(NASA-CR-169000) POLY(ARYL ETHERS) AND
RELATED POLYSILOXANE COPOLYMER MOLECULAR
COATINGS: PREPARATION AND RADIATION
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POLY(ARYL ETHERS) AND RELATED POLYSILOXANE COPOLYMER MOLECULAR COATINGS:

PREPARATION AND RADIATION DEGRADATION

Final Report

Research Grant NAG-1-106

by

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II. EXECUTIVE SUMMARY

A 12 month report describing our initial study of the radiation degradation of poly(arylene ether sulfones) and related materials is proposed. These basic studies are important both as a means to developing stronger, more stable matrix resins for composite materials, as well as to improve the currently meager data base in regard to chemical structure-physical property relationships.

During the first year, over thirty homo-and copolymers have been synthesized, at least partially characterized and, in several cases suitable film casting techniques were developed. Four samples were chosen for initial radiation degradation and films have been submitted. Progress in this area is discussed in detail in the body of this report. Also, during this period, an initial outline of two Ph.D. programs in Materials Engineering Science has begun.

The renewal will continue to expand and indeed accelerate the program, both with regard to synthesis and characterization and radiation degradation/analysis. This will be possible because of new equipment both at NASA and at this University and because of the foundation laid thus far.

Our recent research and that of others has shown that poly(dimethyl siloxane) soft bocks/segments can preferentially migrate to the surface of copolymer films. Since siloxanes are utilized as thermal control coatings, this form of "molecular" coating may be of interest. The chemistry for preparing such copolymers with any of the polymers described has been demonstrated.

We will independently study the radiation induced degradation of these polymers and copolymers and will attempt to develop mechanistic ideas on the basis of spectroscopic, chromatographic and mechanical behavior results.

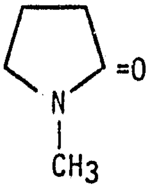
IV. PROGRAM PROGRESS

1. Polymer Synthesis and Characterization

N-Methyl-2-Pyrrolidone (M-Pyrole) has been used extensively as a solvent in the synthesis of polyamides. It is used as a solvent also for the synthesis of acrylonitrile copolymers, various sulfone containing polymers, and also for other phosphorous and nitrogen containing polymer systems. In this paper, we will discuss its use as a solvent for the synthesis of various poly(arylene ethers).

This family of macromolecules have been previously synthesized in this laboratory (1) and elsewhere (2) by using either potassium-carbonate/dimethyl acetamide (DMAC) or via the aqueous caustic/DMSO route. However the scope of those approaches is limited. Relatively low boiling and decomposition points for dimethyl acetamide results in somewhat slow rates of polymerization (perhaps 10-12 hours). The synthesis of high molecular weight semi-crystalline polymers may also be extremely difficult, due to premature polymer precipitation (3). Moreover, tetratogenic activity associated with DMAC restricts its use.

N-Methyl-2-Pyrrolidone has proved to be an excellent alternative solvent. Its physical and chemical properties have several outstanding advantages over other aprotic liquids. It is highly polar as is reflected in its high boiling point of 202°C.



The N-Substituted carboxamide ring has good hydrolytic stability except in the presence of strong aqueous base or acid at elevated temperatures. Also it is relatively non-toxic and non-corrosive. These desirable properties have prompted us to investigate NMP as the solvent for various polyarylene ethers syntheses. A variety of homo-and copolymer structures have been prepared as outlined in Tables I and II.

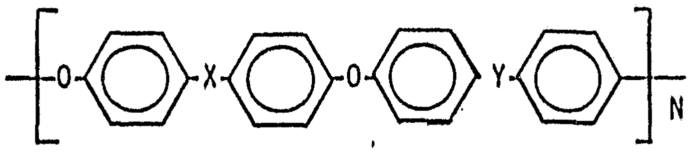


TABLE I

Poly(Aryl Ether) Synthesis Variables

X	Y	Total Reaction Time in Hours	T,°C	$[\eta]^{25°C}_{NMP}$
$-\overset{CH_3}{\underset{CH_3}{C}}-$	SO_2	5	170	0.58
S	SO_2	3	160	0.71
SO_2	SO_2	8	180	0.35
Chemical Bond	SO_2	5	170	0.92

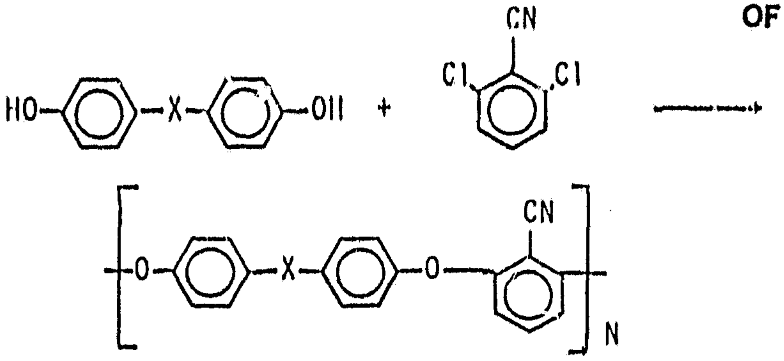


TABLE II

Effect of the Diphenol Linking Agent on Relative Rates of Poly(Aryl Ether) Synthesis

