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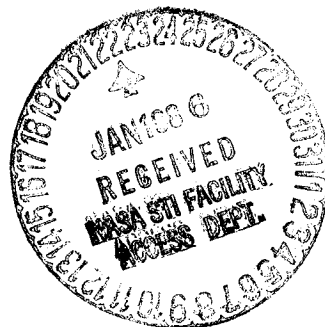
OPTICALLY TRANSPARENT/COLORLESS POLYIMIDES

Anne K. St. Clair, Terry L. St. Clair,
Wayne S. Slemp, and Keziban S. Ezzell

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Hampton, Virginia 23665

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Anne K. St. Clair, Terry L. St. Clair and Wayne S. Slemp

Materials Division, NASA Langley Research Center

Hampton, VA 23665-5225

Keziban S. Ezzell

Aerospace Technologies Division, PRC Kentron Inc.

Hampton, VA 23666

ABSTRACT: Several series of linear aromatic polyimide films have been synthesized and characterized with the objective of obtaining maximum optical transparency. Two approaches have been used as part of this structure-property relationship study. The first approach was to vary the molecular structure so as to separate chromophoric centers and reduce electronic interactions between polymer chains to lower the intensity of color in the resulting polymer films. A second and concurrent approach has been to perform polymerizations with highly purified monomers. Glass transition temperatures of thermally cured polyimide films were obtained by thermomechanical analysis and thermal decomposition temperatures were determined by thermogravimetric analysis. Transmittance UV-visible spectra of the polyimide films were compared to that of a commercial polyimide film. Fully imidized films were tested for solubility in common organic solvents. The more transparent films prepared in this study have been evaluated for use on second-surface mirror thermal control coating systems. Lightly colored to colorless films were characterized by UV-visible spectroscopy before and after exposure to 300 equivalent solar hours UV

irradiation and varying doses of 1 MeV electron irradiation. The effects of monomer purity, casting solvent and cure atmosphere on polyimide film transparency were also investigated.

Introduction

Because of their inherent toughness and flexibility, low density, remarkable thermal stability, radiation resistance and mechanical strength, aromatic polyimides have excellent potential for use as advanced materials on large space structures. A need exists for high-temperature (200°-300°C) stable, flexible polymeric film and coating materials that have high optical transparency in the 300-600 nm range of the electromagnetic spectrum for applications on space components such as multilayer insulation blankets, solar cells, and thermal control coating systems. Although several classes of polymers are available 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. Linear all-aromatic condensation polyimides are generally known for their intense yellow color.[1] Commercial aromatic polyimide film is approximately 70% transparent (depending on thickness) at 500 nm which is the solar wavelength of interest for space applications. After aging in a space environment, however, the film transparency is reduced.

A recent research effort was conducted to synthesize and characterize linear aromatic polyimide film having maximum optical transparency.[2]

Several series of highly optically transparent films were produced by making

variations in the polymer molecular structure aimed at reducing electronic

interactions between polymer chains. Polymerizations were performed with

highly purified monomers. The more transparent films were further evaluated

for use in a space environment.[3] Irradiation experiments were designed to

simulate use of the transparent films as part of second-surface mirror

thermal control coatings.[4] This paper will review past work with the

introduction of several new polymer systems. The effects of changes in

molecular structure on polyimide film transparency/color and solubility have

been investigated in this structure-property relationship study. The

effects of monomer purity, casting solvent, and cure atmosphere on film

transparency have also been investigated.

Experimental Section

Materials. The aromatic diamine monomers used in this study are shown

in Figure 1. The 3,3'-diaminodiphenylsulfone ($DDSO_2$) and 2,2-bis[4-(4-

aminophenoxy)phenyl]hexafluoropropane (BDAF)[5] were obtained from commercial

sources and purified by recrystallization, m.pts. 173° and 162°C respective-

ly. The 1,3-bis(aminophenoxy)benzene (APB) was obtained commercially and

vacuum distilled, m.pt. 105°C. The 3,3'-oxydianiline (3,3'-ODA) was an

experimental material obtained from Mitsui Toatsu, Inc. and was sublimed,

m.pt. 78°C, and the 2,2'-bis(3-aminophenyl)hexafluorpropane (3,3-6F) was an

experimental material obtained from American Hoechst and was recrystallized,

m.pt. 79°C. The aromatic dianhydride monomers used in this study are shown

in Figure 2. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone

tetracarboxylic dianhydride (BTDA), and 2,2-bis(3,4-dicarboxyphenyl)hexa-

fluoropropane dianhydride[6] (6F) were obtained from commercial sources and purified by vacuum sublimation, m.pts. 284°, 222°, and 243°-244°C respectively. The BTDA was also recrystallized prior to sublimation. The 4,4'-oxydiphthalic anhydride (ODPA) was an experimental monomer obtained from Ciba Geigy and was sublimed, m.pt. 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[7] and was used as received, m.pt. 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.

Preparation of Polyamic Acids and Polyimide Films. The reaction route for preparing polyamic acids and polyimide films is shown in Figure 3. The polyamic acid precursor solutions were prepared in closed versels at ambient temperature at a concentration of 15% (w/w) solids in DMAc. The solid dianhydride monomer was added all in one portion to an equimolar amount of diamine dissolved in DMAc. After mechanically stirring for 8-24 hours, the resulting polyamic acid solutions were refrigerated. Polymer films were prepared by casting the polyamic acid resins onto glass plates in an enclosed dust-free chamber at a relative humidity of 10%. Solutions were spread with a doctor blade and gaps were set so as to ensure final film thicknesses of 1 mil, 0.5 mil and 0.2 mil. Polyamic acid films were thermally converted to the corresponding polyimide films by heating in a forced air oven for one hour each at 100°, 200° and 300°C.

Characterization. Monomer melting points were determined on an E. I. DuPont Model 900 Differential Thermal Analyzer at 10°C/min. 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 fully-cured 1 mil thick polymer films were measured by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in static air at 5°C/min. Polymer decomposition temperatures were obtained by thermogravimetric analysis (TGA) on 1 mil thick films heated at 2.5°C/min in either 15 cc/min flowing air or nitrogen. Transmission UV-visible spectra were obtained on 0.5 ± 0.03 or 0.2 ± 0.01 mil thick films using a Perkin-Elmer Lambda 5 UV-Vis spectrometer in the reflectance mode with an Integrating Sphere Attachment. Infrared spectra were obtained on some films before and after irradiation using a Nicolet 60SX Fourier Transform Infrared Spectrometer. Polymer films cured at 300°C were tested for solubility at approximately 1% (w/w) in DMAc, $CHCl_3$ and 2-methoxyethyl ether (diglyme).

Radiation Exposure. Polyimide films measuring 0.50 mil in thickness 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 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. Films were mounted on a reflecting silver surface vacuum deposited on aluminum to simulate a second-surface mirror thermal control coating. 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.

Polyimide film specimens (.5 mil thick) were also 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.

Results and Discussion

The polyimide films prepared from the monomers shown in Figures 1 and 2 are listed in Table I. Reaction of polymer-pure monomers in DMAc yielded pale colored to colorless polyamic acid solutions with a range in inherent viscosities of 0.27 to 1.20 dl/g. Clear, tough and flexible films were prepared from all of the polymer solutions listed. Thermal conversion of the polyamic acid films at 300°C in a forced air atmosphere produced polyimide films which displayed the characteristic imide-related infrared absorption bands at 1770-1790, 1710-1735, and 742-747 cm^{-1}. The polyimide films generally varied in color from yellow for those polymers prepared from the more conventional BTDA and PMDA dianhydrides to pale yellow/colorless for polymers which contained BDSDA, ODPA and 6F dianhydrides. Glass

transition temperatures (T_g) of the fully cured films ranged from 167°-338°C. This vast range in T_g values reflects the wide variation in molecular structures represented in these series of polymers. Polymer T_g increased according to the dianhydride structure used in the following order: BDSDA < ODPA < BTDA, 6F < PMDA. The APB diamine monomer, with its meta-orientation and flexible oxygen links caused an overall depression in T_g compared to other diamines studied. There was a significant reduction in the T_g of polymers prepared using the meta-oriented 3,3'-ODA diamine when compared to those previously reported containing 4,4'-ODA. 6F + 3,3'-ODA displayed a T_g of 244°C compared to a T_g of 307°C[8] for the 6F + 4,4'-ODA polymer prepared from the para-oriented diamine. An even greater difference in T_g was found in comparing that of ODPA + 3,3'-ODA (192°C) and ODPA + 4,4'-ODA (270°C).[8]

Transmission UV-visible spectra of films listed in Table I containing APB, BDAF, and DDSO$_2$ diamines have been previously reported.[2] All of these films and those prepared from 3,3'-ODA and 3,3'-6F diamines displayed strong absorptions with transmission cut offs located between 310 and 388 nm for 0.2 mil films. The cut-off of Kapton H Film is 450 nm by comparison. No distinct peak maxima were obtainable. The positions of the transmission cut-off curves were directly related to the color intensity of the films. Absorption occurred further into the UV range for the more transparent films. The wavelengths for the UV cut-off absorptions of the films listed in Table I were taken from the tangents to the transmission curves. Care should be taken in using these values to judge relative color intensity of the polymer films due to the variation in the slopes of the transmission curves. For example, the UV-vis spectra of polymers prepared from BDAF

diamine in Figure 5 show the PMDA + BDAF transmission curve to be broader in comparison to the other curves. The relatively low cut-off at 340 nm is somewhat misleading for this yellow-colored film. In general, the 6F, ODPA and BDSDA polymers were found to have the greater optical transparency compared to those derived from PMDA or BTDA. The polymer films prepared from 6F dianhydride, absorbed at the lower wavelengths and correspondingly had the highest optical transparency over the broadest range. The 6F + DDSO$_2$ and 6F + 3,3'-ODA[9] films were "water-white" colorless in appearance.

Effect of Film Thickness on Color. Special care was taken in this structure/property relationship study to compare films of the same thickness. The UV-visible spectra of 6F + DDSO$_2$ films of three thicknesses are displayed in Figure 5. UV-visible absorption is known to be a function of concentration (or in this case, film thickness). All of the compared spectra shown in these investigations were obtained on either 0.2 ± 0.01 mil or 0.5 ± 0.03 mil thick films which required extremely tedious attempts at film casting to produce these required thicknesses. The variation in thickness of 6F + DDSO$_2$ films from 0.2 to 0.4 mil produced little change in the position of the transmission cut-off for this particular polymer. However, it was determined that slight variations in the thickness of a more highly colored film produced more of an impact on the UV-visible transmission spectrum. Therefore, only films of the same thickness were compared to completely eliminate this factor as a variable.

