transparency is a requirement for high performance polymeric films used in second surface mirror coatings on thermal control systems. The intensity in color of aromatic polyimide films was lowered by reducing the electronic interaction between chromophoric centers in the polymer molecular structure and by using highly purified monomers. The resulting lightly colored to colorless polyimide films have been characterized by UV-visible and infrared spectroscopy before and after exposure to 300 equivalent solar hours UV irradiation and varying doses of 1

MeV electron irradiation. After irradiation, the films were found to be 2 to 2.5 times more transparent than commercial polyimide film of the same thickness.

1. INTRODUCTION

The need exists for high temperature, flexible polymeric film and coating materials that have high optical transparency in the the 300-600 nm range of the electromagnetic spectrum for applications on such space components as multi-layer insulation blankets, solar cells, and thermal control coatings⁽¹⁾. Although there are available several classes of polymers which are transparent/colorless such as polyesters or aliphatic polyimides, these materials have limited long-term

thermal stability. A major drawback for using thermally stable aromatic polyimides for the above stated space applications has been their poor transparency in the visible range of the electromagnetic spectrum. Traditionally, linear all-aromatic condensation polyimides are known for their bright yellow color. Commercial aromatic polyimide film has been evaluated for applications on space solar cells and thermal control coating systems but was found to be only about 70% transparent (depending on thickness) at the solar wavelength of interest (500 nm). A further drawback for using the intensely colored aromatic polyimides as space films or coatings is that although they are approximately 70% transparent, upon aging in a space environment they become even less transparent.

A recent study was conducted to synthesize linear aromatic polyimide film having maximum optical transparency.⁽²⁾ The use of highly purified monomers and the incorporation of meta-linked diamines, bulky electron-withdrawing groups and flexibilizing groups into the molecular structure greatly increased the transparency of films compared to a commercially prepared polyimide film. It is the object of the present investigation to further

evaluate the most transparent of these pale yellow to colorless polyimide films for actual use in a space environment. The following irradiation experiments were designed to simulate the use of a series of six transparent polyimide films as second-surface mirror thermal control coatings.

2. EXPERIMENTAL

2.1 Materials

The six aromatic diamine and dianhydride monomers used to make polymer films for this investigation are shown in Figure 1. The diamine monomers 3,3'-diaminodiphenylsulfone (DDSO₂), 1,3-bis(aminophenoxy)benzene (APB), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF)⁽³⁾ were obtained from commercial sources and purified by recrystallization, melting points 172°, 105° and 162°C respectively. The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) was obtained by sublimation of the tetraacid received as an experimental material from E. I. DuPont de Nemours and Co., melting point 243°C. The 4,4'-oxydiphthalic anhydride (ODPA) was obtained from Ciba Geigy and purified by vacuum sublimation, melting point 224°C. The 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA) was an experimental

research anhydride obtained from the General Electric Corporate Research and Development Center⁽⁵⁾, melting point 189°-190°C. The dimethylacetamide (DMAc) used as a solvent for polymerization was vacuum distilled at 102°C from calcium hydride. The commercial polyimide film used for comparative purposes in this investigation was Kapton® H film obtained from E. I. DuPont de Nemours and Co.

2.2 Preparation of Polymer Films

Polymerizations were performed in closed vessels at ambient temperature at a concentration of 15% (w/w) solids in DMAc. The polyamic acid precursors were prepared by adding equimolar amounts of the dianhydride monomer to the diamine dissolved in DMAc. These mixtures were stirred mechanically for 8 to 24 hours to insure complete reaction of the monomers. The resulting polyamic acid resins were refrigerated until used for film casting.

The polymer films used in this investigation were prepared by spreading the polyamic acid resins onto soda-lime glass plates using a 7 mil blade gap. Films were cast in an enclosed dust-free chamber at a 10% relative humidity. When tack-free, the polyamic acid films were thermally

converted to the corresponding polyimides by heating in a forced air oven for one hour each at 100°, 200° and 300°C. The resulting polyimide films were tough, flexible and had a final film thickness of 0.50 ± 0.01 mil.

2.3 Characterization

The inherent viscosities of the polyamic acid solutions were obtained at a concentration of 0.5% (w/w) in DMAc at 35°C. Glass transition temperatures (T_g) of the polyimide films were measured by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in static air at a temperature program of 5°C/min. Polymer decomposition temperatures (PDT) were obtained by thermogravimetric analysis (TGA) on polyimide films heated at 2.5°C/min in 15 cc/min flowing air. Solubilities of polyimide films were determined at ambient temperature at 1% (w/w) solids in amide, chlorinated and ether solvents. Transmission UV-visible spectra were obtained on the 0.50 mil thick polyimide films before and after UV and electron irradiation using a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer. Infrared spectra were obtained on specified films before and after irradiation using a Nicolet 60SX Fourier Transform Infrared Spectrometer.

2.4 Ultraviolet Radiation Exposure

The 0.50 mil thick polyimide films were exposed to simulated solar ultraviolet radiation in a high vacuum of 1.3×10^{-5} pascal.

The one inch diameter film specimens were mounted in individual sample holders with their own ion pump. Six specimen chambers surrounded the 1 KW xenon lamp serving as the ultraviolet radiation source. Suprasil quartz optics were used to transfer and focus the ultraviolet radiation onto the film specimens. The films were initially mounted and evaluated against two different backgrounds: (1) a black absorbing surface, and (2) a silver reflecting surface. All of the subsequent experiments were performed with the films mounted on the latter silver surface which was comprised of a vacuum deposited silver coating on aluminum. This silver surface was placed behind the film specimens to simulate a second-surface mirror thermal control coating and to provide an opaque coating for uniform irradiation of the transparent films. The intensity of the ultraviolet light at the exposure position was monitored by a detector calibrated with a secondary National Bureau of Standards standard lamp. The intensity of xenon light for these

exposures was 1.5 solar constants. The film specimens were irradiated for 100 and 200 hour periods which would result in 150 and 300 equivalent solar hours (esh) of film exposure.

2.5 Electron Radiation Exposure

The film specimens were irradiated with 1 MeV electrons in a clean high vacuum chamber at a pressure of 2.7×10^{-5} pascal. The specimens were mounted to a temperature-controlled aluminum plate which was perpendicular to the electron beam. The specimens received doses 1×10^8 , 1×10^9 and 5×10^9 rads at a rate of 5×10^7 rads/hr. Faraday cups mounted in the electron beam were used to measure the flux levels on the films. The films did not exceed a specimen temperature of 30°C during these exposures.