X	Total Reaction Time in hours	Temperature, °C	$[\eta]^{25^\circ C}_{NMP}$
S	3	150	0.72
$-\overset{CH_3}{\underset{CH_3}{C}}-$	4	170	0.56
SO_2	8	180	0.40

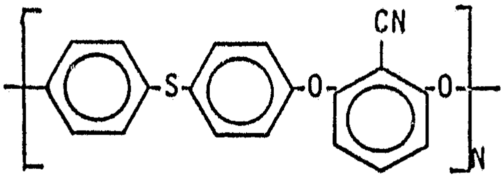
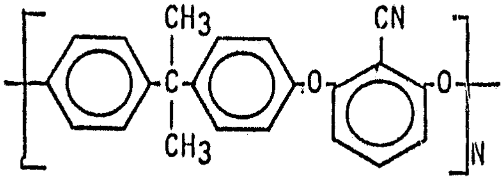
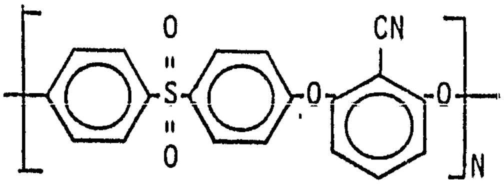
We have also been successful in synthesizing another class of polyarylene ethers which contains aromatic nitrile groups.

The glass temperatures of several representative structures are shown in Table III.

TABLE III

Tg of -(-CN) Containing Poly(Aryl Ether)s by DSC.

Heating Rate: 10°K/min

	Tg = 152°C
	Tg = 173°C
	Tg = 222°C

The major disadvantage associated with the use of m-pyrole is the discoloration of that occurs during some of the polymerizations. The reason for this color change and means to prevent it are presently under investigation. It must be emphasized however that such polymers do not exhibit any inferior physical characteristics. Synthesis of various other classes of polyarylene ethers and copolymers have also been achieved and these are summarized in Table IV.

TABLE IV

Polyarylene Ether Sulfones

Sample Number	Polymer (a)	$[\eta]^{25°C}$
(1)	Bis A PSF P-1700	0.48
(2)	Bis A PSF (-OH terminated)	0.79
(3)	Bis A PSF (-OH terminated)	0.62
(4)	Bis A PSF (-OH terminated)	0.32 (Mn=6760, by titration)
(5)	Bis A PSF (Cl terminated end group)	0.49
(6)	Bis-S	0.35
(7)	Bis-T	0.72
(8)	Biphenol PSF	0.92
(9)	Bis A-Hydroquinone PSF (Hydroquinone 10%)	0.52 also 0.62
(10)	Bis A-Hydroquinone PSF (Hydroquinone 15%)	0.55
(11)	Bis A-Hydroquinone PSF (Hydroquinone 20%)	0.51
(12)	Bis A-Hydroquinone PSF (Hydroquinone 30%)	0.54
(13)	Bis A-Hydroquinone PSF (Hydroquinone 75%)	0.73
(14)	Bis A-Hydroquinone PSF (Hydroquinone 85%)	0.96
(15)	Bis A-Biphenol (50% Biphenol)	0.32

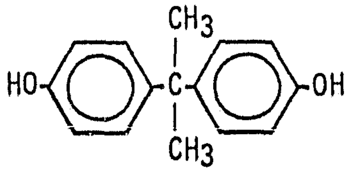
TABLE IV (con't)

Polyarylene Ether Sulfones

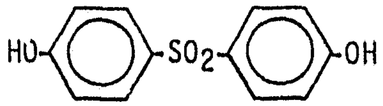
Sample Number	Polymer (a)	$[\eta]^{25^{\circ}\mathrm{C}}$
(16)	Hydroquinone-biphenol PSF (Hydroquinone 50%)	0.85
(17)	Bis A-Bis S PSF	0.36
(18)	Bis-S-Hydroquinone	0.49

(a)

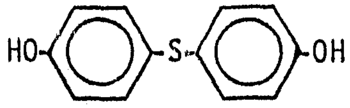
Bis-A,



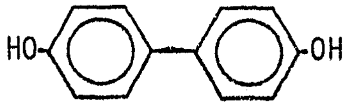
Bis-S,



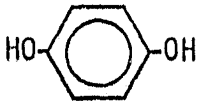
Bis-T,



Biphenol,



Hydroquinone,



The activated aryl halide was usually 4,4'-dichlorodiphenyl sulfone

2. Detailed Casting Procedure for Polyarylene Ether Sulfones

The first step in the preparation of the films is to dissolve the polymer in an appropriate solvent, so as to yield an approximately ten percent (w/v) solution. Where possible, chloroform is a preferred solvent. In order to prepare four films, 4 gms of polymer were placed in a 250 ml beaker containing a magnetic stirring bar and 40 mls of chloroform. This solution was stirred and was covered with a watch glass to prevent the introduction of large impurities from the atmosphere. After the solution was formed, it was filtered. For this purpose a disposable 10cc syringe was used to transfer the polymer solution. The needle was removed and the solution was filtered through a disposable Gelman's syringe filter into a 250 ml Erlenmeyer flask. The polymer solution was examined to see if refiltering was required. If not, the flask was next gently swirled to displace any bubbles.

