THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

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PREPARATION, CHARACTERIZATION, PHYSICAL TESTING AND PERFORMANCE OF FLUOROCARBON MEMBRANES AND SEPARATORS

Submitted by

Prof. Richard J. Lagow

and

Dr. Earl T. Dumitru

Prepared for:

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

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PREPARATION, CHARACTERIZATION, PHYSICAL TESTING AND PERFORMANCE OF FLUOROCARBON MEMBRANES

1.0 INTRODUCTION

Polymeric films five to fifteen mils thick and bearing carboxylate or sulfonate groups have been used in some processes for many years to separate charged species, or to desalt water. New uses have become possible because of dramatic improvement in the chemical and thermal stability of the inert portion of the membranes which depends upon the use of TFE (tetrafluoroethylene) as a major constituent of the polymerizing mixture of polymers. The required breakthrough involves the preparation of perfluoroether monomers which could be modified to include sulfonic acid or carboxylate functions and copolymerize with TFE. There are now two commercial materials, Nafion (from Dupont, USA), and Flemion (Asahi Glass Company, Japan), the former being the sulfonate and the latter the carboxylate membrane. These membranes are capable of years of use at 120°C in the presence of 40% caustic solution and chlorine gas. They also function well in electrolizers and fuel cells designed to produce hydrogen and oxygen from water at elevated temperatures. G.E. has produced SPE fuel cells with catalysts coated on both sides of the membrane. Despite their tremendous technical significance, these materials have some technical deficiencies which are not easily remedied under the conditions of their manufacture. In particular the polymers are not susceptible to crosslinking, and therefore tend to imbibe substantial quantities of electrolyte; a characteristic which limits their current efficiency and therefore their economic significance relative to processes not requiring membranes.

1.1 Objectives

The objective of the present program is to develop new synthetic methods of preparing fluorocarbon membranes bearing carboxyl or sulfonate groups and to over come the swelling problem by introducing carbon-carbon crosslinks.

A second objective is to find a lower cost route to perfluoro-membranes.

The third objective of this project is to extend the usefulness of the direct fluorination method to the preparation of strong, useful polymeric objects having functional groups as part of the structure. The direct fluorination method is also being applied to the preparation of new perfluorocarbon crosslinked elastomers for use in severe environments up to 300°C.

2.0 DIRECT FLUORINATION

Some years ago, Lagow and Margrave reported a breakthrough in control of the reaction of elemental fluorine with organic compounds, inorganic compounds and polymers. The method has been extended by Lagow and coworkers to include polymer powders such as polyethylene, polypropylene, ethylene-propylene copolymers, polyacrylamide, and the alternating copolymer of ethylene with hexafluoroacetone. The powders, greases, and liquids produced were shown to be perfluoro and partially fluorinated compounds corresponding to the original molecular architecture, showing that carbon-carbon and carbon-oxygen (ether) bonds could survive fluorination. It was also shown that acyl fluoride groups could be formed during fluorination of oxygen-containing polymers. The deliberate addition of oxygen to fluorine during fluorination also introduces acyl fluoride. Steady improvements in technique allowed yields of desired products to be increased, and permitted fluorination of more delicate structures such as dioxane, ethyl acetate, and pivaloyl fluoride.

Despite these successful fluorinations, the challenge of preserving the physical strength of a polymeric structure, as for example a film 1 to 10 mils thick, while achieving complete penetration of the thickness and conversion to perfluoro structure remains. The additional challenge of preserving functionality during this process must also be met for success in preparing membranes by direct fluorination.

3.0 SELECTION OF STARTING MATERIALS

3.1 Functionality and Film Forming

The equivalent weight of Nafion at useable conductivities is in the region of 1200. This implies that 5 to 10 TFE units are copolymerized per functionalized perfluorovinylether unit. The Flemion structure is believed to be quite similar. It seemed reasonable to us to begin our synthetic efforts with copolymers of acrylate esters or acrylic acid with ethylene, for reasons that such polymers are readily available in a wide range of copolymer ratios, and because the ester grouping has been shown to survive treatment with elemental fluorine rather well.