Effects of Monomer Purity, Casting Solvent and Cure Atmosphere on Color. A preliminary study has shown that the purity of the aromatic diamine and dianhydride monomers has a direct effect on the transparency of the resulting polyimide film. A number of polymer films have been prepared

with monomers of varying purities and their UV-visible spectra compared.[10]
In Figure 6, the effects of monomer purity on the UV-visible spectra of a
colorless film 6F + DDSO$_2$ are compared to that of a more conventional yellow
BTDA + 4,4'-ODA film. As should be the case, the purity of the starting
monomers had a pronounced effect on the inherent viscosities of the polyamic
acid precursors. The methods of purification and the melting points of the
monomers from which these two polymers were made are listed in Table II.
Melting points were determined by differential thermal analysis (DTA) as
described earlier in the experimental section. In Table II, DTA melt peak
values are compared to the onset of melting determined as the intersection
of tangents to the DTA curve. A comparison of these two values is an
indication of the degree of purity of the monomer. The closer together
these numbers occur, the more pure the material. The peak and onset melts
would be identical for a material of 100% purity. As shown in Table II, the
difference between peak and onset melting points was greater for the "as
received" monomers than for those which were recrystallized and/or
sublimed. Purification of monomers had a relatively small but observable
effect on the transparency of the 6F + DDSO$_2$ polymer system (Figure 6). A
more significant effect on transparency was noted when spectra of BTDA +
4,4'-ODA films prepared from polymer-pure versus as-received monomers were
compared. In subsequent studies, the use of impure BTDA with its high acid
content was found to be the major cause of reduced optical transparency and
low inherent viscosity.[10] Spectra shown in Figure 6 were obtained on 0.2
mil films prepared from the same solvent and cured under identical
conditions.

Additional experiments were conducted to determine the effects of casting solvent and cure atmosphere on the transparency of polyimide film. Several 6F + APB polyamic acids containing identical monomers were prepared in dry DMAc, N-methylpyrollidone (NMP), and a 20:80 mixture of NMP and diglyme solvents. Films cast from each resin were cured under identical conditions and had a final film thickness of 0.2 mil. No effect on transparency was noted in the comparison of the UV-visible spectra of the 6F + APB films prepared from the three different solvent systems. Likewise, no apparent effect on film transparency was observed by varying the cure atmosphere. Films of all the APB, DDSO$_2$ and BDAF polymers listed in Table I were cast and cured in a dry inert nitrogen atmosphere at 300°C. The UV-visible spectra of these 0.2 mil films were compared to those prepared from identical monomers and solvents but cured in a forced air atmosphere at 300°C. Essentially no changes in the UV-vis spectra of the films studied were obtained upon varying the cure atmosphere from air to nitrogen. Previous studies have shown that substantially darker colored films are produced when polyamic acids are thermally converted in air versus inert nitrogen or vacuum.[8,11,12] These studies, however, have shown that darkening of films cured in air is due to oxidative crosslinking and degradation of such polymer moieties as aliphatic CH$_2$ groups. The polymer films of the present study had no such groups present.

Effect of Polymer Molecular Structure on Color. Alterations in the molecular structure of linear aromatic polyimides have been shown in previous[2] and the present studies to have an effect on the optical transparency of fully imidized films. These studies were specifically designed for the purpose of reducing color intensity in polyimide films by

separating or removing chromophores, eliminating conjugation, and reducing overall electronic interactions between polymer chains. Introduction of oxygen or sulfur "separator" groups; incorporation of bulky electron withdrawing groups such as $-CF_3$ or $-SO_2$ groups; use of meta isomerism in the aromatic diamine portion of the polymer; and removal of known chromophores such as $-C=O$ groups have all contributed in the reduction of color intensity of these polyimide films compared to conventional bright to dark yellow (depending on thickness) polyimide film. As shown by preceeding experiments, pure monomers are also a necessary factor in obtaining pale to colorless polyimide film. We believe, however, that the major contributing factor to obtaining colorless polyimide film is due to the reduction or removal of electronic interactions due to charge transfer complexing.

The first mention of charge transfer complex (CTC) formation in polyimides was made in 1971 by Dine-Hart and Wright[13] in a study of model imide compounds. The Russian literature later offered that once condensed, the imide portion of a polyimide chain may retain its electron donor character enough to form CTC with an electron acceptor such as n-chloranyl.[14] It had previously been shown that phthalimides can form CTC with electron donors such as biphenyl, naphthalene or anthracene.[15] In 1977, Kotov et al confirmed the occurrence of CTC in polyimides in a study of the electron absorption spectra of several polypyromellitimides and their model compounds.[16] In this work, donor-acceptor electronic interaction in linear aromatic polyimides was explained in terms of ionization potentials and electron affinities of corresponding structural elements. Gordina and Kotov's work is supported by Fainshtein, et al[17] who report the donor-acceptor reaction of separate polymer fragments and CTC formation as being

responsible for the high-pressure electro-conductance of aromatic polyimides. The reduction of CTC formation and thereby the T_g is reported by Fryd[18] to occur upon: (1) introduction of separator groups into the dianhydride portion of a polyimide to reduce electron affinity, and (2) introduction of meta diamines which distort chain packing.

Introduction of bulky electron-withdrawing groups such as $-CF_3$ or $-SO_2$ groups as proposed in the present study used in conjunction with meta-oriented diamines appears to essentially eliminate CTC in aromatic polyimides resulting in colorless films. Although the use of separator groups such as -O- or -S- in both dianhydride and diamine portions served to reduce overall color intensity in the polymers of this study, meta-isomerism and the placement of bulky groups in the chain had a greater effect in reducing color. For example the transmission cut-offs or absorption per the electronic spectra of polymers containing BDSDA and ODPA were shifted to lower wavelengths in comparison to PMDA polymers with the same diamine. This supports Fryd's[18] statements that the electron affinity of the powerful electron withdrawing anhydride groups is reduced by incorporation of separator groups and thus reduces CTC. However, if we substitute 6F dianhydride for BDSDA or ODPA the cut-off moves to even lower wavelength. The $-C(CF_3)$ group in this dianhydride is exceedingly electronegative and should contribute toward increasing the overall electron affinity of the dianhydride. Here, however, the sheer bulkiness of the group overrides the effects of electron affinity by blocking or hindering chain packing and any ability for CTC to occur. When 6F dianhydride is coupled with 3,3'-6F and $DDSO_2$ diamines, which each contain meta-orientation and bulky electron withdrawing groups, totally colorless polymers are produced. Evidence for

the above discussion is given in Table III where various aromatic polyimides prepared from 6F dianhydride are listed with their molecular structures and film color.

The structure of the aromatic diamine has also been found to affect the resulting color of aromatic polyimide films in this study. As noted in Table III, replacing 3,3'-ODA diamine for 4,4'-ODA in 6F dianhydride-containing polyimides results in a film color change from light yellow to pale/colorless. This color change is believed to be caused by a reduction in CTC due to the presence of the meta-oriented diamine. This work supports Fryd's[18] explanation of why meta isomerism in the diamine had a greater effect on lowering the T_g than did the introduction of flexibilizing groups. Preliminary data[19] from UV-visible spectral studies on 6F-ODA polyimides show the color/CTC of these polymers to decrease in the following order:

6F + 4,4'-ODA > 6F + 2,4'-ODA, 6F + 3,4'-ODA > 6F + 3,3'-ODA.
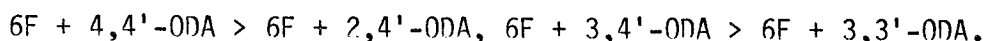
Effect of Polymer Molecular Structure on Solubility. The most popular method for obtaining soluble polymers in general has been the incorporation of organic groups pendant to the main chain. This approach has been reported and determined successful in obtaining soluble polyimides.[20-22] A second, less traditional approach to obtaining soluble fully aromatic polyimides has been the introduction of separator bridging groups in the dianhydride portion of the polymer and incorporation of isomeric diamines for further enhancement.[8] Solubilities of films prepared in the present study and cured at 300°C in air are given in Table IV. The data show the necessity of the dianhydride separator groups as previously reported in producing a soluble polyimide. However, the most soluble polymers produced

contained the bulky $-C(CF_3)_2$ group in the dianhydride. Although meta-isomerism of the aromatic diamine enhanced overall solubility of the polymer, use of this technique by itself did not produce soluble polymers. For example, the BTDA and PMDA polymers in Table IV which contained meta-oriented APB and $DDSO_2$ diamines were totally insoluble in all solvents tested. Likewise the incorporation of 3,3'-diaminobezophenone, 3,3'-methylenedianiline and m-phenylenediamine into both BTDA and PMDA polymers has produced insoluble films.[8]

The increased solubility of polymers in this and previous studies[8] can be explained in terms of the variation of molecular structure to reduce electronic interactions or charge transfer complex formation. Linking groups in the dianhydride which serve to reduce electron affinity, bulky $-CF_3$ and $DDSO_2$ groups, and meta-oriented diamines all serve to reduce CTC. Reduction or elimination of CTC should greatly facilitate the solvation of polymer chains.

In addition to the changes in polymer properties observed herein, preliminary data in our labs show that changing the molecular structure to reduce electronic interactions between chains in aromatic polyimides may affect not only film transparency and solubility, but may also enhance flow properties to provide improved processability.

Effect of UV Irradiation on Film Color. The UV-visible spectra of the more transparent films produced in this study (Table I) are reproduced in Figures 7 and 8. Transmission spectra of all of the 6F dianhydride-containing films are compared in Figure 7 to that of commercial Kapton® H film. The 0.5 mil films were approximately 95% transparent at 500 nm, the wavelength of peak intensity for solar radiation, compared to approximately

35% for the commercial film. All of these films except for the 6F + 3,3'-6F
were subjected to UV irradiation. After 300 esh irradiation (Figure 9), the
films containing 3,3'-ODA, APB and BDAF retained 82-84% transparency at 500
nm. The 6F + DDSO$_2$ retained 62% transparency. Prior to irradiation the
transparency of ODPA- and BDSDA-containing films ranged from 85-93% at the
solar maximum λ (Figure 8). Upon subjection to UV irradiation, the trans-
parency of these films was reduced to between 64 and 86% as shown in Figure
10. From the results in Figures 9 and 10, it is evident that the presence
of sulphur in the backbone of the polymers 6F + DDSO$_2$ and BDSDA + APB
enhanced UV degradation. Polymers containing oxygen and -C(CF$_3$)$_2$ groups,
however, performed exceedingly well. The 6F + 3,3'-ODA and ODPA + 3,3'-ODA
were the most UV-resistant films tested having 84 and 86% transparency at
500 nm after 300 esh aging. The loss in transparency from UV irradiation
was a minimal 9% and 6% for 6F + 3,3'-ODA and ODPA + 3,3'-ODA respectively.
All films including Kapton were flexible after UV irradiation.

Effect of Electron Irradiation on Film Color. The UV-visible spectra
of 6F-containing films after exposure to 5 x 10^9 rads 1 MeV electrons are
displayed in Figure 11. Surprisingly, the transmission curves converged
upon exposure of the films to electron irradiation with the average cut-offs
in the area of 380 nm. Transparency at 500 nm of these 6F films, however,
remained excellent ranging from 85 to 91%. The 6F + 3,3'-ODA film sacrific-
ed only 2% in transparency at 500 nm. The UV-visible spectra of ODPA and
BDSDA films after electron exposure are shown in Figure 12. The cut-offs of
these films also converged in the neighborhood of 380 nm though transparency
at 500 nm remained as high as 82 to 89%. Of the films shown in Figure 12,
ODPA + BDAF and ODPA + 3,3'-ODA were the best performers and lost only 4 to

5% in transparency at 500 nm upon irradiation. All of the films of this study remained flexible upon submission to 1 MeV electrons. The Kapton film, however, was found to be brittle when creased.