The next step was the actual casting of the film. A large stainless steel base was used as a level base to cast the films. The actual casting was done on a clean 9" x 6" glass plate. The device used to spread the polymer solution over the glass plate is a doctor's blade. Casting was conducted so as to yield a six inch long film. That is, the nine inch length of the plate was perpendicular to the doctor's blade. The actual procedure involves placing 8-10 mls of the dissolved polymer on the edge of the plate, and in one continuous motion, transferring the blade over the solution. The glass plate was then covered with a watch glass to prevent dust from settling on the drying film.

This cast film was allowed to sit overnight (20 hrs) to partially dry. The films were then transferred into a vacuum oven and heated to 60°C at low pressure for at least 8 hours to remove the chloroform. Since the films were ~1 mil or less, this is believed to be sufficient. This film thickness is critical for the radiation degradation studies.

The films were removed from the oven and from the plate by running cold water over the plate. The thin film then can usually be easily stripped off the plate.

The films were stored between two Kimwipes which were themselved within 2 pieces of rail board. This procedure helps the film to remain straight and prevents creases. The film which is now within the rail board, was transferred into a Ziploc bag which was left open and placed in the vacuum oven for 24 hours to remove any traces of water. Then the bags were removed from the oven, and stored in a desicator until the radiation degradation experiments are initiated.

3. Fourier Transform Infrared Spectra (FTIR)

The Polymer Materials and Interfaces Laboratory (PMIL) has very recently been able to purchase a Nicolet MX-1 FTIR Instrument. We believe that this instrument can play a major role in helping to characterize the bulk and surface effects of radiation degradation, as well as many other structural phenomena. We have recorded and stored the spectra of all the important polymers and copolymers synthesized to date. Spectra of the first four polymer films chosen for radiation degradation studies are shown in Figures 1-4. Excellent Spectra can be produced with ease and rapidity. We will comment further on this technique in Section V.

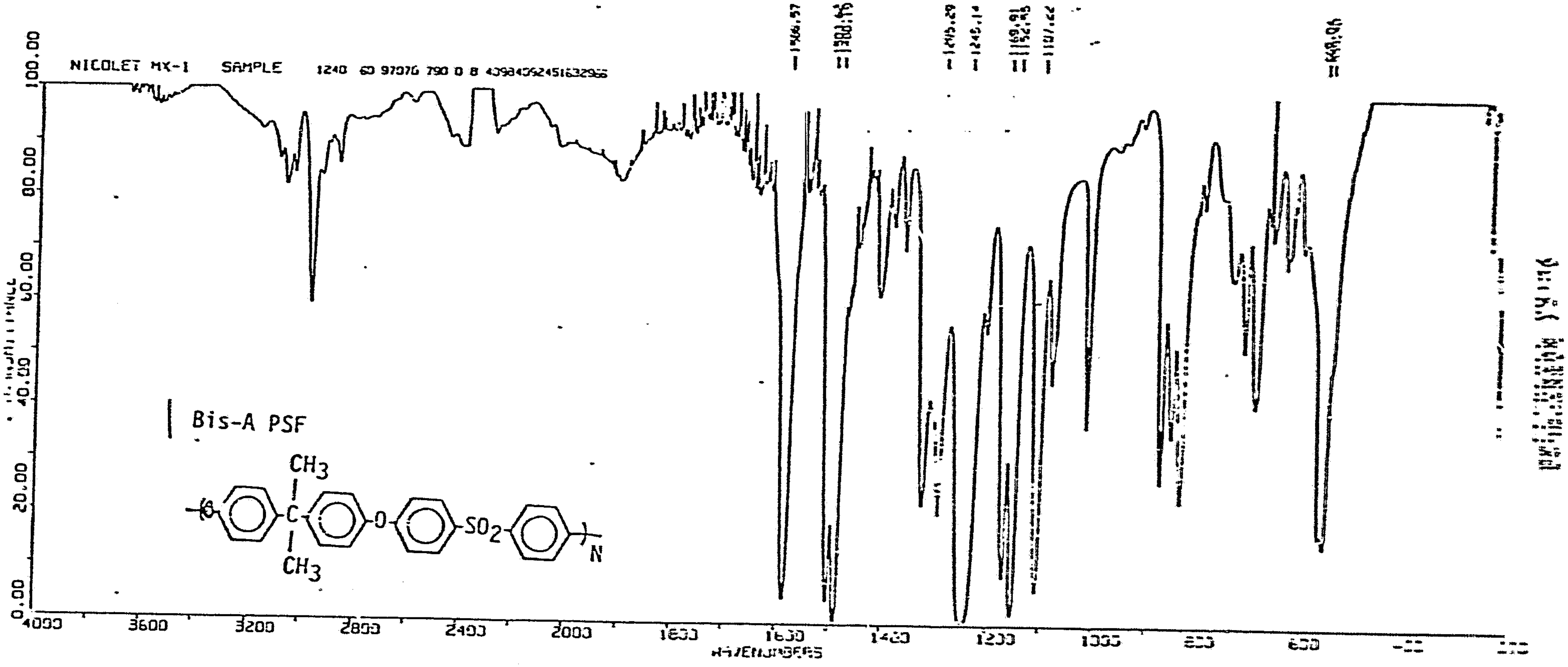

NICOLET MX-1 SAMPLE 1240 60 97070 790 0 8 4398439245163296
% TRANSMITTANCE
100.00
80.00
60.00
40.00
20.00
0.00
4000
3600
3200
2800
2400
2000
1600
1600
1400
1200
1000
800
600
400
200
WAVENUMBERS
1586.57
1488.45
1295.29
1245.14
1169.91
1152.45
1107.22
689.96
Bis-A PSF
CH3
CH3
O
SO2
N