Homopolymers and copolymers selected as substrates must, in addition to bearing the desired functional groups, also form strong films capable of being crosslinked.

3.2 Crosslink Ability

The introduction of crosslinks to the ethylenic copolymer and blends mentioned above can be readily accomplished with electron beam radiation. We chose to investigate the range of doses from 1 MRAD to 100 MRAD in order to provide sufficient variability in crosslink density to demonstrate the effect on the swelling properties of the resulting membranes.

3.3 Fluorination

The use of elemental fluorine diluted with inert gas and cooled to appropriate temperatures to synthesize new perfluorochemical structures has been thoroughly investigated and reviewed by R.J.Lagow in his review article. We are here concerned with the additional challenge of producing physically useful articles from this process. The possibility is enhanced by the proclivity of direct fluorinations to proceed from the surface inwards with a gradation of fluorine contents from the skin towards the center. Such asymmetric membranes may be especially interesting despite the possibility of elimination of HF and production of unsaturation.

The selection of ester groups, anhydride groups, acid halide groups, and ethylenic units, as the substrates for fluorination is based on the accumulated experience of the investigators. Other oxygen-bearing groups are likely to release oxygen during fluorination, and to promote formation of hydroperoxides followed by chain scision, and enbrittlement of the product. The introduction of crosslinks before the fluorination is expected to mitigate the effects of chain scision, but we have chosen to reduce the risk of oxygen damage by limiting our attention to the foregoing functional groups initially.

4.0 EXPERIMENTAL

4.1 Preparation of Films

Solutions containing 5% of the chosen polymer or polymers are prepared by gentle mixing on a hot plate and approximately 20 g portions are poured onto 4" x 4" or 8" x 8" aluminum foil trays which have been secured to glass plates to ensure flatness, and levelled to ensure uniform thickness. The solvents are carefully evaporated at temperatures which avoid bubble formation and other non-uniformities.

Two or three layers of cast films were hot pressed together at 120^o and 400 psi for 3 minutes to produce thicker films.

4.2 Crosslinking

The foil trays containing the dried films are subjected to 1 MEV electron beam bombardment inside of polyethylene bags which have been flushed with nitrogen to reduce the undesired oxidation which would otherwise occur. Since the crystallization of blocks of ethylene units in polymers of this type cannot be prevented below approximately 60^{o}C, samples were radiated at elevated temperature (e.g. 85^{o}C); thus ensuring uniformity of distribution of crosslinks. The electron beam is sufficiently intense to maintain a temperature of 85^{o}C over the approximately one hour of radiation time.

4.3 Fluorination

The films were separated from the aluminum supports and placed on copper gauze inside the fluorination reactors, which were flushed with inert gas. Fluorination was carried out beginning with low concentrations of fluorine in helium and gradually increasing the concentration of fluorine until pure fluorine surrounds the sample. For some experiments the fluorination was intensified by increasing the pressure of pure fluorine to 30 psi and for some the temperature of the fluorination was also raised to 60^{o}C.

5.0 CHARACTERIZATION

5.1 Weight Increases

The primary indication that hydrogen has been replaced by fluorine is the weight increase due to the difference in atomic weight. Weight increases are recorded as percent of the original weight, the assumption being that no weight is lost from the sample except hydrogen, which leaves as HF.

5.2 Infra-Red Spectroscopy

The infrared spectrum of the polymers before and after fluorination reveals decreases in CH vibrations, and the appearance of CF vibrations, the appearance of $-CF_2-COO$ vibrations and the decrease of $-CH_2-COO$ vibrations. The qualitative results used in this program should be superceded by quantitative FTIR spectra of the samples, but the problems of special sample preparation, time, and money have so far prevented this.

5.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry d tects the melting temperature of crystalline polymers and the amount of crystalline sequences present, and comparison of various samples permits the deduction of solubility, or the presence of mixtures, or the progress of reactions such as fluorination. As fluorine replaces hydrogen in the polymer films, the melting point and the area under the curve representing the amount of crystalline material remaining will change. These changes may be correlated with the weight increases of the films on fluorination.