As found previously,[3] no changes in the UV or electron-irradiated films were detectable by Fourier transform infrared spectroscopy.

Thermal Stability of Transparent Films. Polymer decomposition temperatures (PDT) of the films studied are listed in Table I. PDT were taken as the intersection of tangents drawn to the zero and maximum weight loss portions of the dynamic TGA curves. The PDT ranged from 510° to 555°C as should be expected of linear aromatic polyimides. However, because the PDT do not fully indicate the thermal performance of a polymer at a given temperature, isothermal TGA data were obtained on the more transparent films.

Because weight loss in air of the films was minimal at 300°C, a higher temperature of 350°C was chosen to observe discrimination of curves for isothermal aging. Isothermal TGA curves of the 6F-containing films are presented in Figure 13 in comparison to that of Kapton film. Only the thermal stability of the 6F + DDSO$_2$ film was as excellent as Kapton after aging 300 hrs at 350°C in flowing air. The thermal stability of the remaining polymers decreased with the amount of oxygen present in the diamine portion of the polymer backbone as expected. Results from isothermal aging of the ODPA and BDSDA films were similar as shown in Figure 14. In general, the presence of -CF$_3$ groups enhanced thermal stability, while the presence of -O- enhanced degradation.

Because the desired application of these transparent films is for use in a space environment, two of the best performing films from the

irradiation experiments were isothermally aged in inert nitrogen at 350°C. The air and nitrogen isothermal TGA curves of 6F + 3,3'-ODA and ODPA + 3,3'-ODA are compared in Figure 15. After 300 hrs, the % weight loss for 6F + 3,3'-ODA was approximately the same for the film whether aged in air or nitrogen. From the slopes of these two curves, however, we would predict continued superior performance for the film aged in nitrogen but beginning degradation of the film aged in air. The ODPA + 3,3'-ODA performed better upon aging at 350°C in nitrogen than in an oxygen-containing environment.

Conclusions

Several series of linear aromatic polyimide films have been synthesized with the objective of obtaining maximum optical transparency. This goal was achieved by the removal of existing chromophores, the purification of start-ing materials, and by the reduction of conjugation and electronic interac-tions between polymer chains due to charge transfer complex formation. Changes in the polymer molecular structure such as the incorporation of oxygen or sulphur separator links, bulky electron withdrawing groups such as $-CF_3$ or $-SO_2$, and meta-orientation of the aromatic diamine portion all contributed to reducing the color intensity of these transparent films. The UV transmission cut-offs of these films ranged from 310 to 388 nm compared to 450 nm for commercial polyimide film of the same thickness. Although the presence of separator groups contributed to improved film transparency, the presence of bulky electron withdrawing groups coupled with meta-oriented diamines were major factors in producing colorless films. These changes in

molecular structure also rendered many of the fully imidized polymers soluble in common organic solvents. Solubility of these transparent aromatic polyimides in a low boiling solvent such as chloroform makes them particularly attractive as spray-coatings for space applications where the the substrate cannot endure the traditional 300°C polyimide cure temperature.

Some of the more optically transparent of the polyimide films produced in this study were evaluated for their potential use in a space environment. Upon irradiation with 300 equivalent solar hours UV irradiation and 5×10^9 rads 1 MeV electron irradiation the films were 2 to 2.5 times more transparent at 500 nm than commercial polyimide film. The polymer films which performed best upon irradiation were those containing -C(CF$_3$) or -0- in the dianhydride portion of the molecule in combination with 3,3'-oxydianline diamine. All films were relatively thermally stable at 300°C in air. Stability at 350°C was reduced by increasing amounts of oxygen in the diamine portion of the polymer chain. This study indicates that these polymers should be extremely attractive as coating materials for any application where thermal stability, solubility and high optical transparency are needed.

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TABLE I. Properties of Polyimides Films

Polymer	η_{inh} (dl/g)	Tg (°C)	PDT (°C)	Film Color (0.5 mil Thick)	UV Cut-Off, nm (0.2 mil Films)
6F + APB	1.20	206	550	Pale to Colorless	336
6F + 3,3'-ODA	1.00	244	540	Pale to Colorless	330
6F + BDAF	0.92	263	530	Pale Yellow	328
6F + DDSO$_2$	0.47	279	520	Colorless	312
6F + 3,3'-6F[9]	0.60	260	510	Colorless	316
ODPA + APB	0.87	187	535	Pale Yellow	349
ODPA + 3,3'-ODA	1.09	192	540	Pale to Colorless	352
ODPA + BDAF	1.08	241	515	Pale Yellow	346
ODPA + DDSO$_2$	0.51	258	555	Pale Yellow	352
BDSDA + APB	0.41	167	520	Pale to Colorless	368
BDSDA + BDAF	1.10	210	520	Pale to Colorless	353
BDSDA + DDSO$_2$	0.43	213	520	Pale Yellow	365
BTDA + APB	0.80	202	520	Yellow	378
BTDA + BDAF	0.94	249	545	Yellow	388
BTDA + DDSO$_2$	0.42	257	535	Pale Orange	365
PMDA + APB	0.44	221	530	Yellow	366
PMDA + BDAF	0.47	305	520	Yellow	340
PMDA + DDSO$_2$	0.27	338	535	Pale Orange	360

Table II. Effect of Monomer Purity on Polyamic Acid Viscosity

Polymer	η_{inh} (dl/g)	Dianhydride		Diamine	
		m.pt. (°C)[a]	PM[b]	m.pt. (°C)[a]	PM[b]
6F + DDSO$_2$	0.5	244 (243)	Rx/Subl.	173 (171)	Rx
	0.2	239 (235)	None	169 (166)	None
BTDA + 4,4'-ODA	1.3	222 (220)	Subl.	187.5 (187)	Rx/Subl.
	0.3	209 (199)	None	186.5 (184)	None

[a]Melt peak by DTA; melt onset obtained from intersection of DTA tangents is given in parentheses

[b]Purification method: Rx = recrystallization, Subl. = Sublimation

Table III. Comparison of Polyimide Films Containing 6F Dianhydride
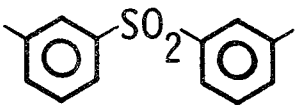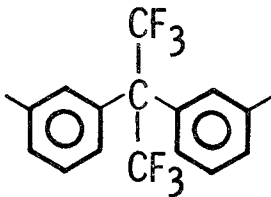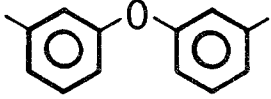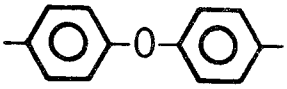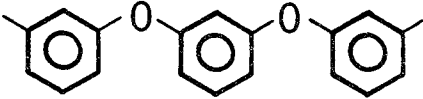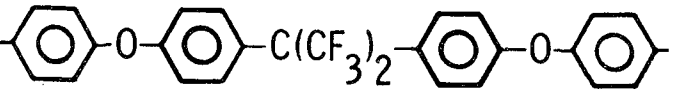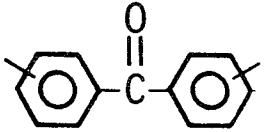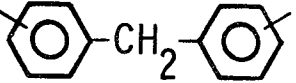
Polymer	-Ar-	Physical Appearance
6F + DDSO$_2$	(phenyl)-SO$_2$-(phenyl)	Colorless
6F + 3,3'-6F	(phenyl)-C(CF$_3$)$_2$-(phenyl)	Colorless
6F + 3,3'-ODA	(phenyl)-O-(phenyl)	V. pale yellow/colorless
6F + 4,4'-ODA	(phenyl)-O-(phenyl)	Light yellow
6F + APB	(phenyl)-O-(phenyl)-O-(phenyl)	V. pale yellow/colorless
6F + BDAF	(phenyl)-O-(phenyl)-C(CF$_3$)$_2$-(phenyl)-O-(phenyl)	pale yellow/colorless
6F + DABP	(phenyl)-C(=O)-(phenyl)	Light yellow
6F + MDA	(phenyl)-CH$_2$-(phenyl)	Yellow

TABLE IV. Solubilities Of Transparent Polyimide Films

Polymer	Film Solubility[a] in		
	DMAc	$CHCl_3$	Diglyme
6F + APB	P. Sol.	P. Sol.	P. Sol.
6F + 3,3'-ODA	Soluble	Soluble	Soluble
6F + BDAF	Soluble	Soluble	I
6F + $DDSO_2$	Soluble	Soluble	I
6F + 3,3'-6F	Soluble	Soluble	Soluble
ODPA + APB	P. Sol.	P. Sol.	I
ODPA + 3,3'-ODA	Soluble	Soluble	I
ODPA + BDAF	P. Sol.	P. Sol.	I
ODPA + $DDSO_2$	P. Sol.	I	I
BDSDA + APB	P. Sol.	P. Sol.	I
BDSDA + BDAF	Soluble	Soluble	Soluble
BDSDA + $DDSO_2$	Soluble	P. Sol.	I
BTDA + APB	I	I	I
BTDA + BDAF	I	I	I
BTDA + $DDSO_2$	I	I	I
PMDA + APB	I	I	I
PMDA + BDAF	I	I	I
PMDA + $DDSO_2$	I	I	I