FIGURE 1

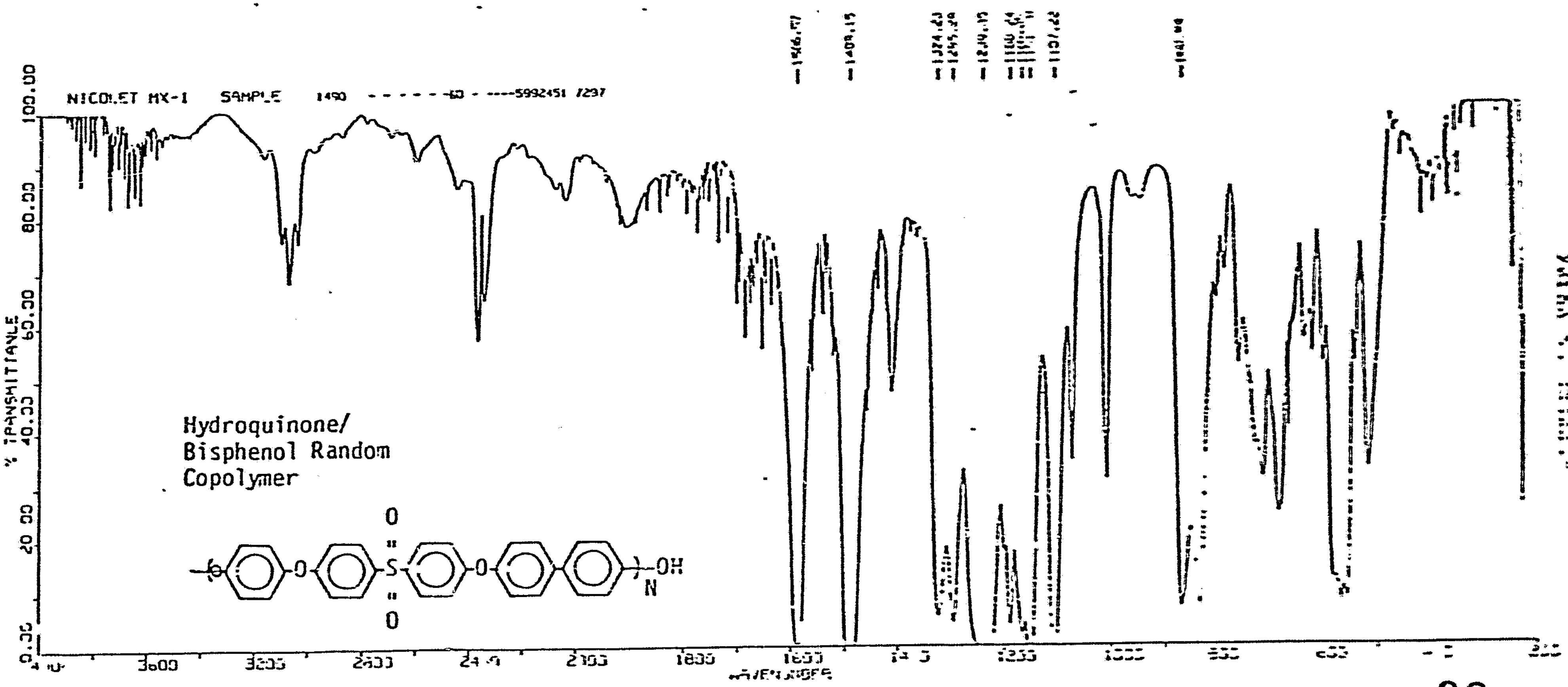

NICOLET MX-1 SAMPLE 1490 - - - - - - 60 - - - - -5992451 7297
100.00
80.00
60.00
40.00
20.00
0.00
% TRANSMITTANCE
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER
—1586.07
—1488.15
—1324.23
—1245.28
—1240.15
—1160.64
—1107.22
Hydroquinone/
Bisphenol Random
Copolymer
O
S
O
O
O
OH
N