5.4 Swelling

The weight of the electrolyte absorbed in the films over extended periods of soaking under liquid electrolyte are observed and correlated with the crosslink density and the concentration of ionizing groups in the membrane. Swelling of the unionized membrane in non-ionizing solvents may be used to distinguish the crosslink density effect from the ionic effects.

5.5 Physical Properties

The strength of the membranes is measured by tensile testing of the swollen materials in an Instron tester. The dry ionic polymers are frequently brittle and the strength tests would not be representative of conditions of use.

5.6 Conductivity

Conductivity of the crosslinked membranes before and after fluorination is measured in an electrochemical cell after the membrane has been boiled in acidic aqueous media for many hours to condition the membrane. The conductivity is also measured at several elevated temperatures, partly because the structure of the polymer film will be temperature-sensitive if there are crystalline regions present, and because of differential swelling with temperature. It is of interest to detect the upper limits of usefulness in terms of temperatures for these membranes, and to observe the decrease in electrical resistance with rising temperature.

5.7 Thermogravimetric Analysis

Determination of the temperature at which weight is lost from dry films in inert atmospheres is a useful indicator of the thermal stability of the materials. Accordingly such data has been accumulated for polymer films of interest.

6.0 MATERIALS AND EQUIPMENT

6.1 Polymers which form Films

6.1.0. Copolymer DPD6169-NT is nominally a film-forming random copolymer of ethylene with 6 mol % ethyl acrylate supplied by Union Carbide Corp.

6.1.2. C.P. 32 is a random copolymer of ethylene with 23% methyl acrylate by weight

6.1.3. 1P-105 is a random copolymer of ethylene and 20% methyl methacrylate by weight

6.1.4 TD 7551 is a random copolymer of ethylene with 30% isopropyl acrylate by weight

6.1.5. A random copolymer of ethylene with acrylic acid 17% by weight.

The latter 4 samples were supplied as experimental materials by Gulf Oil and Chemical Company through the courtesy of Dr. B. H. Clampitt of the Houston, Texas Research Laboratory.

6.2 Polymers bearing functional groups

6.2.1 PA-18 is an alternating copolymer of maleic anhydride and 1-octadecene

6.2.2. PA-14 is an alternating copolymer of maleic anhydride and 1-tetradecene

6.2.3. PA-10 is an alternating copolymer of maleic anhydride and 1-decene

6.2.4. PA-6 is an alternating copolymer of maleic anhydride and 1-hexene

6.3 Radiation Source

Crosslinking was accomplished in the Vandegraaf electron accelerator at the Western New York Nuclear Facility of the State University of New York at Buffalo, N.Y., using approximately 1 MEV electrons, and at the Center for Fast Kinetic Reaction at the University of Texas, Austin, TX.

7.0 RESULTS AND DISCUSSION

7.1 Mixing of Polymers

One gram of the film-forming polymer described in Section 6.1.1 above was dissolved in 30 ml. of $CHCl_3$ or CCl_4, and mixed with an equally concentrated solution of the polymers described in 6.2.1, 6.2.2, 6.2.3, and 6.2.4. The mixed solutions were reversibly clear above 60°C, and cloudy below 60°C. This is also true of 6.1.0 solutions in the absence of other polymers, presumably because the polyethylene sequences crystallize below 60°C in these solvents. These observations are collected in Table I, along with observations on the dried films. The fact that precipitation does not occur above 60°C when both polymers are present in solvents means that they are compatible pairs.

The above is a surprising result since most polymers are mutually insoluble.

TABLE 1. Compatibility of Polymer Mixtures in $CHCl_3$

Polymer 1	Conc. g/ml	Polymer 2	Conc.	Observation
DPD	1/30			Clear above 60°, cloudy below
		PA-18	1/30	Clear
DPD	1/30	PA-18	1/30	Mixed solutions clear above 60°C
		PA-14	1/30	Clear
DPD	1/30	PA-14	1/30	Clear above 60°C
		PA-10	1/30	Clear
DPD	1/30	PA-10	1/30	
		PA-6	1/30	Clear
DPD	1/30	PA-6	1/30	Clear above 60°C, cloudy below

7.1.1 Films of Polymer Mixtures

Evaporation of solvent at 50-60°C on 8" x 8" glass plates produced thin films of all the above mixtures. The films are flexible but difficult to remove from the glass because they are too thin.