[a]performed on 1% w/w solutions; P. Sol. = partly soluble;
I = insoluble

Figure 1. Aromatic Diamine Monomers

6F

H_2N — CF$_3$ — C — CF$_3$ — NH$_2$

ODA

H_2N — O — NH$_2$

BDAF

H_2N — O — CF$_3$ — C — CF$_3$ — O — NH$_2$

APB

H_2N — O — O — NH$_2$

DDSO$_2$

H_2N — SO$_2$ — NH$_2$
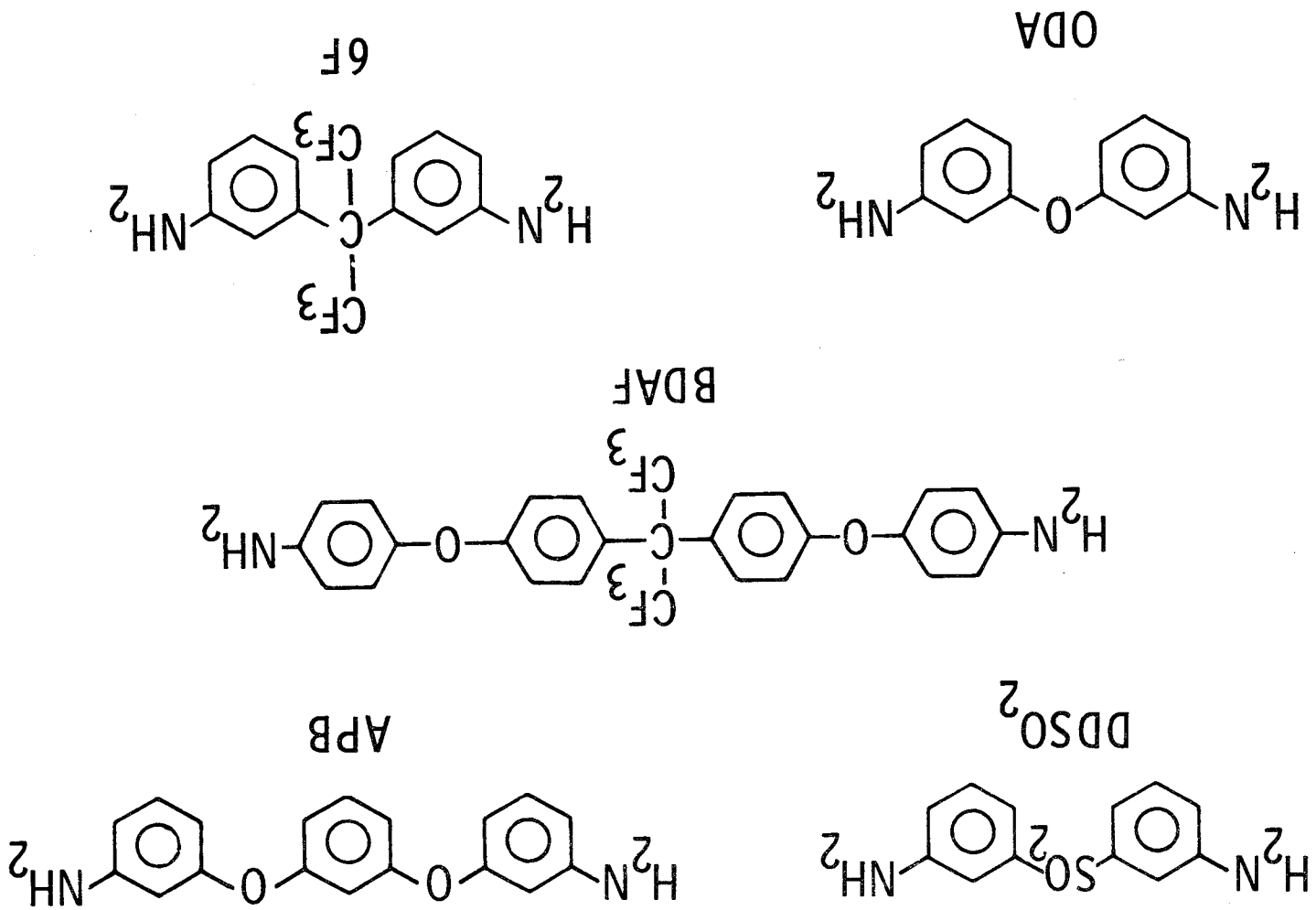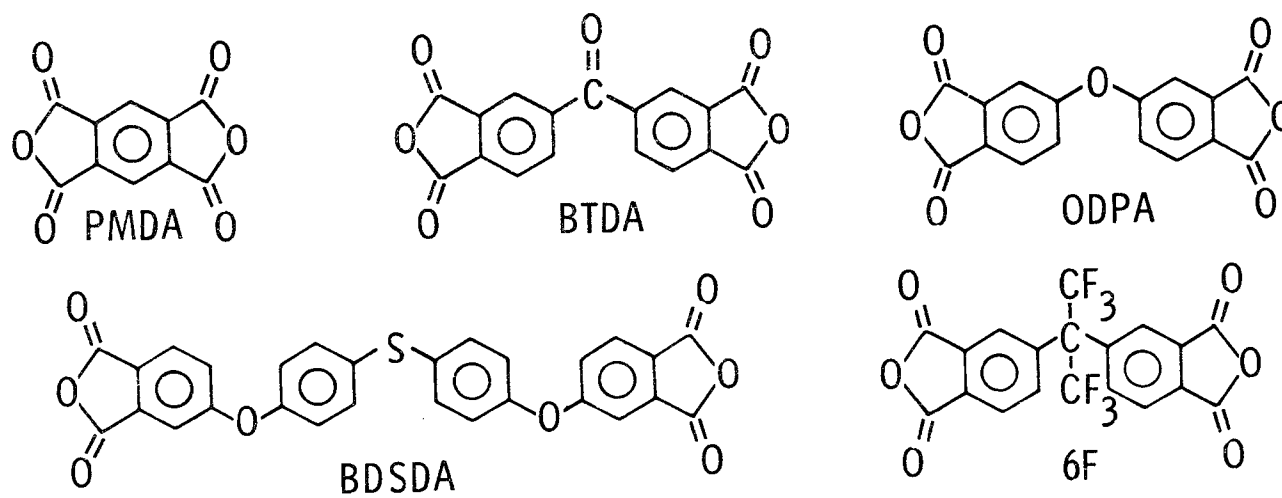
Figure 2. Aromatic dianhydride monomers
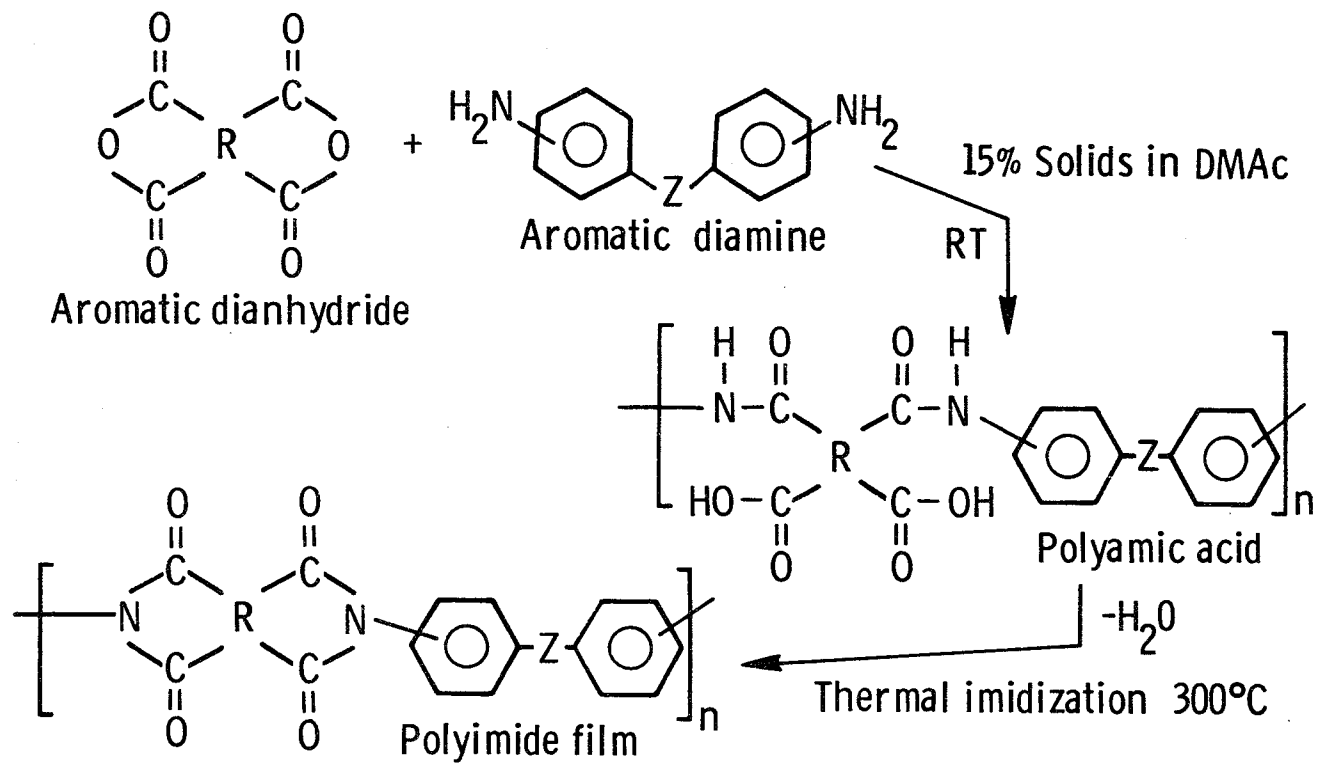
Figure 3. Reaction route for preparation of polyimide films
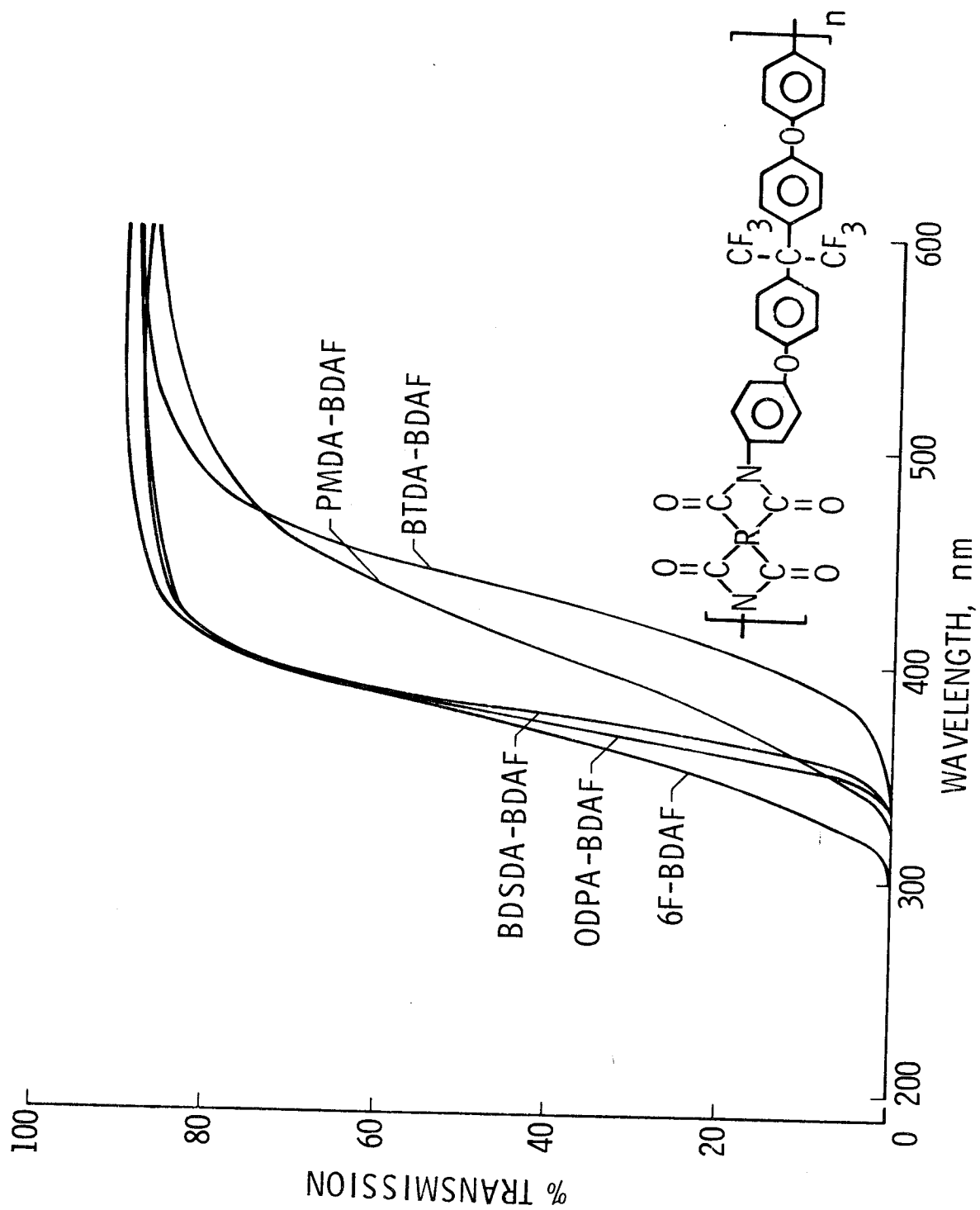
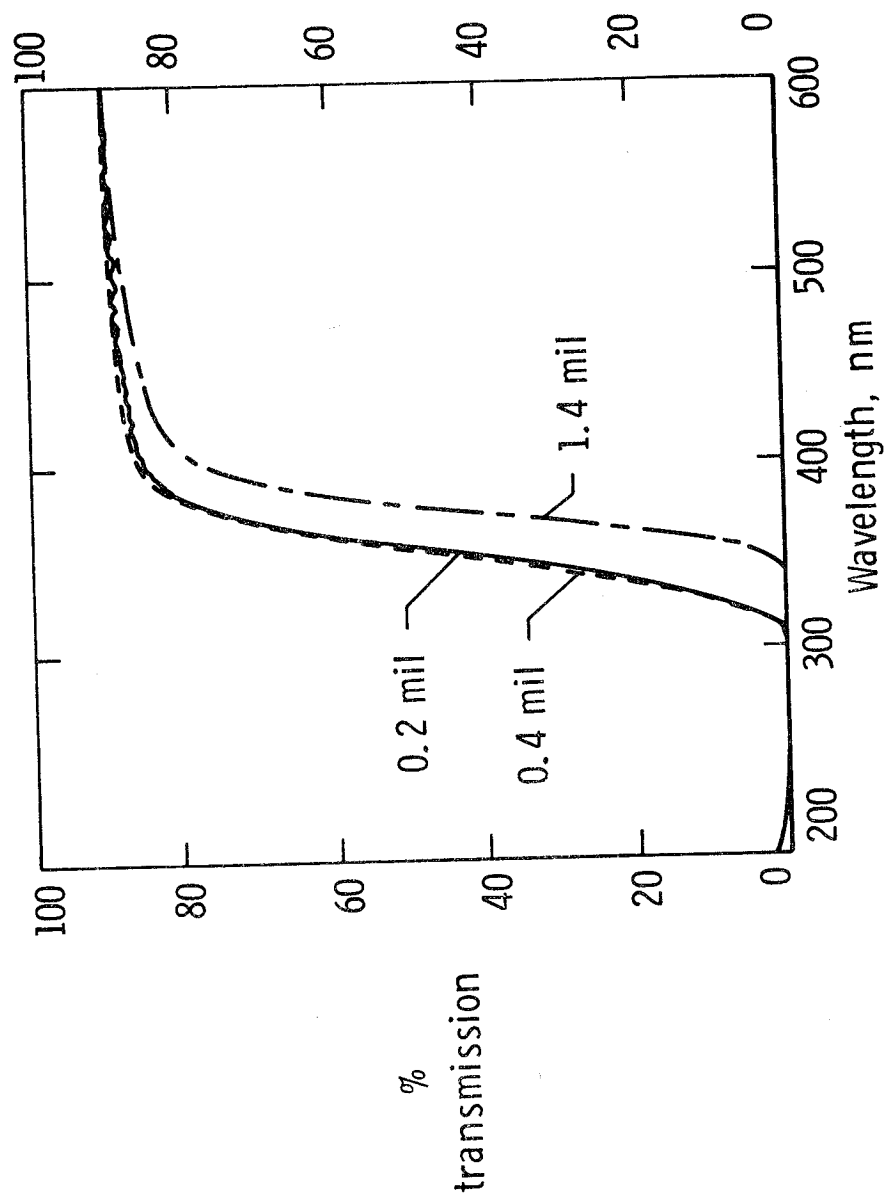Figure 4. UV-visible spectra of 0.2 mil BDAF-derived polyimide films