FIGURE 2

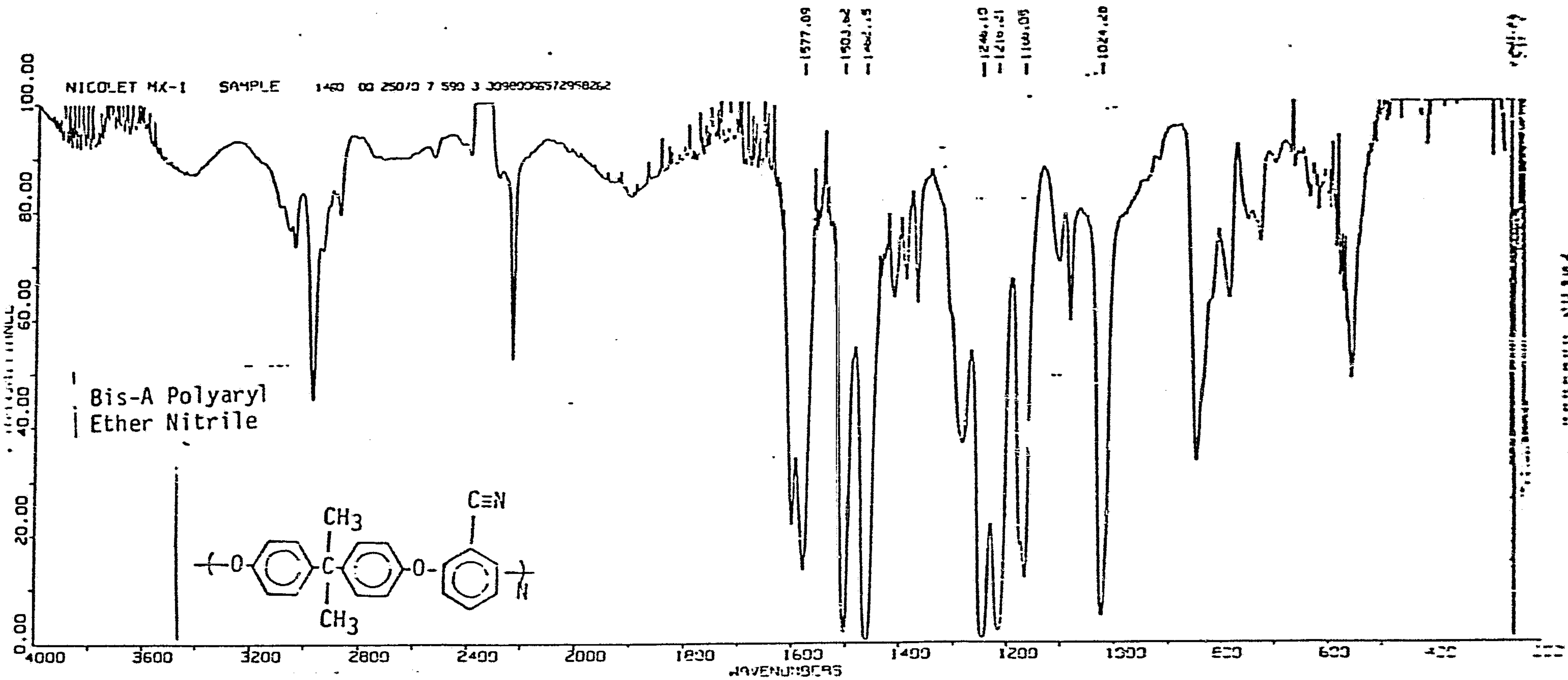


FIGURE 3

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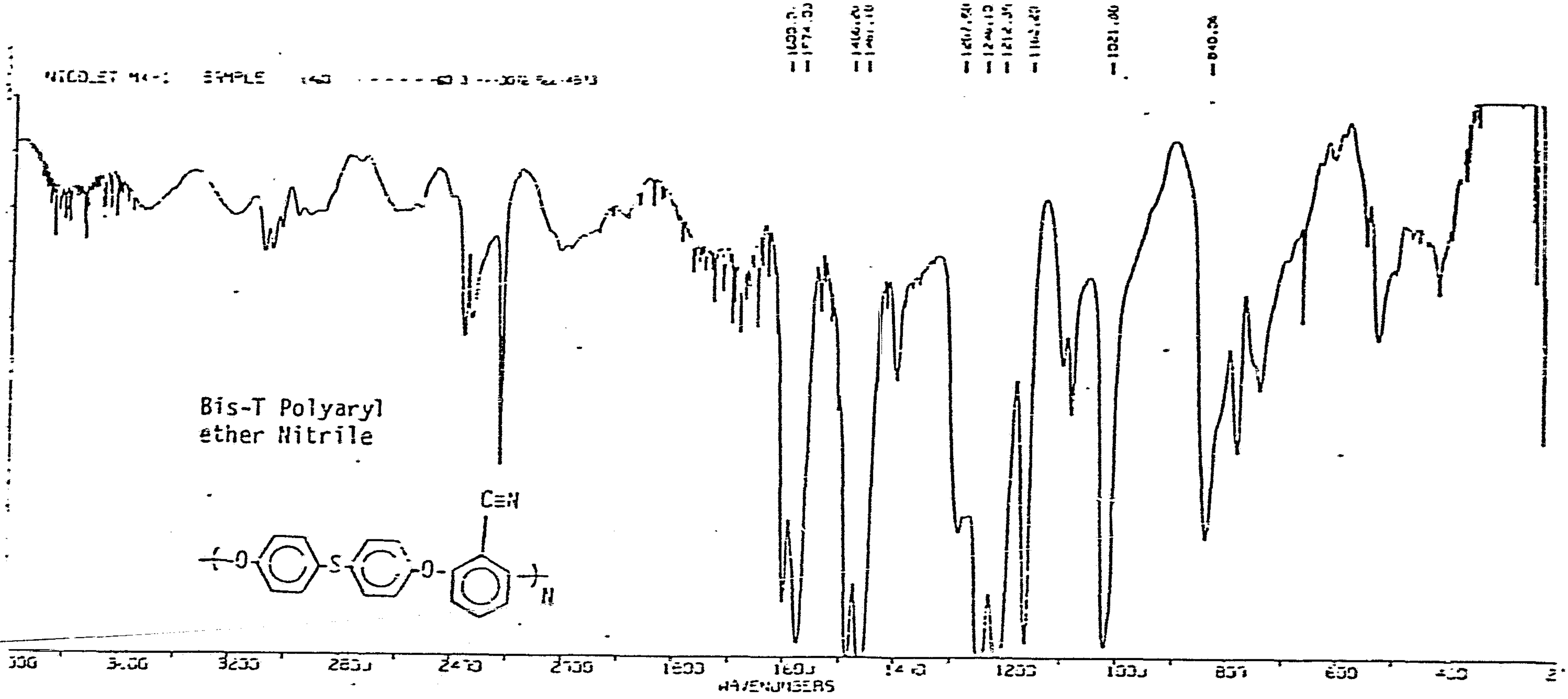