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		PA-14	1/30	Clear
DPD	1/30	PA-14	1/30	Clear above 60°C
		PA-10	1/30	Clear
DPD	1/30	PA-10	1/30	
		PA-6	1/30	Clear
DPD	1/30	PA-6	1/30	Clear above 60°C, cloudy below

7.1.1 Films of Polymer Mixtures

Evaporation of solvent at 50-60°C on 8" x 8" glass plates produced thin films of all the above mixtures. The films are flexible but difficult to remove from the glass because they are too thin.

Double and triple thickness films were prepared by pouring a second layer over the first, evaporating solvent, then heating to about $120^{o}C$ to ensure fusion of the two layers. On cooling, these films are slightly cloudy or translucent, strong enough and flexible enough to peel from the glass.

Table 2. Films of Polymer Mixtures Cast from $CHCl_3$

Polymer 1	Polymer 2	
DPD (1g)	PA-18(1g)	Strong, flexible, hazy
DPD (2g)	PA-18(2g)	double layer, cloudy at $120^{o}C$, but clears to hazy on cooling.
DPD (1g)	PA-14(1g)	Cloudy, flexible, adheres strongly to glass
DPD (2g)	PA-14(2g)	Double layer strong, flexible, peels without breaking, clears on cooling from $120^{o}C$.

Press-heated films were also prepared by folding 8" x 8" sheets to 4" x 4" square, preheating in a compression press at $120^{o}C$ for 3 min., pressing for 3 min. at 400 psi, and then cooling to room temperature. The compositions of the films were varied to observe the range of film-forming capability. The data are collected in Table 3 including the equivalent weights of the mixtures.

TABLE 3: Hot-Pressed Films of Polymer Mixtures

No.	Polymer 1	Polymer 2	Eq.wt.(g/eq)	meq/g
1	DPD (0.7788g)	PA-18 (0.1728g)	970	1.03
1.5	DPD (0.6967g)	PA-18 (0.2587g)	649	1.54
2	DPD (0.6115g)	PA-18 (0.3458g)	483	2.07
3	DPD (0.6956g)	PA-18 (0.5192g)	410	2.44
4	DPD (0.6136g)	PA-18 (0.6912g)	331	3.02
5	DPD (0.7788g)	PA-18 (0.8640g)	333	3.00
6	DPD (1.000g)	PA-14 (1.000g)	294	3.40
7	DPD (1.000g)	PA-14 (2.000g)	220	4.53

7.1.2 Crosslinking

Samples of the above films were exposed to 1 MEV electrons for sufficient time to absorb the doses recorded in Table 4. Swelling experiments were performed in CCl_4 at 25°C and 50°C to demonstrate that the PA-18 was not extractable, and the crosslinked films were not soluble. The uptake of solvent was measured by quickly blotting and weighing specimens immersed in liquid solvent.

Table 4: Radiation Dose and Swelling of Polymer Films in CCl_4 (by weight)

Sample No.	Film No. (Table 3)	Dose Mrad	Weight (g)	Time t=0	30 Sec.	5 min	15 min	30 min	16 hrs	Max % Swelling
1	3-1.5-10X	10	0.0511		.087	0.165	0.185	0.188	0.181	254
2	3-1.5-20X	20	0.060		0.093	0.163	0.169	0.170	0.164	173
	heated to 50°C			0.164	0.277	0.318	0.297	0.302		403
3	3-1.5-30X	30	0.053		0.087	0.142	0.150	0.153	0.151	184
	heated to 50°C				0.245	0.287	0.286	0.290	0.271*	411
4	3-1.5-40X	40	0.0589		0.0750	0.131	0.136	0.142	0.141	139
	heated to 50°C				0.194	0.200	0.202	0.188	0.190	222
5	3-1.5-40X	40 (unpressed, cast film)								
			0.035		0.043	0.041	0.045	0.045	0.045	28.5
	heated to 50°C				.058	.061	.065	.063	0.058	65.7

* Sample torn in half overnight

The observed decrease in maximum swelling with increasing radiation dose is expected, as more crosslinks are produced. The surprisingly low swelling of #5, the unpressed, cast film 3-1.5-40Mrad compared to #4, may reflect a difference in morphology of the crystalline portion of the sample. This change would probably be reflected in the Transport properties of the resulting membrane.