3. RESULTS AND DISCUSSION

3.1 Film Synthesis and Properties

The polyamic acid polymers and corresponding polyimide films prepared for evaluation in this investigation are listed in Table I. Reaction of the polymer-pure monomers in DMAc yielded pale yellow to colorless, viscous polyamic acid solutions with inherent viscosities ranging from 0.41 to 1.20 dl/g. The thermal

imidization of these polymers resulted in tough flexible linear polyimide films ranging in color from very pale yellow to essentially colorless at a thickness of 0.50 mil. The high optical transparency of these films was due to changes in molecular structure which caused a reduction in both inter- and intra-chain electronic interactions.⁽²⁾

As shown in Table I, glass transition temperatures (T_g) of the polyimide films measured by TMA ranged in value from 167° to 279°C. Polymer decomposition temperatures (PDT) were taken from the intersection of tangents drawn to the zero and maximum weight loss portions of the dynamic TGA curves. PDT ranging from 515° to 550°C indicate thermal stabilities expected of linear aromatic polyimides.

3.2 Ultraviolet Irradiation of Films

UV-visible transmission spectra of the transparent polyimide films under investigation are compared to that of commercial Kapton® H film in Figure 2. No distinct peak maxima were obtained. The position of the UV-Vis transmission cut-off was directly related to the color intensity of the film. The most intensely colored yellow Kapton® film exhibited a

transmission cut-off at approximately 500 nm. The very pale yellow to colorless films displayed transmission cut-offs between 350 and 400 nm. The most transparent of these was the 6F + DDSO₂ polymer which was characterized by a UV cut-off at the shortest wavelength (350 nm) of those studied. The spectra of the "control" films shown in Figure 2 provided a basis for comparison with subsequent irradiated films. Great care was taken to irradiate only those films measuring a nominal 0.50 mil in thickness so that any differences noted in UV-Vis spectra after irradiation could be deemed due to changes in polymer molecular structure or degradation.

The first UV irradiation experiment was conducted to determine the effect of background on film degradation during irradiation. The least colored 6F + DDSO₂ film and the most intensely colored of the transparent films ODPa + APB were chosen for this experiment. UV-Vis spectra were obtained on these films after 150 esh and 300 esh UV irradiation mounted against both a black absorbing surface and a silver reflecting surface (Figures 3a and 3b). Considerable absorption occurred upon irradiation of 6F + DDSO₂. Irradiation against a reflecting background reduced the transparency of the film to a higher degree than

an absorbing background. This phenomenon was to be expected as the incident radiation is reflected off of the highly reflecting silver surface and can make a second pass through the film causing further degradation. No discernible difference could be detected in the UV-Vis spectra of ODPA + APB against Ag vs. black background after 150 esh irradiation. However, a greater loss in transparency was detected for this film on a silver background after 300 esh irradiation (Figure 3b). All subsequent UV irradiation experiments were performed on films against silver-deposited surfaces to best simulate a second-surface mirror thermal control coating.

The UV-Vis spectra of films irradiated for 150 esh are shown in Figure 4. Transmission of the polyimide films ranged from 72 to 88% compared to 35-37% for Kapton® at 500 nm, the wavelength of peak intensity for solar radiation.⁽¹⁾ After 300 esh irradiation (Figure 5), the films prepared for this evaluation retained 62% (6F + DDSO₂) to 82% (6F + BDAF) transparency at 500 nm compared to 35% transparency for Kapton® film. From these results, it is evident that the transparent polyimide films of the present study would provide 2 times greater efficiency as coatings in

second-surface mirrors than commercial polyimide film based upon UV irradiation data.

It should also be noted that those polymers containing both oxygen and -C(CF₃)₂ linkages, 6F + BDAF and 6F + APB, performed best upon UV irradiation. On the other hand, the presence of sulfur atoms in the polymer molecular structure seemed to enhance degradation.

3.3 Electron Irradiation of Films

The first in a series of three electron irradiation experiments was a 2 hour exposure of the polyimide films to 1 MeV electrons at 5×10^7 rads/hr resulting in a total dosage of 1×10^8 rads. The UV-Vis spectra of films after exposure in this initial screening are shown in Figure 6. There was overall little sacrifice in the transparency of the films after exposure to 1×10^8 rads. The positions of transmission cut-offs remained close to the same order as for the control films (Figure 2) with 6F + DDSO₂ having a cut-off at the shortest wavelength and ODPA + APB having a cut-off at the longest wavelength other than Kapton®.

The second experiment was comprised of a 20 hour exposure of the polyimide films to 1 MeV electrons at 5×10^7 rads/hr

resulting in a total dosage of 1×10^9 rads. The UV-Vis spectra of films after exposure to 1×10^9 rads are displayed in Figure 7. All of the transmission cut-offs are displaced to the right toward longer wavelength as compared to the Control Films in Figure 2. However, overall transparencies compared to Kapton® remain excellent.

The third experiment was comprised of a 100 hour exposure to 1 MeV electrons at 5×10^7 rads/hr giving the films a total dosage of 5×10^9 rads. Results from this final exposure are shown in Figure 8. Surprisingly, there is very little difference in the position of the UV-Vis cut-off peaks for all of the transparent films prepared for this study. The peaks seemed to have converged with the average cut-off in the area of 400 nm. The transparent polyimide films retained excellent transmission (80-90%) at 500 nm after exposure of 5×10^9 rads compared to Kapton® (35%).

3.4 Infrared Spectroscopy

FTIR spectra were obtained on 6F + DDSO₂, 6F + BDAF and Kapton® film before and after exposure to 300 esh UV radiation and 5×10^9 rads 1 MeV electron radiation. Spectra were then obtained by subtracting spectra of the

irradiated films from the control film spectrum before irradiation. No changes in spectra of the films could be detected upon irradiation by UV or electrons. Changes in molecular structure due to UV or electron irradiation as per the above experiments were therefore not detectable by FTIR.

3.5 Film Solubilities

Particular attention should be given to the fact that reduction of inter- and intra-chain electronic interactions in polyimides not only can reduce the intensity of color of the resulting polymer but also can enhance polymer solubility.⁽²⁾ Solubilities of the films used in this investigation are shown in Table II in comparison to Kapton® H film. The 6F + DDSO₂ and 6F + BDAF polymers exhibited full solubility at 1% solids (ambient temperature) in both amide-type and chlorinated solvents. Solubility in a low-boiling solvent such as CHCl₃ should make these polymers especially attractive as spray-coatings for space applications where the substrate cannot endure the normal 300°C cure of conventional polyimides.