FIGURE 4

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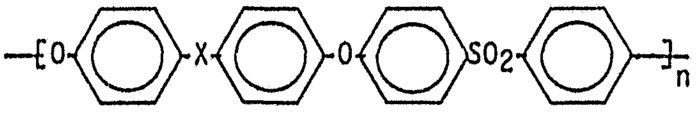
VI. PROPOSED RESEARCH

1. Polymer and Copolymer Synthesis

A. Poly(Arylene Ether Sulfones)

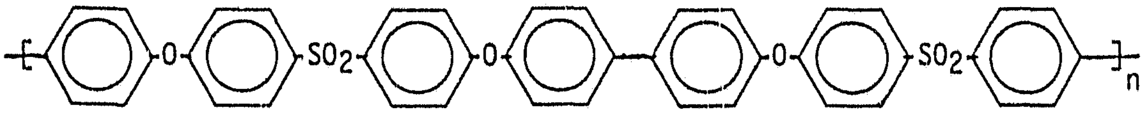
The basic structure 1 will continue to be the principal standard for comparison:



1

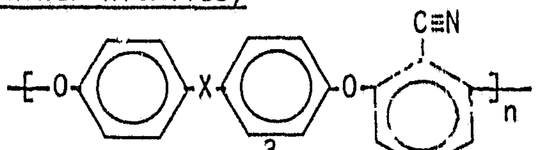
where X = $C(CH_3)_2$ (Bis-A), as chemical bond (Biphenol)

Copolymers of hydroquinone and biphenol with 4,4'-dichlorodiphenyl sulfone will also be prepared, since they can serve as amorphous and soluble, but all aromatic model structures. Introduction of some tetramethylbisphenol A to enhance gelation will also be investigated.



2

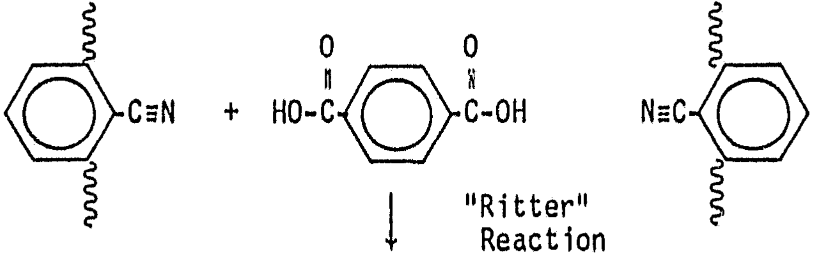
B. Poly(Arylene Ether Nitriles)



3

X= $C(CH_3)_2$, chemical bond

Almost nothing is known about novel structures such as 4. The aromatic nitrile groups is electron withdrawing, does provide a measure of polarity and even a site for crosslinking. It may be possible to introduce and react diacids such as terephthalic or adipic, at relatively high temperatures.



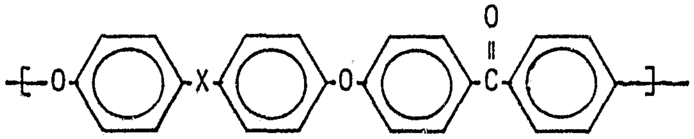
Amide Crosslinked Polyether

4

The concentration of the nitrile group could also be controlled by copolymerization with 4,4'-dichloro diphenyl sulfone.

C. Poly(Arylene Ether Ketones)

Poly(arylene ether ketones) such as 5 are relatively recently (4) prepared materials which are more easily crystallized than sulfone containing polymers.



5

We have already prepared a preliminary polymer from bisphenol A and 4,4'-difluorobenzophenone.

D. Polysiloxane Modified Poly(Arylene Ethers) and Related Structures

Our recent research and that of others has shown that poly(dimethyl siloxane) soft blocks/segments can preferentially migrate to the surface of copolymer films. Since siloxanes are utilized as thermal control coatings, this form of "molecular" coating may be of interest. The chemistry for preparing such copolymers with any of the polymers described has been demonstrated.