Samples of the above films were cut and weighed, then boiled for 6 hours in 1M aqueous HCl solution. The weight of the swollen films at room temperature is reported in Table 5.

Table 5 Swelling of Hydrolysed Polymer Films in Aqueous HCl (1M) (measured at room temperature)

Sample No. (Table 4)	Meq/g	Rads Dose	Wt. Inc.
1	1.54	10 Mrad	158
2	1.54	20	100
3	1.54	30	115
4	1.54	40	87
5	1.54	40 cast film	18

It appears that higher dose rates of radiation may be required to lower the swelling even further. The behavior of cast film #5 should be re-investigated.

7.1.3 Differential Scanning Colorimitry

The Dupont 990 D.S.C. was used to compare the melting temperatures and fraction of crystalline material present in the crosslinked mixtures to the starting materials.

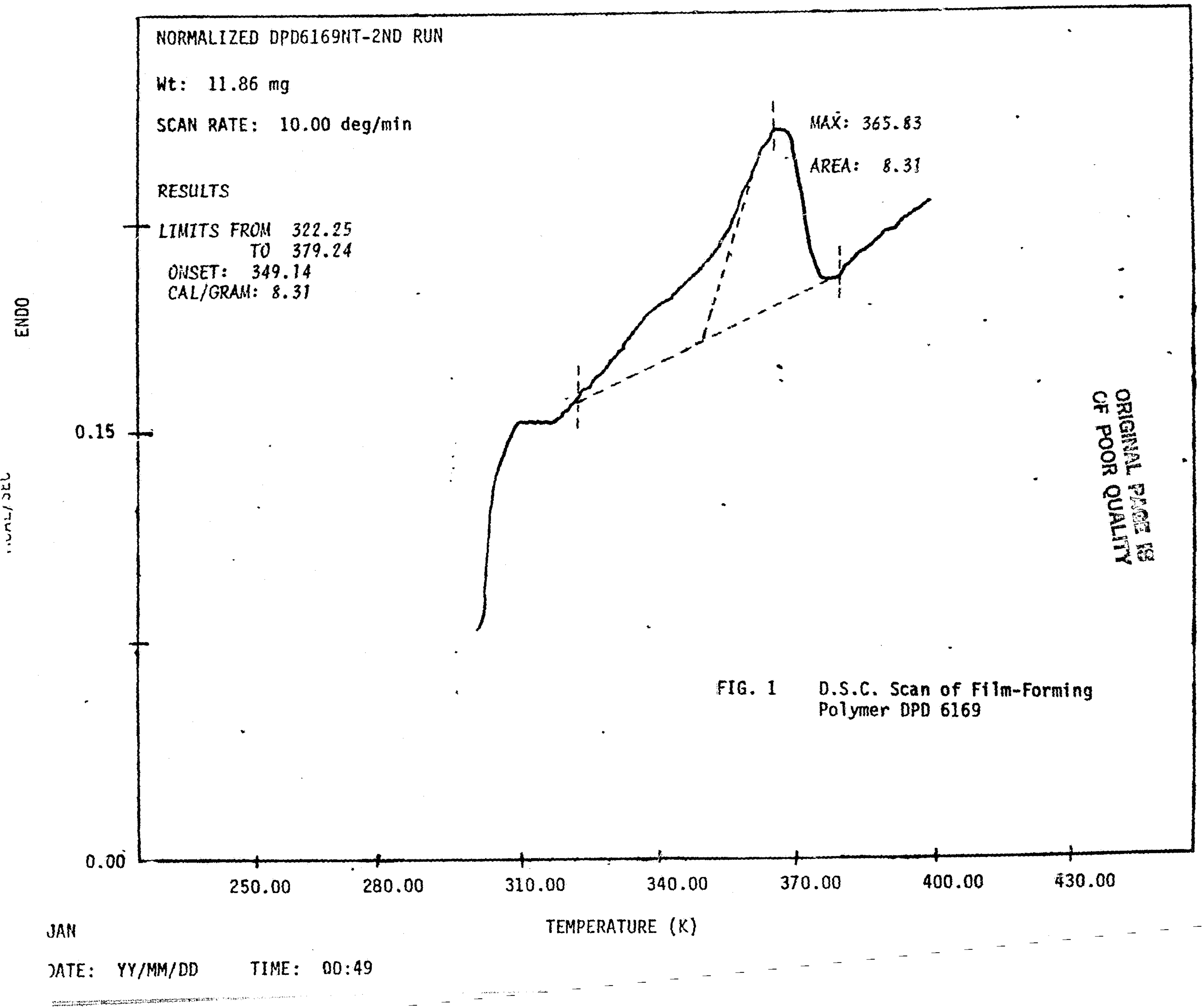

FIG. 1 D.S.C. Scan of Film-Forming Polymer DPD 6169

7.2 Fluorination

Crosslinked polymer films (4" x 4") were mounted on copper gauze and sealed in a 6" dia. x 2" deep fluorination reactor. The reactor was flushed for 6 hours with dry Helium flowing at 100 cc/min. through 1/4" tubing, and then the outlet was blocked and the pressure raised to 10 psi to test for leaks. Helium pressure was then released, and fluorine introduced on the following schedule:

Flow F_2 cc/min	Flow He cc/min	Time Interval
0.5	100	91.5
0.5	70	33
1.0	75	49.5
2.0	50	23.7
2.0	0	44
3.0	0	16 optional pressurize to 11 psi

Table 6: Weight Increases on Fluorination of Crosslinked Polymer Films

Sample (Table 3)	Rad Dose Mrad	% Wt. Increase
4	20	23
4	40	18
7	15	56.3

7.2.1 Water Pickup of Fluorinated, Crosslinked Films

Samples were boiled in 1M HCl for 24 hours

Table 7: Water Pickup of Fluorinated, Crosslinked Films

Sample No. (Table 3)	meq/g	Crosslinks (Mrad)	Wt. Inc. Inc. (F_2)	Water Pickup
7	4.53	15	56.3	15

7.3 Physical Properties

The boiled samples were tested for tensile strength in an Instron Tester at room temperature.