4. CONCLUSIONS

Six optically transparent aromatic polyimide films were prepared and evaluated as potential materials for use in space on future thermal control coating systems. The polyimide films of this investigation were 2 to 2.5 times more transparent than commercial polyimide film after both UV and electron irradiation experiments designed to simulate a second-surface mirror thermal control coating. Before irradiation the films were approximately 95% transparent at 500 nm, the wavelength of peak intensity for solar radiation, compared to approximately 40% for commercial polyimide film. After 300 equivalent solar hours of UV exposure the films retained a transparency between 62 and 82% at 500 nm compared to 35% transparency for commercial polyimide film. Films containing oxygen and $-C(CF_3)_2$ linkages in the backbone structure performed best after exposure to UV irradiation. The presence of sulfur atoms in the molecular structure seemed to enhance UV degradation. The films were less affected by electron irradiation, retaining 80-90% transparency at 500 nm after exposure to 5×10^9 rads 1 MeV electrons compared to 35% transparency for commercial polyimide film. No changes in the molecular structures of these polymer films

were discernible by FTIR upon UV or electron radiation exposure. Several of the polyimides studied were found to be soluble in low boiling solvents, which should increase their potential for spray-coating applications. The increased transparency (which translates into increased efficiency) and the enhanced solubility of these optically transparent polyimides make them viable candidates for further consideration for thermal control coating systems.

5. ACKNOWLEDGEMENTS

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7. BIOGRAPHIES

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Center, Hampton, VA. She received a B.A. degree in Chemistry from Queens College in 1969 and an M.S. in Chemistry from Virginia Polytechnic Institute and State University in 1972. From 1972 to 1977, she was employed as a Research Associate at NASA Langley Research Center. Mrs. St. Clair's field of research has included the synthesis and development of high temperature aerospace polymers for composites, adhesives, films and coatings applications.

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TABLE I. PROPERTIES OF TRANSPARENT POLYIMIDE FILMS

POLYMER	INHERENT			
	VISCOSITY (dl/g)	T _g (°C)	PDT (°C)	FILM COLOR (0.50 mil)
6F + DDSO ₂	0.47	279	520	COLORLESS
6F + APB	1.20	206	550	PALE YELLOW/COLORLESS
6F + BDAF	0.92	263	530	PALE YELLOW
ODPA + APB	0.87	187	535	PALE YELLOW
ODPA + BDAF	1.08	241	515	PALE YELLOW
BSDA + APB	0.41	167	520	PALE YELLOW/COLORLESS

TABLE II. SOLUBILITIES OF POLYIMIDE FILMS

POLYMER	FILM SOLUBILITY IN		
	DMF/DMAc	CHCl ₃	DIGLYME
6F + DDSO ₂	SOLUBLE	SOLUBLE	INSOLUBLE
6F + APB	PARTLY SOLUBLE	PARTLY SOLUBLE	PARTLY SOLUBLE
6F + BDAF	SOLUBLE	SOLUBLE	INSOLUBLE
ODPA + APB	PARTLY SOLUBLE	PARTLY SOLUBLE	INSOLUBLE
ODPA + BDAF	PARTLY SOLUBLE	PARTLY SOLUBLE	INSOLUBLE
BSDA + APB	PARTLY SOLUBLE	PARTLY SOLUBLE	INSOLUBLE
Kapton®	INSOLUBLE	INSOLUBLE	INSOLUBLE

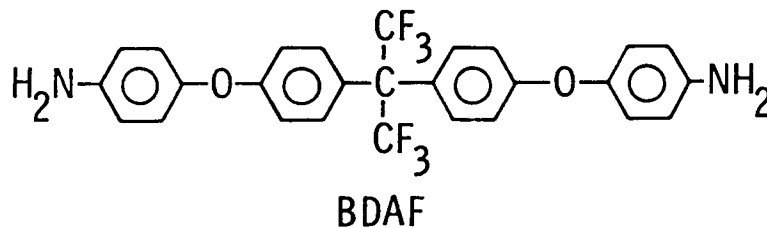
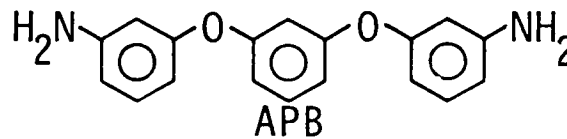
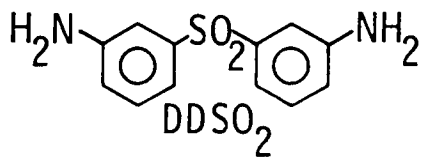
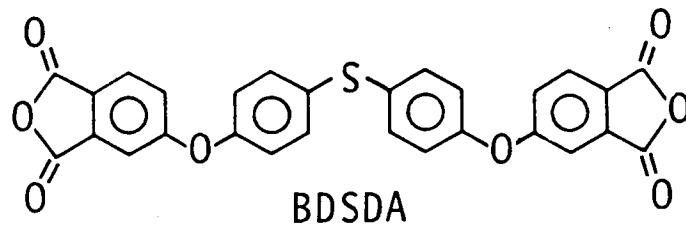
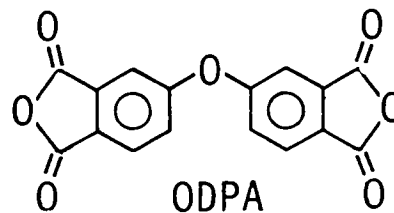
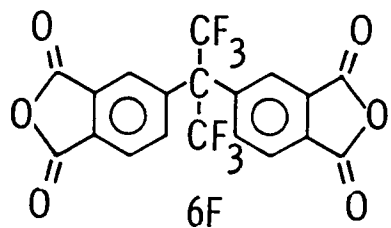


FIGURE 1. DIANHYDRIDE AND DIAMINE MONOMERS.