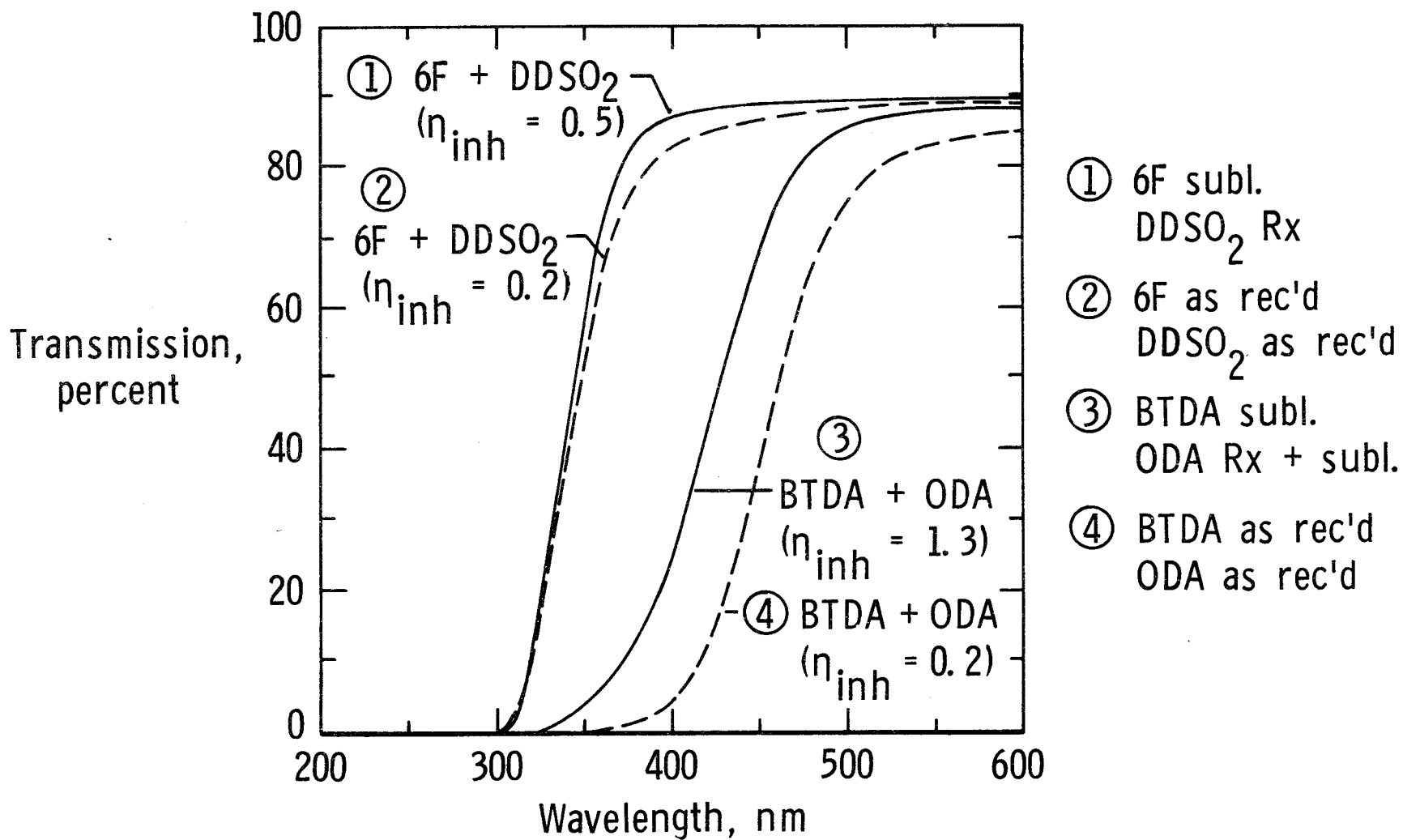Figure 5. UV-visible spectra of 6F + DDSO$_2$ films varying in thickness

Figure 6. Effect of monomer purity on the UV-visible spectra of 6F + DDSO$_2$
) and BTDA + 4,4'-ODA films

The chart shows the following labeled curves:

- 6F + APB
- 6F + 3,3'-ODA
- 6F + BDAF
- 6F + DDSO$_2$
- 6F + 3,3'-6F

Control films (before irradiation)

Kapton®

Solar maximum (500 nm)

Y-axis: Transmission, percent (0, 20, 40, 60, 80, 100)