7.4 Thermogravimetric Analysis

Samples of the above films were analyzed for thermal stability using the Dupont 990 thermogravimetric analyzer. Temperatures for 1% and 3% weight loss are indicated.

7.5 Electrical Conductivity of Fluorinated Films

Conductivity of fluorinated and unfluorinated films was determined after the membranes were conditioned in boiling aqueous acid for 4 hours, 24 hours, and 48 hours. The lowest resistivity reported by NASA-Lewis was 5 ohm-cm^{-1}.

8.0 Comparison with Commercial Fluorocarbon Membranes

Published information from DuPont and Asahi Glass indicate that electrical resistivity and water pick up of our fluorinated carboxylic acid crosslinked membranes are essentially equivalent. The subject membranes of this report have the additional flexibility of a wide range of crosslink density and a considerable, independent range of carboxyl concentration.

The physical properties of the membranes reported here are, of course, inferior to the highly developed commercial products. We plan to develop physical properties concurrently with the selection of optimum crosslink and carboxyl group concentrations for specific applications.

9.0 CONCLUSIONS

The direct fluorination method of converting carefully selected hydrocarbon substrates to fluorinated membranes has been successfully applied to produce promising, novel membranes for electrochemical devices.

A family of polymer blends has been identified which permits wide latitude in the concentration of both crosslinks and carboxyl groups in hydrocarbon membranes.

The membranes of paragraph two have been successfully fluorinated and are potentially competitive with commercial membranes in performance, and potentially much cheaper in price.

Further investment is justified to improve physical properties and establish cost advantages.