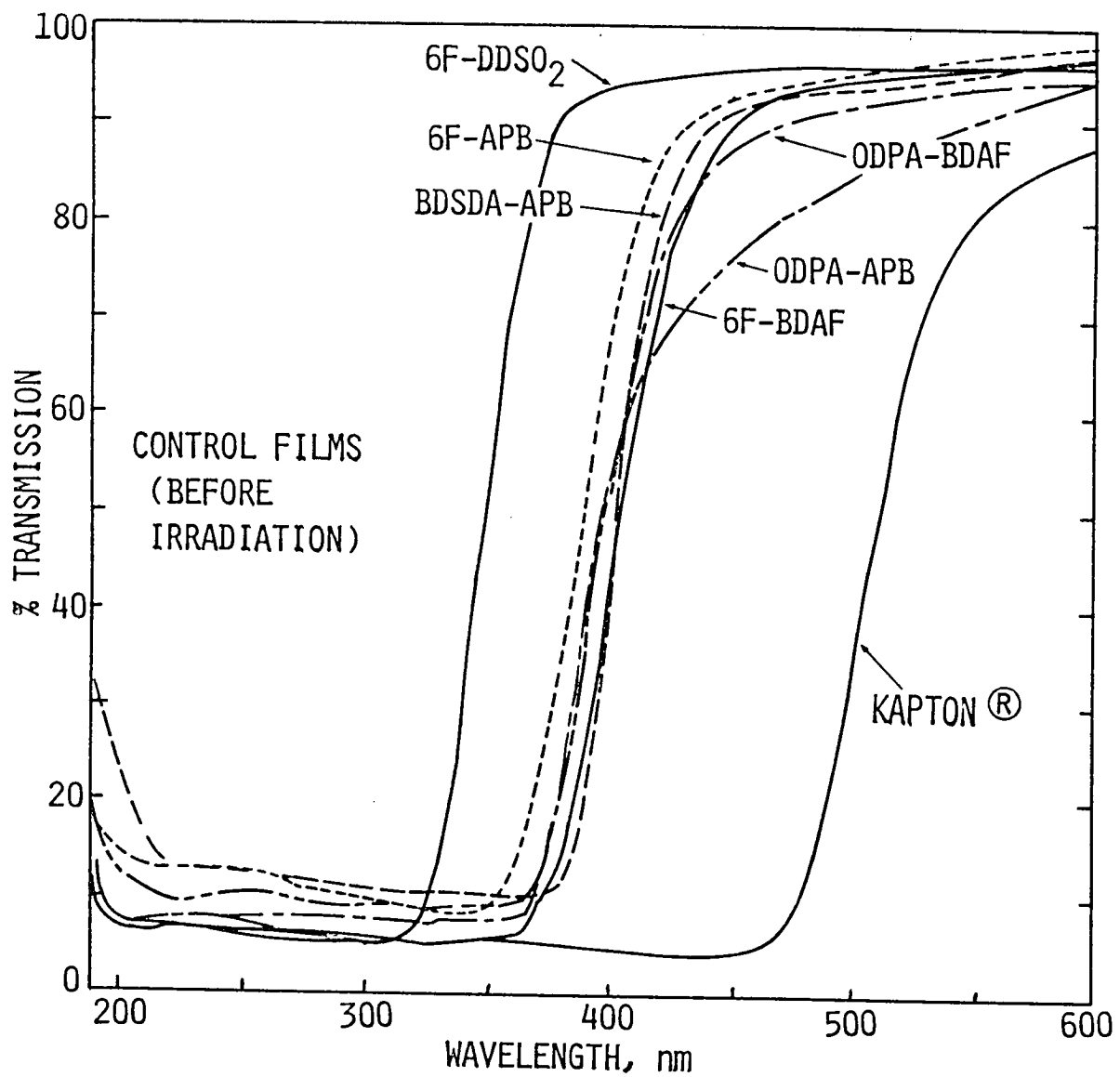


FIGURE 2. UV-VIS SPECTRA OF POLYIMIDE CONTROL FILMS.