It is now generally recognized that the physical blending of additives with low surface tensions will modify the surface properties of polymers. For example, a certain lubricity is imparted to polyethylene (11) and to polyvinylidene chloride-acrylonitrile copolymers (12) with the incorporation of low concentrations of long chain amides. Certain fluorocarbon additives reduce wettability and friction in poly(methylmethacrylate) and poly(vinyl chloride) (13).

It has become increasingly evident in the past few years that, in well phase separated block copolymer films, preferential (air) surface migration of the component of lower surface free energy occurs (14-18, 19-26). Moreover, when small amounts of some block copolymers possessing one low energy component are physically blended with a homopolymer of similar structure to the higher surface energy block, the lower energy structure also concentrates at the surfaces of the films (16, 18, 13, 22, 27). The block copolymers have been shown to be particularly suitable as additives because of their high resistance to removal from the surfaces by rinsing or solvent extraction (27). Copolymers used for these types of systems wherein one block structure is polydimethylsiloxane have a high potential for industrial use since this surface phenomena occurs at quite low concentrations of the additive (27).

Gaines and Bender (27) studied the surface tensions of blends containing an (A-B) polystyrene-polydimethylsiloxane block copolymer and polystyrene homopolymer (<Mn> = 9290). Copolymer concentrations were varied from 0.05-5 wt. percent. Results for the 5% and 0.2% copolymer blends at 185°C were within 1 dyne/cm of that for pure polydimethylsiloxane and 16 dynes/cm below the surface tension of polystyrene. In addition, surface tensions of the blends in the melt were all observed to decrease quite rapidly with time up to ∿ 25 minutes.

Owen and Kendrick (10) investigated the surfaces of a series of (A-B-A) triblock styrene-dimethylsiloxane-styrene copolymers at compositions of siloxane ranging from 20-77 wt. percent. Surface tensions of solutions of these polymers in styrene and critical surface tensions of blends (1.0 wt. % of the respective copolymers with polystyrene homopolymer) in film form were measured. Results of the blend study yielded critical surface tensions ranging from 28.3 dynes/cm for the lowest percentage of siloxane to 22 dynes/cm (identical to that of siloxane homopolymer) for the two highest percentages (59% and 77% siloxane in the copolymer). Films of all copolymers (neat) had critical surface tensions identical to that observed for the polydimethylsiloxane homopolymer.

Gaines and LeGrand (18) measured ethylene glycol contact angles of films made from blends of polycarbonate-polydimethylsiloxane copolymers (28) with Lexan polycarbonate. They observed all of the blends studied (lowest copolymer wt. % = 0.1%) to possess contact angles close to those observed on pure polydimethylsiloxane. This wettability was also found to be almost totally insensitive to silicone content or silicone block length over the range investigated (0.1-4.0 wt. % copolymer with silicone blocks of 1500 g/mole or higher).

O'Malley (22) performed a similar study of hexamethylene sebacate-polydimethylsiloxane perfectly alternating block copolymers and their blends with polyhexamethylene sebacate homopolymer. The number average molecular weight of the crystalline polyester block was held constant at 3160 g/mole while the siloxane block length was varied from 1400-10,600 g/mole. Critical surface tensions of 28 and 21 dynes/cm were determined for the homopolymers (hexamethylene sebacate and polysiloxane respectively) whereas all of the copolymers had γ_c's of 22 dynes/cm. Polyblends containing 1.0 - 10.0 wt. percent of the copolymer with the lowest siloxane content also all exhibited γ_c's of 22 dynes/cm. It should be noted that this is the only study which has been done of this type wherein one of the block structures was crystalline.

Sung and Hu (29-32) conducted several studies of a segmental polyurethane-polysiloxane system (Avcothane) known to be biocompatible. It is not clear whether this is a physical blend or a copolymer (or both). The patent literature suggests a very complicated structure. However, because of its blood compatibility, it is included herein. It is produced (33) by blending (in solution under high shear) a preformed, hydroxy terminated segmented polyether-urethane with 10% by weight of a diacetoxy terminated polydimethylsiloxane. To what extent the acetoxy terminated siloxane reacts with the hydroxy terminated oligomer is not defined. X-ray photoelectron spectroscopy (XPS or ESCA) yielded Si/C, O/C, and Si/O intensity ratios for the blood contact side of the films essentially equal to those obtained for pure polydimethylsiloxane. FTIR internal reflectance and Auger electron spectroscopy results supported the data obtained via ESCA.

Clark et al. (14-15) studied the surfaces of A-B diblock polystyrene-polydimethylsiloxane copolymers using ESCA coupled with contact angle measurements. Copolymers containing 23 and 59 wt.% polystyrene possessing number average molecular weights of approximately 120,000 g/mole both exhibited critical surface tensions of 22 dynes/cm (identical to that for polydimethylsiloxane homopolymer). In addition, the effect of varying the film casting solvent on surfaces of the copolymers was investigated. Normal angle ESCA results showed intensity ratios for the copolymer with 23% polystyrene (films cast from chloroform) to be closely matched to those of pure polydimethylsiloxane. Moreover, the data obtained for the copolymer containing 59% polystyrene revealed the same results when films were cast from solvents selective for the polystyrene phase (styrene and bromobenzene). The siloxane surface layers were estimated to be ∿ 40 Å deep based on ESCA depth profiling results. Analogous ESCA data on the copolymer (59% polystyrene) cast from solvents preferential for the siloxane suggested varying amounts of polystyrene to be in the surface area sampled.