X-axis: Wavelength, nm (200, 300, 400, 500, 600)
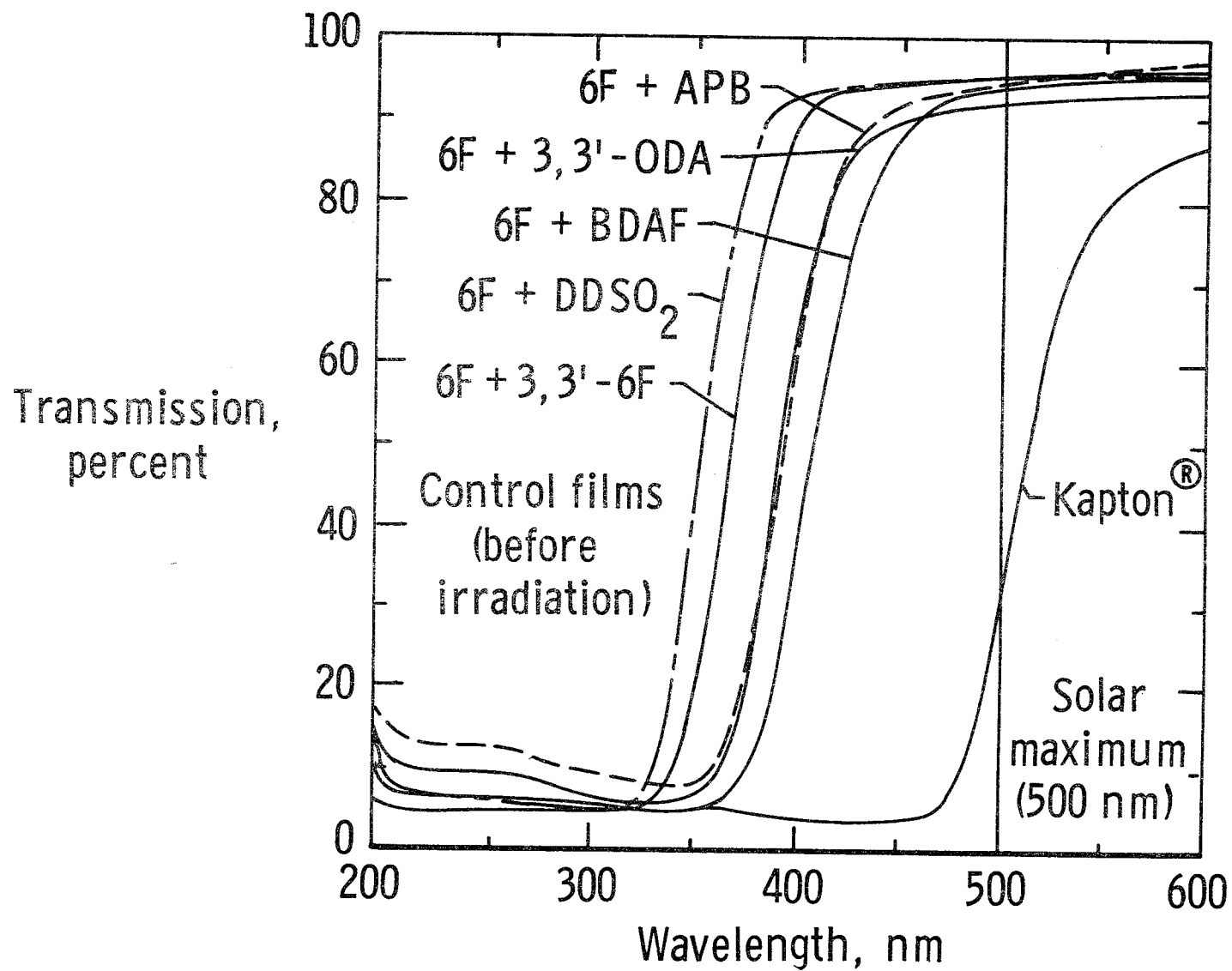
Figure 7. UV-visible spectra of 0.5 mil 6F-containing polyimide films before irradiation
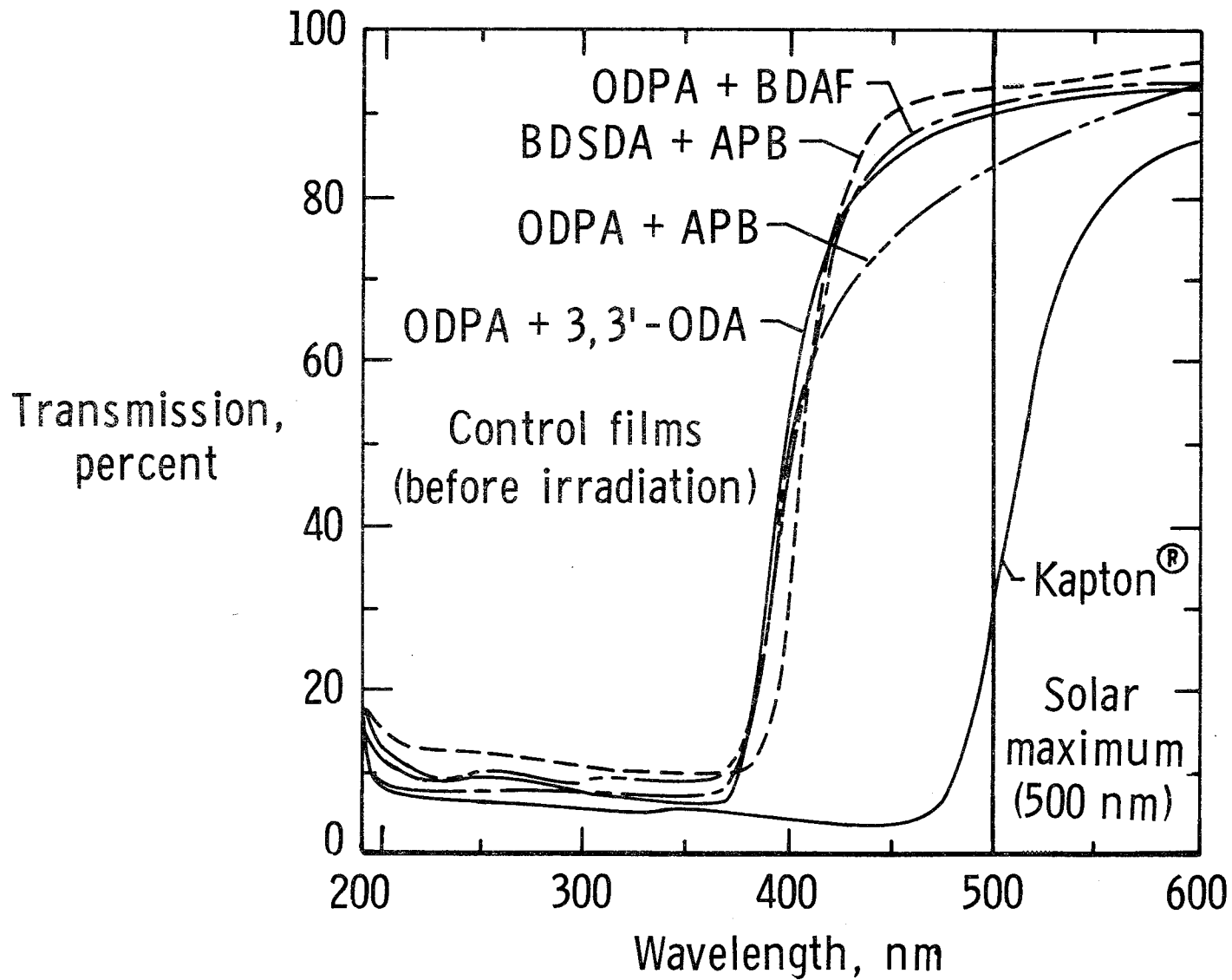
Figure 8. UV-visible spectra of 0.5 mil ODPA and BDSDA-containing films before irradiation
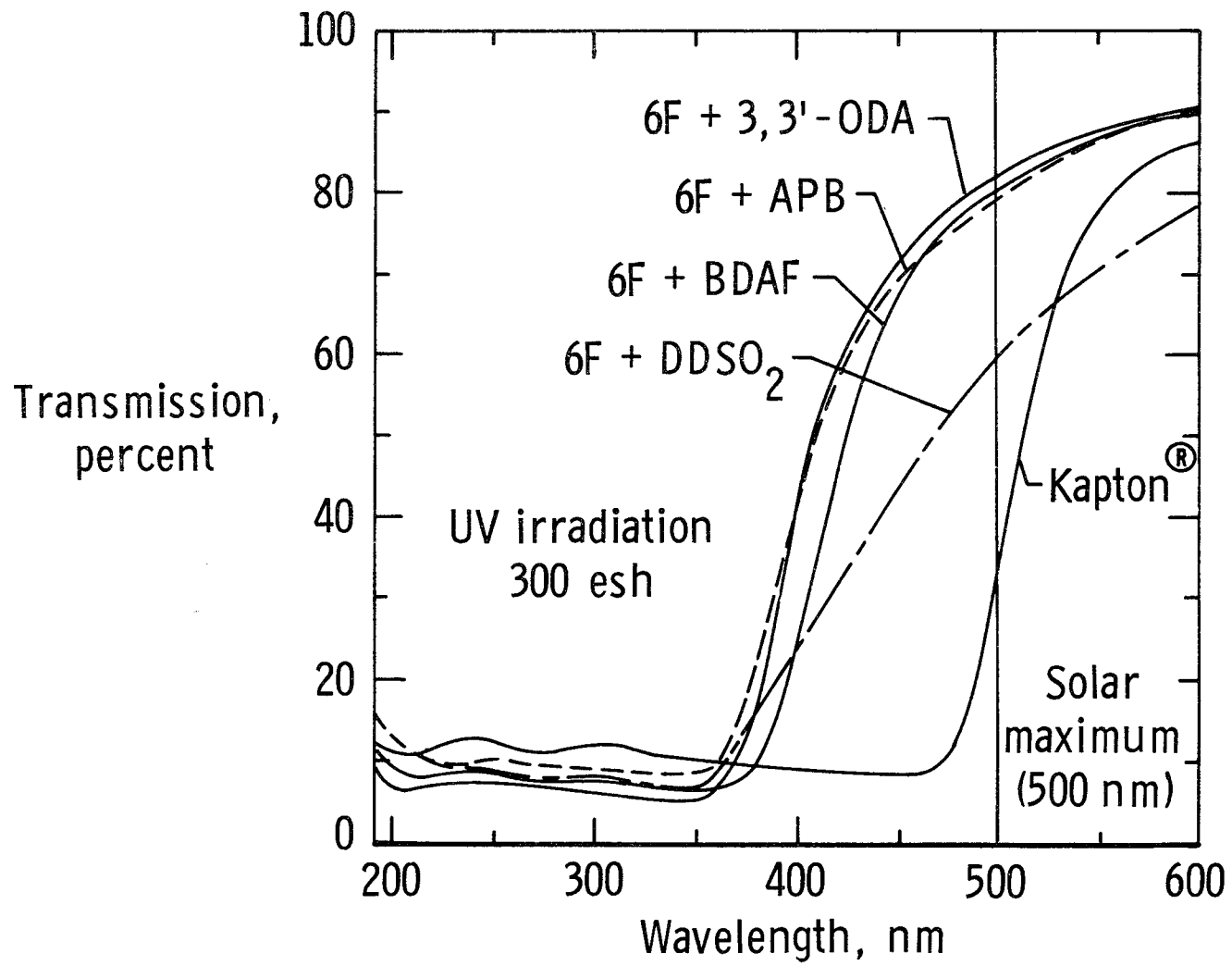
Figure 9. UV-visible spectra of UV-irradiated 6F-containing polyimide films
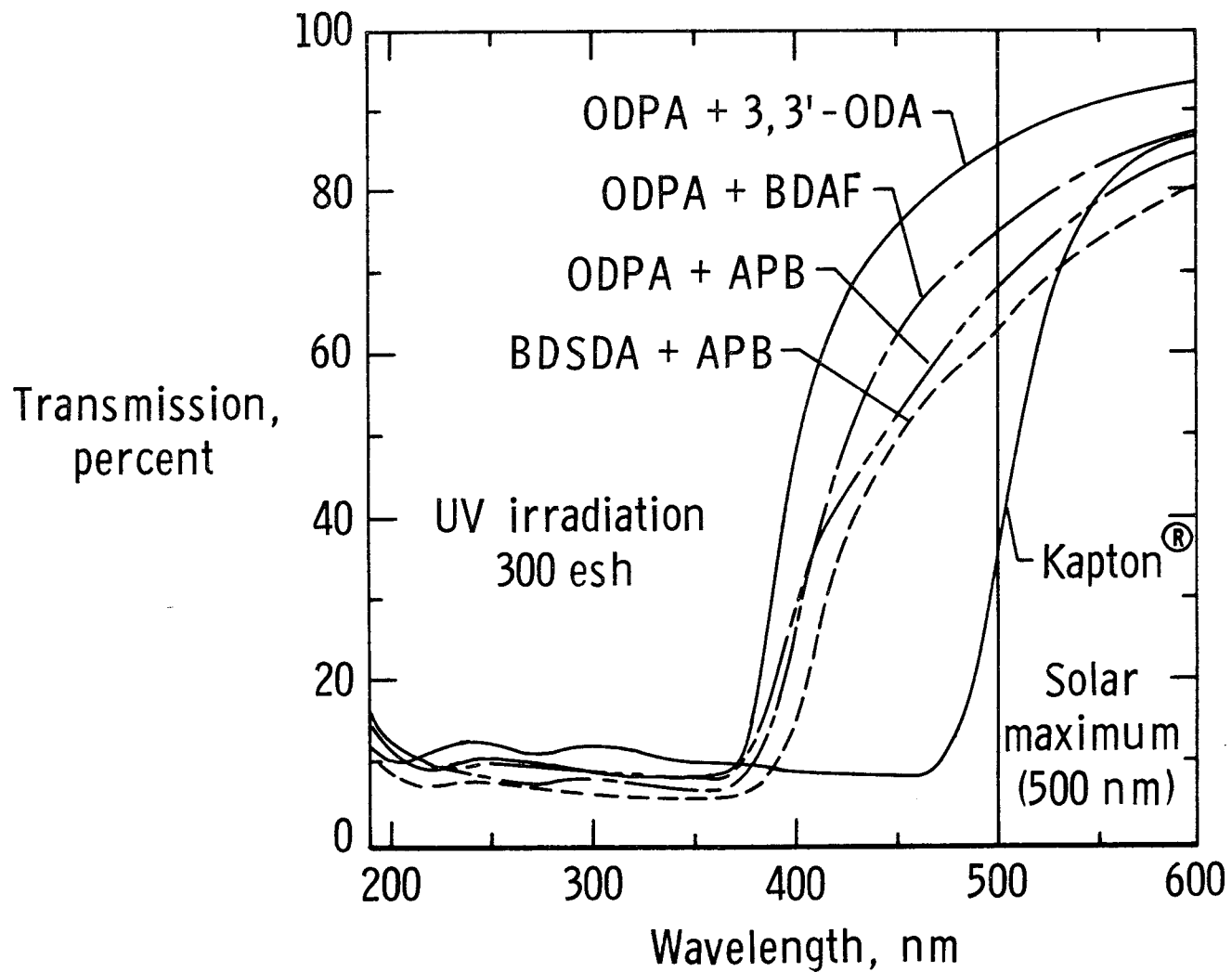
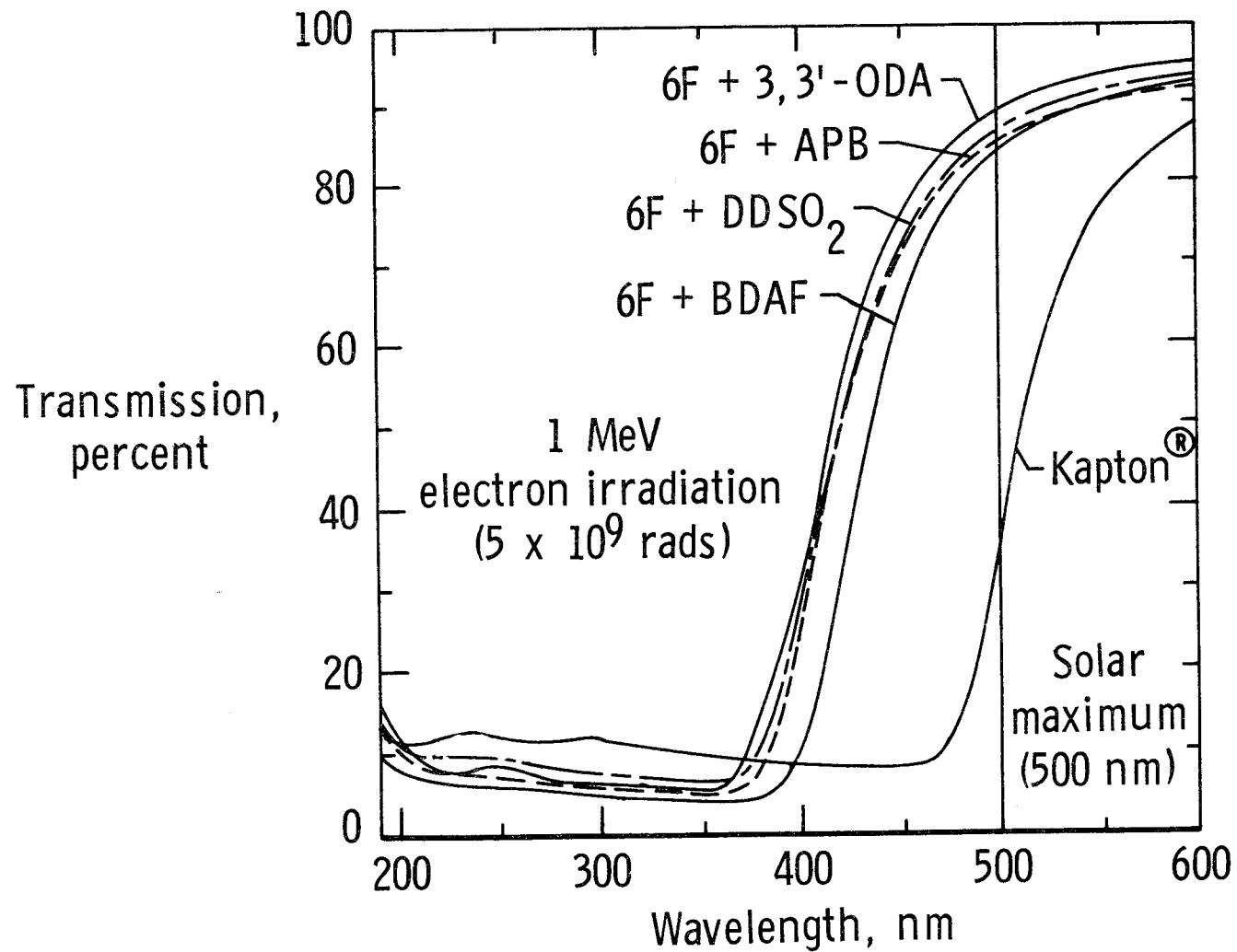Figure 10. UV-visible spectra of UV-irradiated ODPA and BDSDA-containing polyimide films