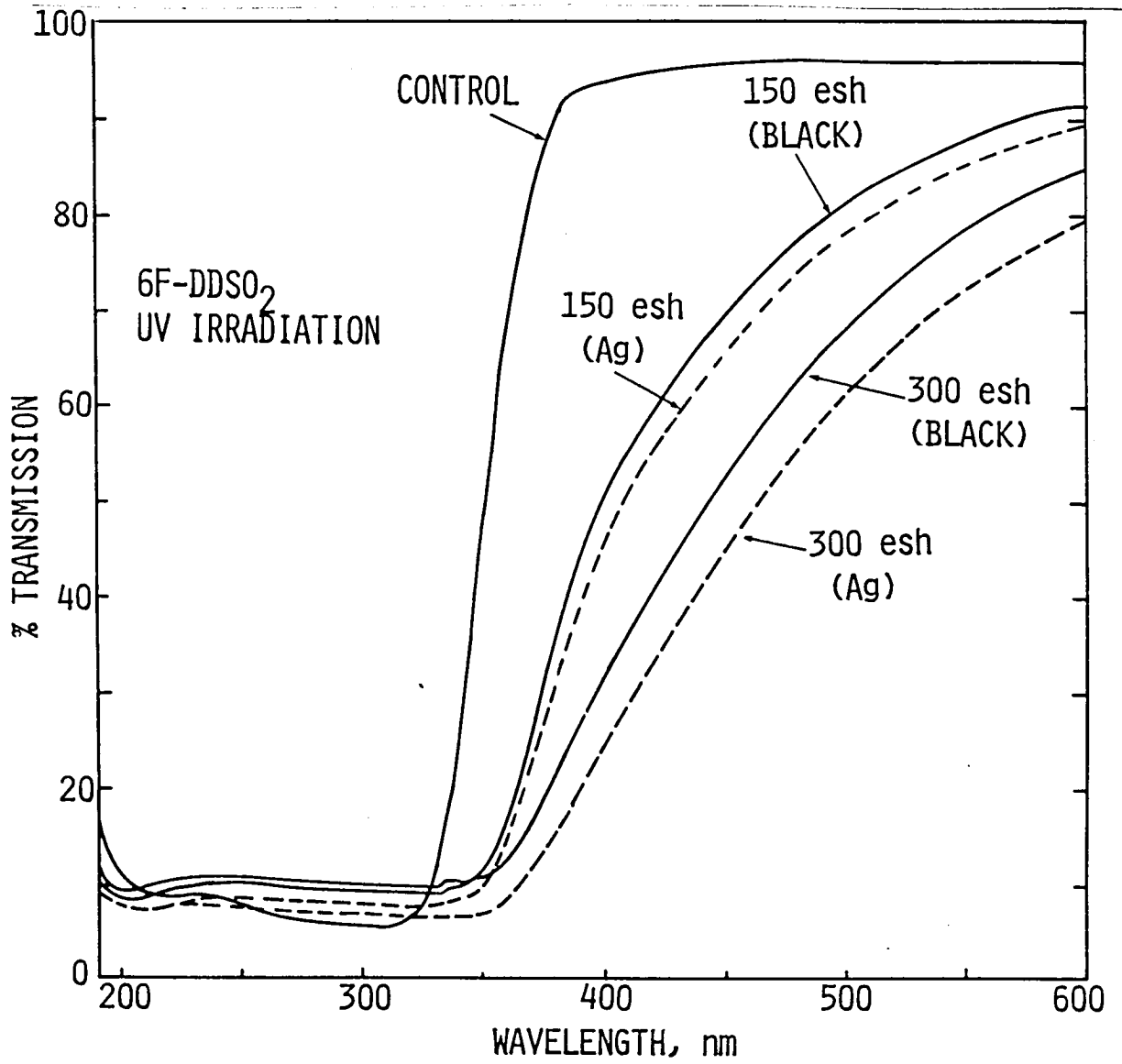


Figure 3a. UV-VIS Spectra of UV-Irradiated 6F-DDSO₂ vs Background.

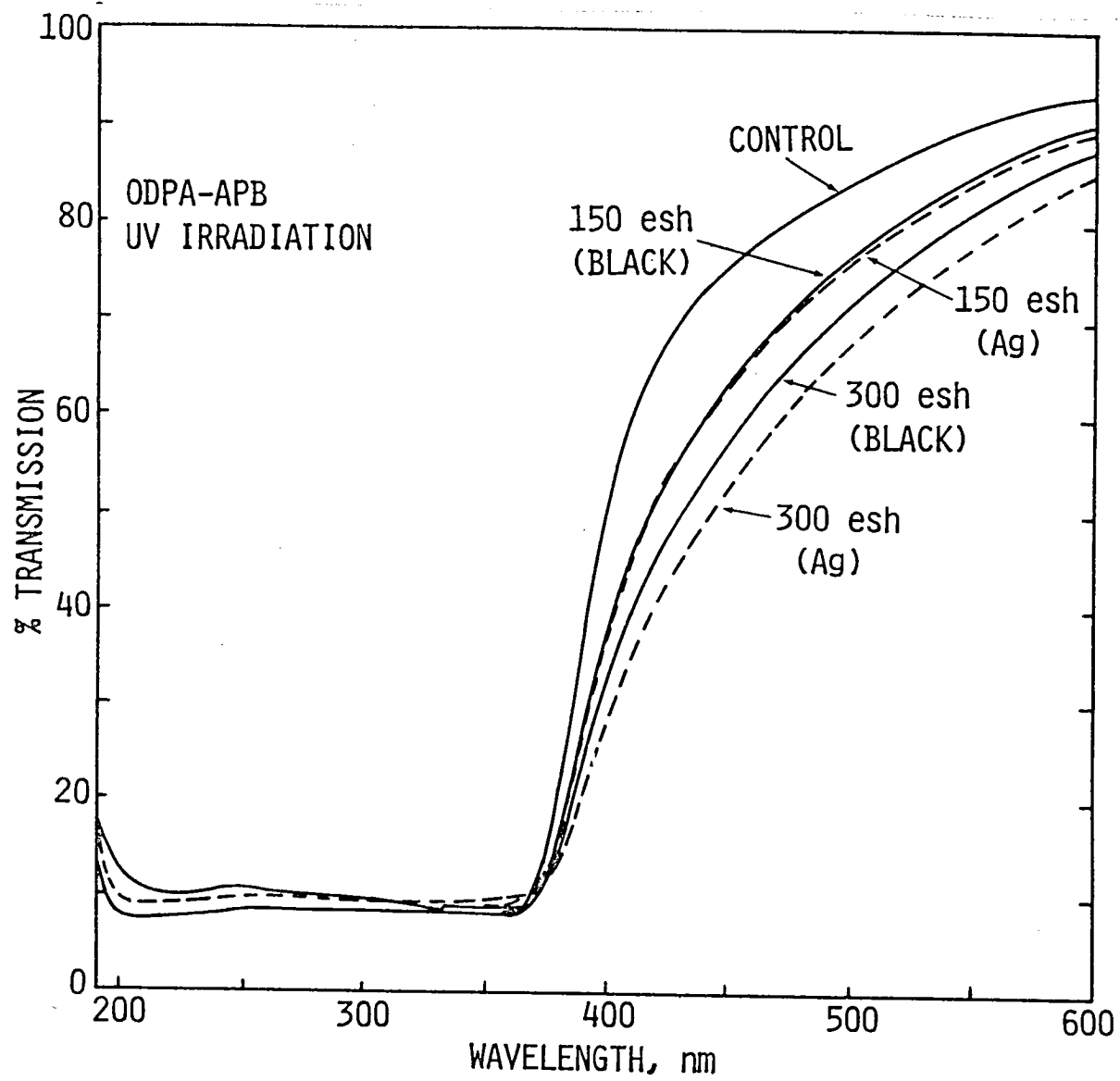


Figure 3b. UV-Vis Spectra of UV-Irradiated ODPA-APB vs Background.