2. Characterization

A. Intrinsic Viscosity

Intrinsic Viscosity (or limiting viscosity number) is a simple, yet rapid and valuable technique for assessing relative molecular weights. With proper calibration, viscosity average molecular weights can be obtained. This technique should be quite useful in following radiation degradation below the gel point. We hope to obtain an automatic timer from Wescan to further accelerate these measurements.

B. Membrane Osmometry

This is, of course, the most important technique for measuring number average molecular weights, $\overline{M}_n$. Our Wescan 321 instrument allows calculation of $\overline{M}_n$ from the equation:

$$\left(\frac{\pi}{C}\right)_{C\to 0} = \frac{RT}{\overline{M}_n} + A_2C$$

where π = osmotic pressure

R = gas constant

T = absolute temperature

A_2= second virial coefficient

c = concentration

The possible variation of A_z with radiation degradation (again in the pregelation stage) may also be of value.

C. Gel Permeation Chromatography

Gel Permeation Chromatography (for a recent reference see (7)), GPC or size exclusion chromatography (SEC) is by far the most important method to attempt to assess changes in molecular weight and molecular weight distribution during radiation degradation: We have a Waters High-Pressure GPC, with refractive index, UV and infrared detectors, which is capable of operating efficiently at room temperature. At this time, we do not have a laser light scattering detector which would permit direct $\overline{M}_w$ determination. It is, however, high on our priority list.

D. Fourier Transform Infrared Spectroscopy (FTIR) (8,9)

As stated earlier, we now have a Nicolet MX-1 FTIR which is quickly proving to be very valuable and useful. It is rapid, automated and precise. Moreover, optically dense, essentially opaque materials may be utilized, because of the high energy throughput of the FTIR. The latter is a direct advantage of the ability of the interferometers to collect relatively large amounts of energy at high resolutions (the "Jacquinot" advantage). Storage of the data in a dedicated minicomputer allows one to perform mathematical manupulations on the spectrum. For example, one can substract the spectra of an original polymer and compare it with, for example a radiation degraded specimen. The preliminary results of Sykes and Santos on degraded P-1700 suggest a decrease in the ratio of O/S. Reduction of the sulfone groups to a sulfide in the reducing atmosphere would be consistent with this data. Such a hypothesis could be easily studied with the FTIR, and we would propose to include this type of study.

E. Thermal Analysis and Dynamic Mechanical Behavior

Our laboratory is equipped with a Perkin-Elmer Model 2 Differential Scanning Calorimeter (DSC), Thermogravimetric Analyzer (TGA), Thermomechanical analyzer (TMA) and a System 4 microprocessor. We will use the DSC to study T_g, possibly T_m and crystallization phenomena and perhaps auto-oxidation behavior. The TGA can be used to determine weight loss, either isothermally or at programmed rates anc controlled atmospheres. The TMA (in the penetration mode) provides rapid, useful pseudo-modulus-temperature profiles. Thus, it should be possible to partially characterize the post gel stage from the presence of a "rubbery" modulus.

Rheovibron forced tensile resonance experiments will also be conducted. These will provide storage (E'), and loss (E") moduli, as well as damping characteristics. Moreover, crosslinked samples will show a rubbery modulus above T_g which should be proportional to the $\overline{M}c$ or molecular weight between crosslinks.

F. Radiation Degradation Studies

This subject, of course, is the central thrust of the proposed effort. However, currently at VPI and SU we do not have a suitable source of high energy radiation. There is a small source in Physics, but it appears to be much too small for the current proposed research. It will, however, be possible for us to expose our new polymer and copolymer films to radiation sources available in industrial and governmental laboratories. We will then attempt to characterize the damage by

(A) gel permeation chromatography
(B) Fourier Transform Infrared Spectroscopy
(C) sol-gel analysis
(D) mechanical property retention

A major additional part of our effort will be to properly synthesize and structurally characterize the polymers as described in sections A through E. A second objective will be to provide suitably cast films to NASA-Langley Research Center for radiation exposure. A third and difficult objective will be characterize the degradation mechanisms and extent of physical property decay and to try to correlate chemical structure-physical property relationships. Several ways of approaching the question of structural characterization were outlined in Sections A-E. In addition, post gelation behavior may be investigated by sol-gel analysis and possibly swelling, as outlined by Saito(10). Quite a bit of information can be obtained by application of equations relevant to molecular weight, molecular weight distribution, gel content and sol fraction. For example, for a random molecular weight distribution (which most of the polyaryl ethers should possess), the sol fraction may be related to the radiation dose by the Charlesby-Pinner expression (10).

$$S + S^{1/2} = \frac{Y}{2X} + \frac{1}{X\ Pw\ (0)}$$

where S = sol fraction (e.g. 1- gel fraction

y = main chain scissions

X = density of crosslinks

Pw= original weight average degree of polymerization

Since the density of crosslinks is usually related linearly to the radiation dose, a plot of $S + S^{1/2}$ is the reciprocal of the dose may provide information on the scission to crosslink ratio (intercept) and the efficiency of the process (slope).

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