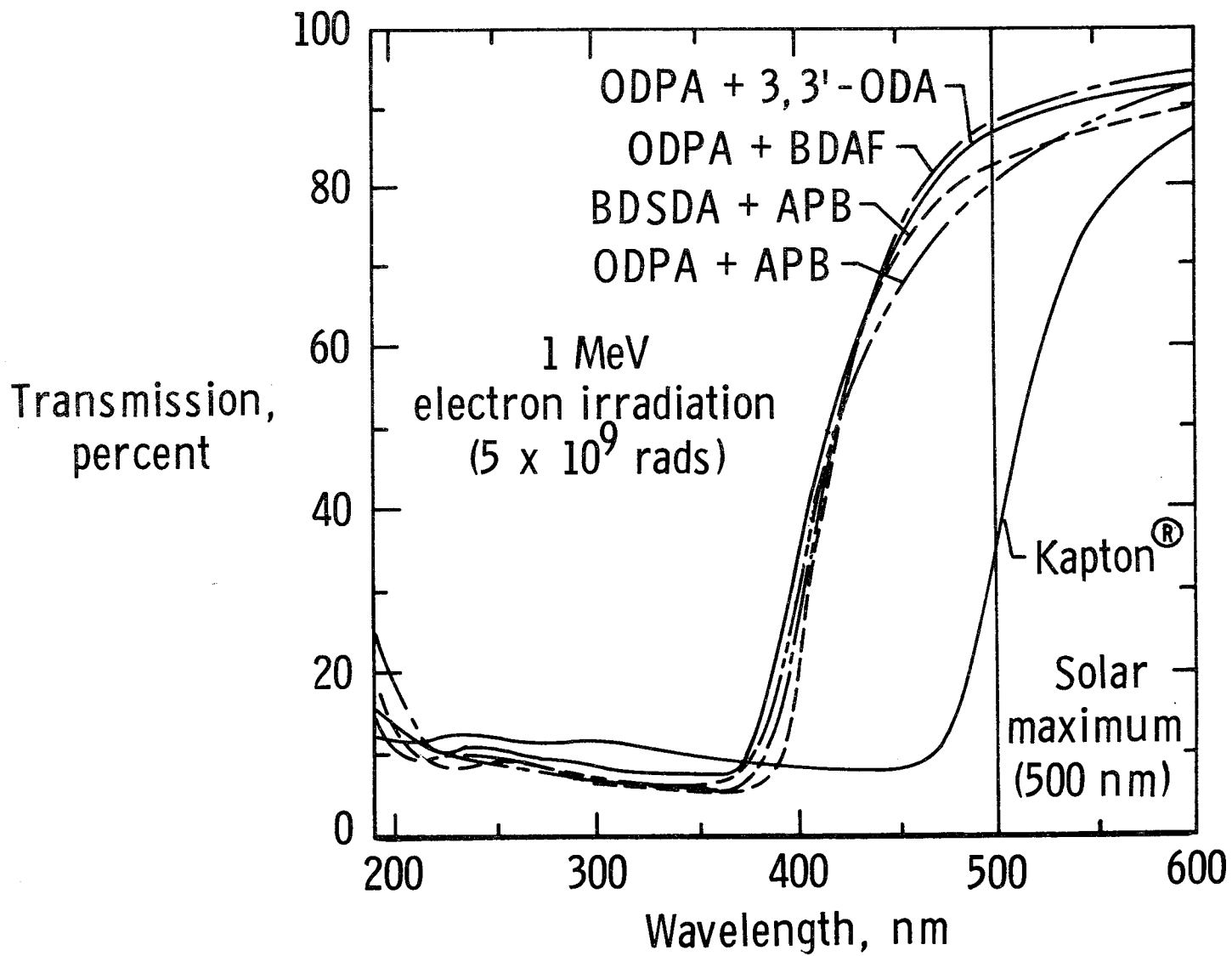Figure 11. UV-visible spectra of e-irradiated 6F-containing polyimide films