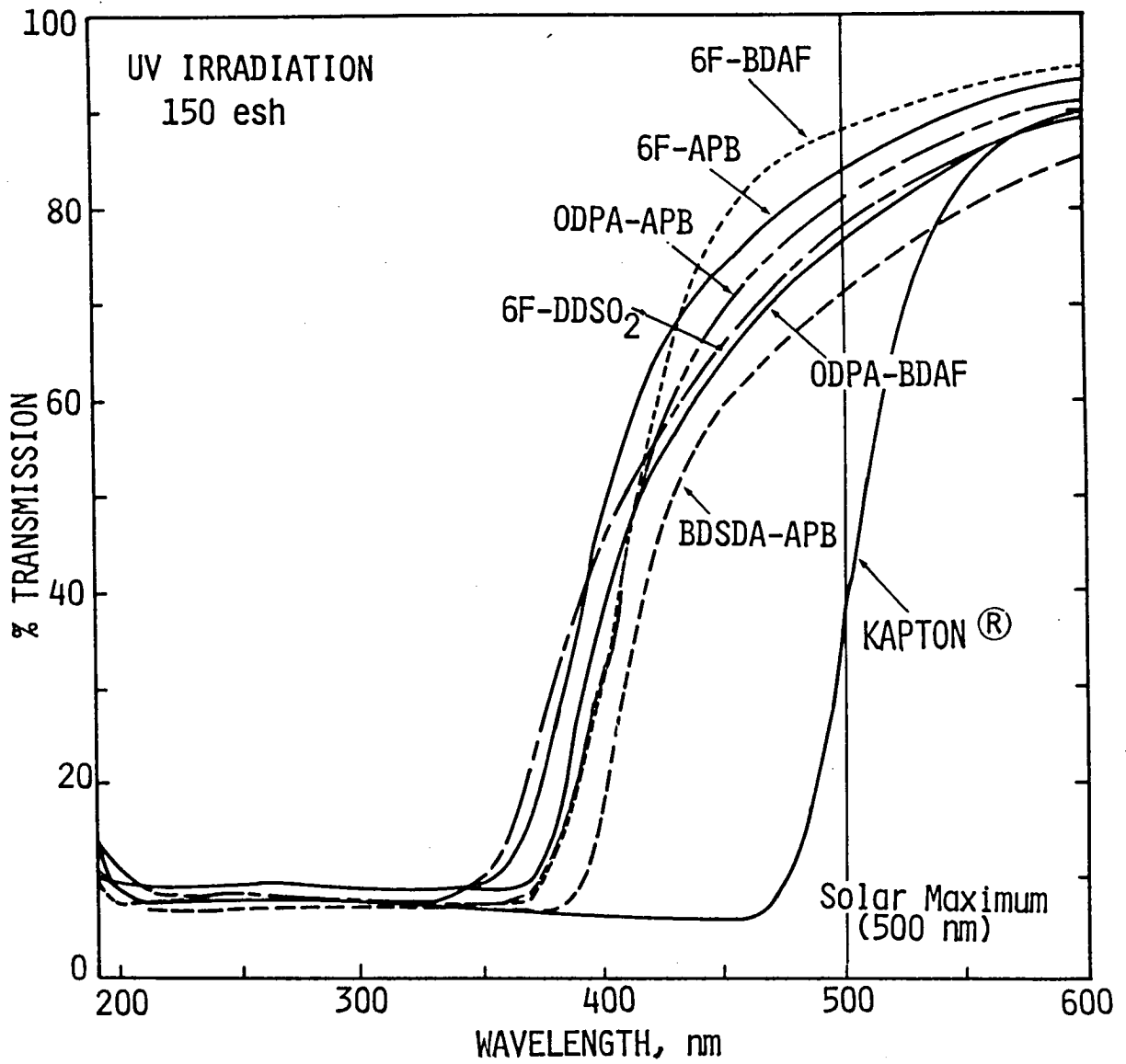


FIGURE 4. UV-VIS SPECTRA OF UV IRRADIATED POLYIMIDE FILMS.

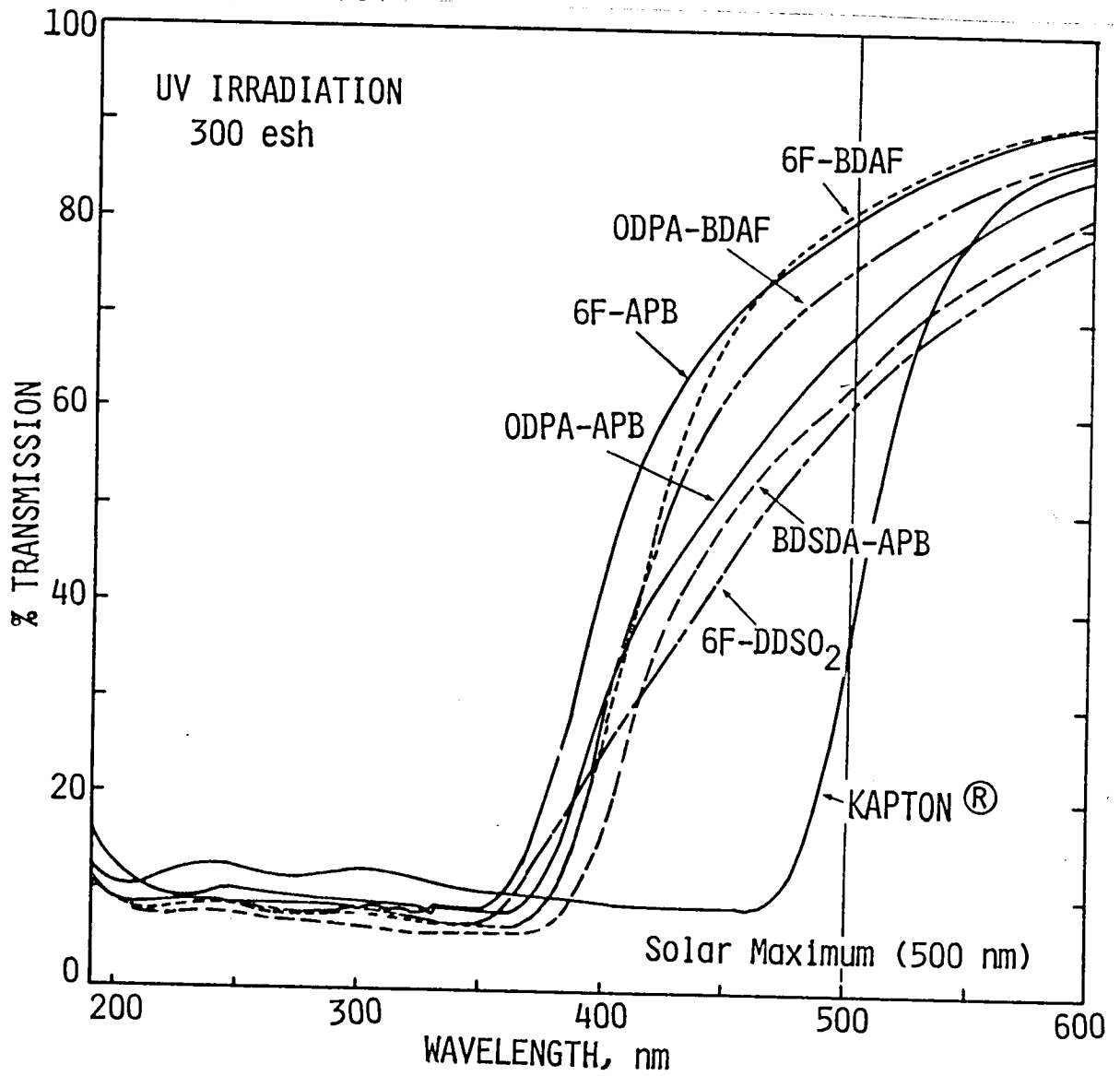


FIGURE 5. UV-VIS SPECTRA OF UV IRRADIATED POLYIMIDE FILMS.

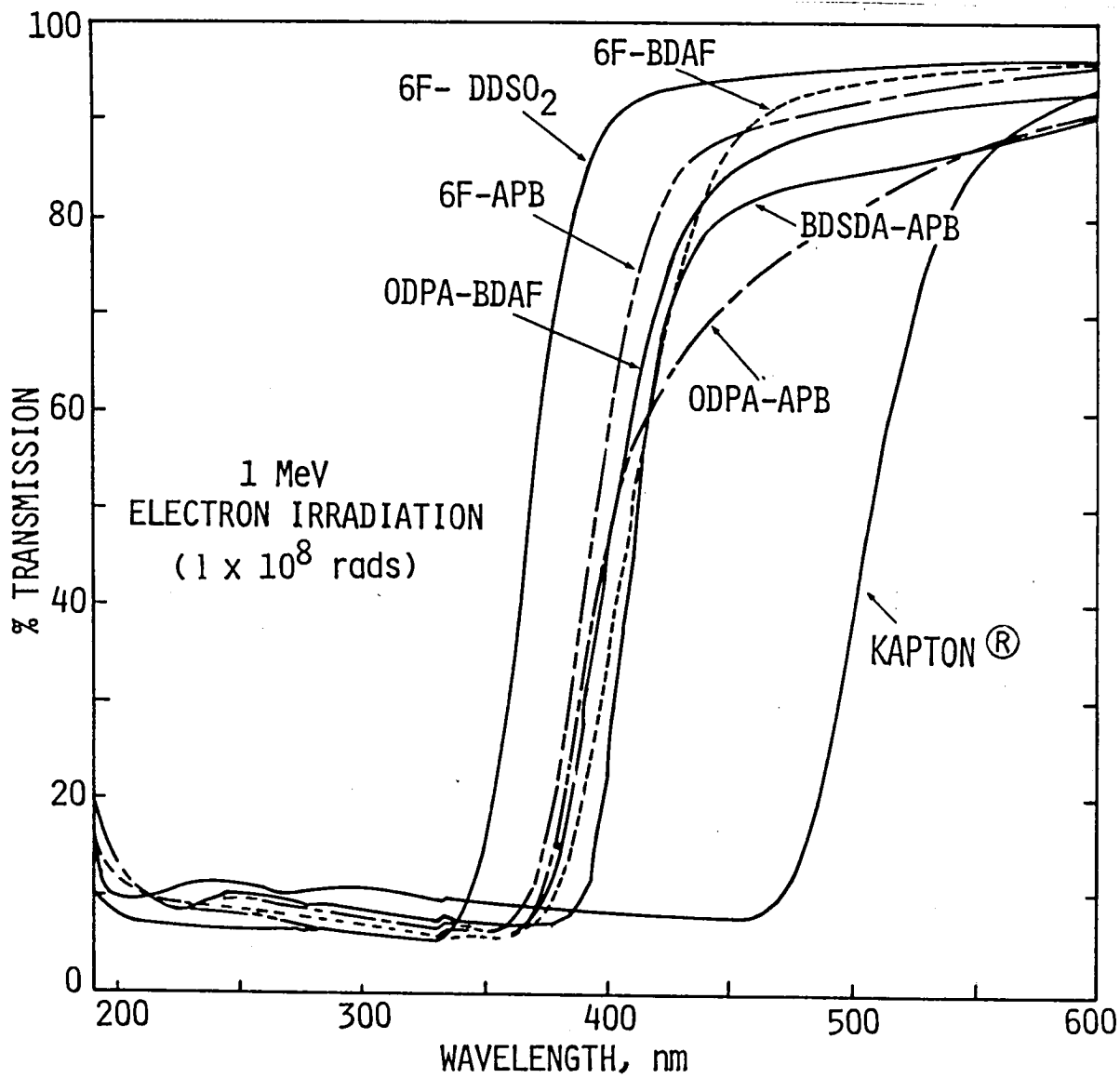


FIGURE 6. UV-VIS SPECTRA OF ELECTRON IRRADIATED POLYIMIDE FILMS.