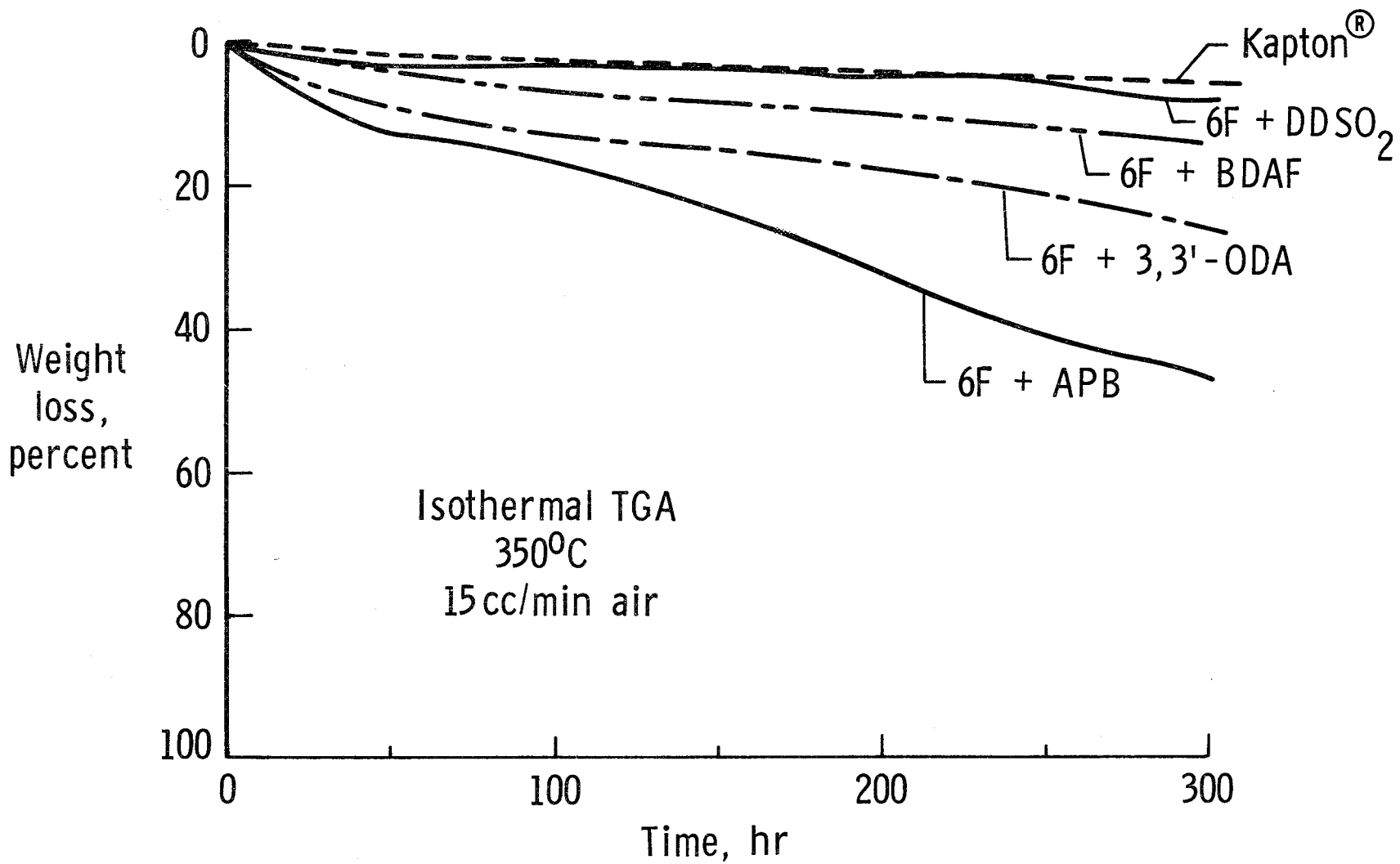Figure 12. UV-visible spectra of e-irradiated ODPA and BDSDA-containing polyimide films

Figure 13. Isothermal weight loss of 6F-containing polyimide films at 350°C in air
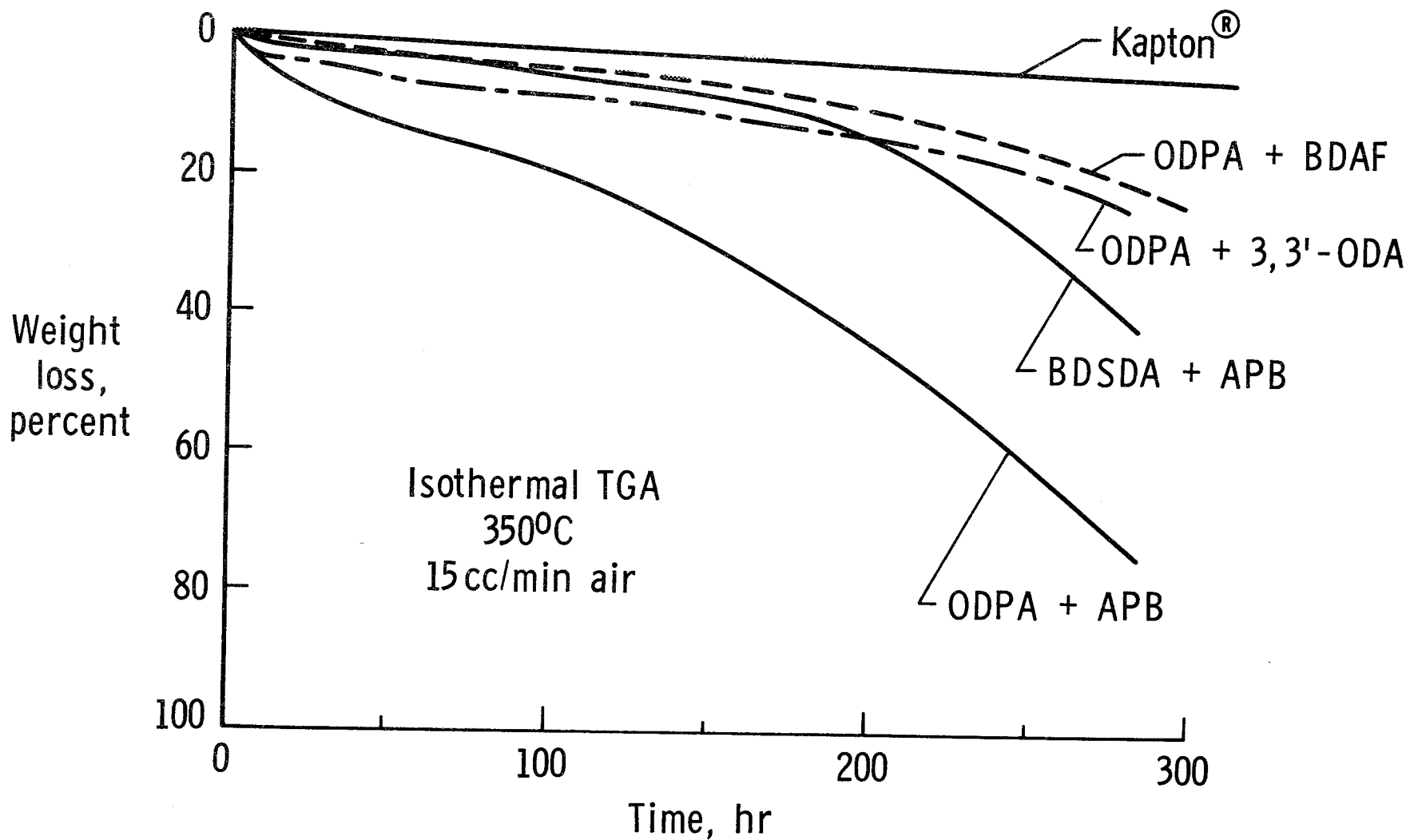
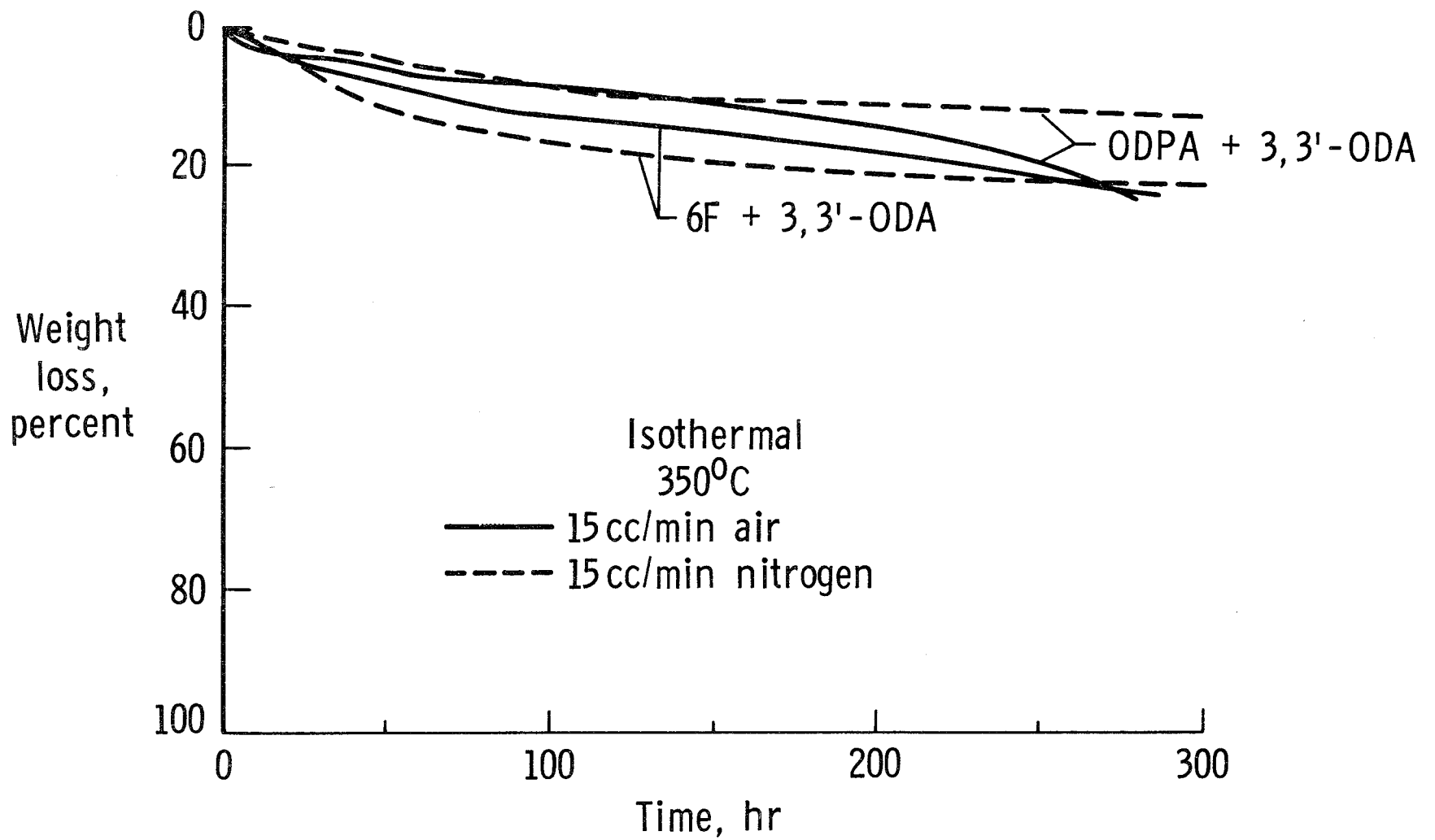Figure 14. Isothermal weight loss of ODPA and BDSDA-containing films at 350°C in air

Figure 15. Isothermal weight loss of 3,3'-ODA films at 350°C in air versus nitrogen

Standard Bibliographic Page

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16. Abstract

Several series of linear aromatic polyimide films have been synthesized and characterized with the objective of obtaining maximum optical transparency. Two approaches have been used as part of this structure-property relationship study. The first approach was to vary the molecular structure so as to separate chromophoric centers and reduce electronic interactions between polymer chains to lower the intensity of color in the resulting polymer films. A second and concurrent approach has been to perform polymerizations with highly purified monomers. Glass transition temperatures of thermally cured polyimide films were obtained by thermomechanical analysis and thermal decomposition temperatures were determined by thermogravimetric analysis. Transmittance UV-visible spectra of the polyimide films were compared to that of a commercial polyimide film. Fully imidized films were tested for solubility in common organic solvents. The more transparent films prepared in this study have been evaluated for use on second-surface mirror thermal control coating systems. Lightly colored to colorless films were characterized by UV-visible spectroscopy before and after exposure to 300 equivalent solar hours UV irradiation and varying doses of 1 MeV electron irradiation. The effects of monomer purity, casting solvent and cure atmosphere on polyimide film transparency were also investigated.

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