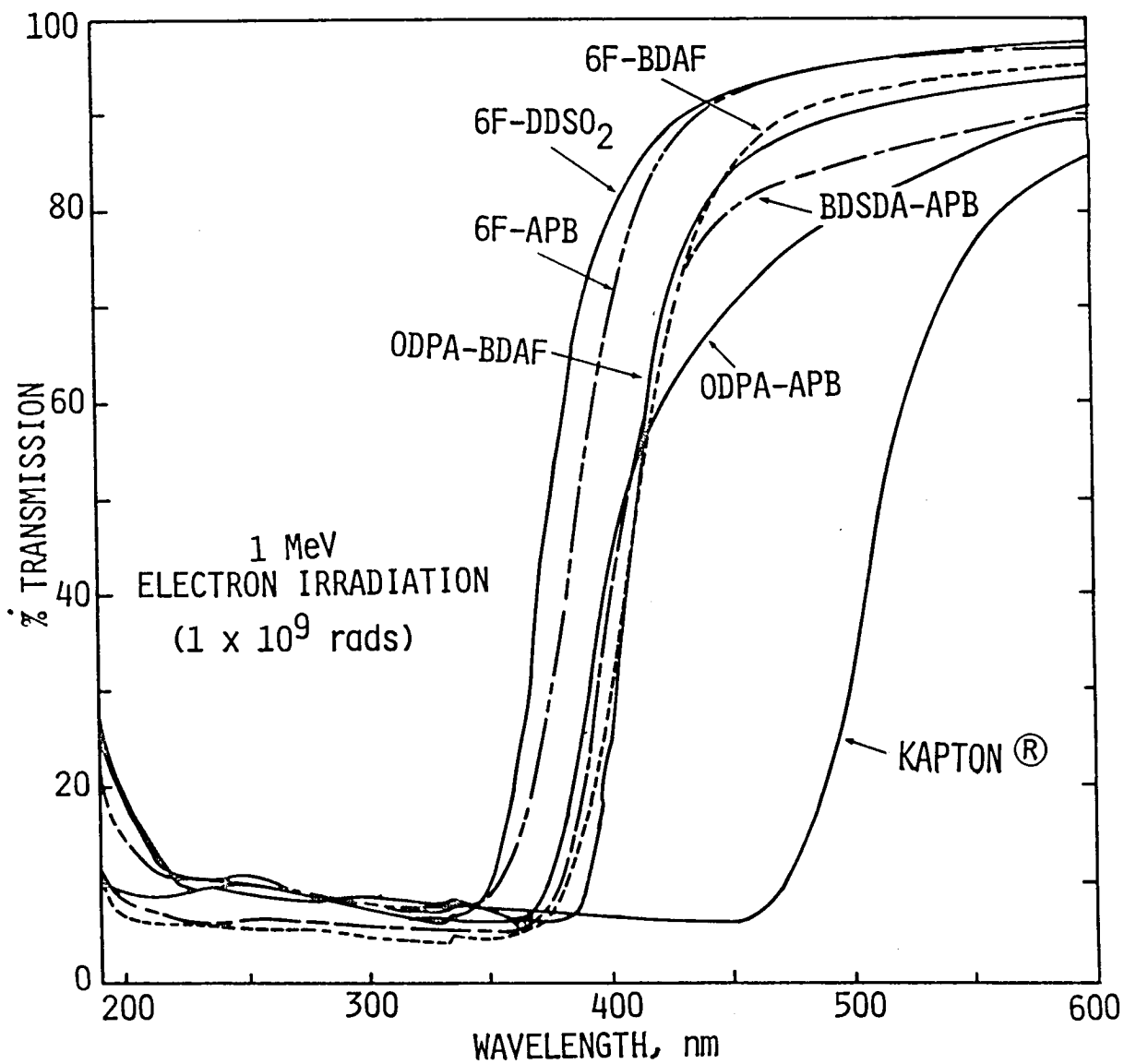


FIGURE 7. UV-VIS SPECTRA OF ELECTRON IRRADIATED POLYIMIDE FILMS.

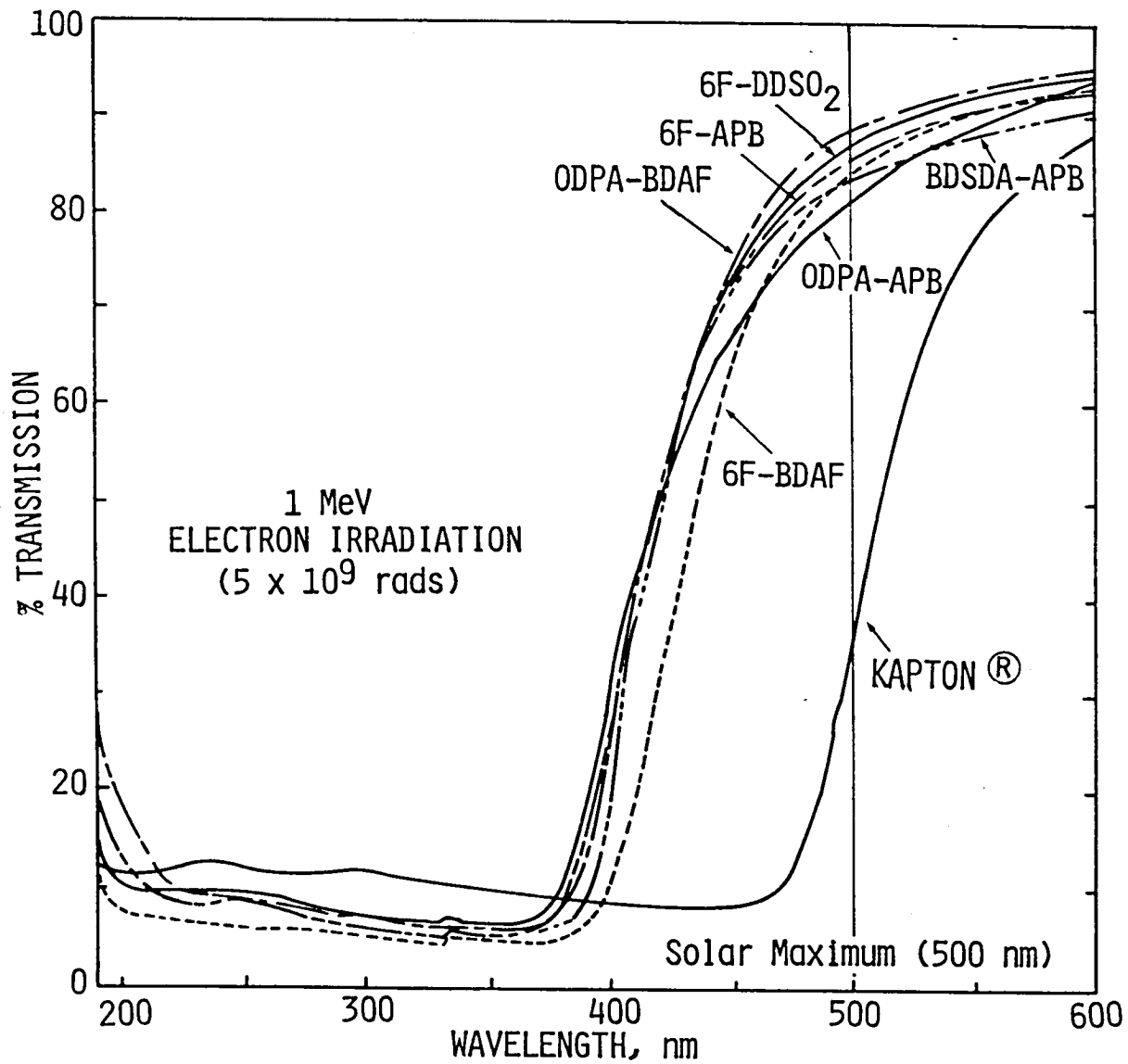


FIGURE 8. UV-VIS SPECTRA OF ELECTRON IRRADIATED POLYIMIDE FILMS.

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9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665				10. Work Unit No.	
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12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
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