[illegible] ~~CR# 166276~~

SQT

NASA-CR-166276

FINAL REPORT

TO THE

NATIONAL AERONAUTICS SPACE ADMINISTRATION

Contract #NAS2-10064

(1) *MANUFACTURE OF DPFC-DMS POLYMER IN THE 5KG RANGE.*

B. Mason Hughes
Principal Investigator
Flammability Res. Center
University of Utah
Salt Lake City, Utah 84108

Donald R. Owen
Sub-contract - Tulane University
Principal Investigator

Jean H. Futrell
Director, Flammability Research Center
University of Utah
Salt Lake City, Utah 84108

(NASA-CR-166276) MANUFACTURE OF DPFC-DMS POLYMER IN THE 5KG RANGE Final Report (Utah Univ.) 25 p HC A02/MF A01 CSCL 11G

N84-27888

Unclas
G3/27 19786

TABLE OF CONTENTS

Page

A. SUMMARY

BPFC-DMS block copolymers have been synthesized on a pre-pilot scale (i.e., to 5 Kg lots) and subsequently fabricated into clear, colorless films. Details of the synthesis procedures, property determinations, and film casting techniques are presented. Solubility, viscosity and molecular weight characteristics of the resulting product are reported.

B. SYNTHESIS OF BPFC-DMS BY INTERFACIAL CONDENSATION

Approximately 10 Kgs of the dried polymer has been produced by a procedure involving the following three stages of batch processing:

1. Raw material synthesis
2. Oligomer synthesis
3. Block copolymerization

These steps will be discussed in sequence.

1. Raw Material Synthesis

Purification of Chloroform and Dichloromethane

Because of availability and storage convenience, chloroform was substituted for dichloroethane by this laboratory because of availability and storage for the endcapping procedure. Reagent grade $CHCl_3$ was purified by passing 4 liters of solvent under a slight N_2 pressure through a 4 ft., 1 in. diameter glass column packed with #20 active alumina. The filtrate was discharged directly into a fired, N_2 blanketted, oven dried, dark glass (or foil covered) container and stored in a cool place. Dichloromethane, later used to replace $CHCl_3$ in the final oligomer solution, was purified in a similar manner. The solvents were stored for 1 week or less under these conditions. Solvents not used within a week were repurified by the above procedure before they were used.

BPF Storage and Usage

To minimize skin irritation and handling complications, BPF was kept in solution (or slurry) form. Freshly recrystalized BPF was placed in a vacuum oven at 90°C overnight then placed in a N_2-filled oven at 110°C for 24 hours. 315 g of BPF was then added to a fired, N_2-dried 1 gallon dark glass container containing 2700 ml of the purified $CHCl_3$. This procedure was carried out in a solvent hood with N_2 flowing over the bottle neck at approximately 2 liters/min. The bottle was purged by placing the teflon N_2 delivery tubing into the container and bubbling N_2 through the solution for a minimum of 2 minutes. The container was then tightly capped and stored in a dark, cool area. Similarly, 300 g of BPF per 2700 ml of CH_2Cl_2 was charged to a 1 gallon brown glass container. Approximately 40 ml of acetone was added to dissolve all the BPF. The latter solution was retained for use in the copolymerization step.

Silicone Fluid Synthesis

D-4 silicone fluid was synthesized according to the procedure outlined in Sorenson [1]. After the distillation and pyrolysis steps, a mixture of approximately 50/50, D3/D4 siloxane fluid was obtained. Under a slow stream of N_2, 1426.4 g of the D3/4 solution was added to a 1 gallon, fired, N_2 oven-dried, dark glass container. Then 80 g $Si(CH_3)_2Cl_2$ and 0.329 g $FeCl_3$ (anhydrous) were added to the mixture. After loosely capping the container, it was placed in an N_2 drying oven for 24 hours at 48°C. 1500 ml of the purified $CHCl_3$ was then added under a slow stream of N_2, and the bottle was tightly capped and stored in the refrigerator. Shelf lives appear to be in excess of 1 year without any loss in reactivity for solution prepared to this stage.

2. Oligomer Synthesis

A 10 liter three-neck flask was assembled with thermometer, vented dropping funnel, and a gas inlet tube and vent for N_2/NH_3. The inlet tube was made from a long-stem dropping pipette which reached nearly to the bottom of the flask. During assembly, a 2 liter/minute flow of N_2 was directed through the flask and was left on for several minutes after charging with reactant, in order to purge the system. 4500 ml of the $CHCl_3$-BPF slurry was then charged to the vessel. The N_2 stream was switched to NH_3, which was bubbled through the slurry at a rate of 1.84 liters/minute for 30 minutes. At the 20 minute mark a white precipitate begins to appear. At 25 minutes reaction time stirring of the mixture is facilitated by the addition of another 800 mls of purified $CHCl_3$. The NH_3 is then switched off and the N_2 purge (0.2 ℓ/min.) is started. Equilibriated silicone fluid is slowly charged to the dropping funnel until 1140 ml have been added (two additions are necessary). Then the silicone fluid is added to the reaction mixture at a rate of 30 ml/min and an exotherm is observed. The resulting purple suspension was stirred for 1 hour and then refluxed for 2 hours at 60-61°C.

The resulting fluid is an off-white suspension with pH $\simeq$ 7.0. Two liters of distilled H_2O were then added and the mixture was acidified with 2.4 N HCL to a pH of 3.0. Reagent grade acetone is added to clear the solution (approximately 150-200 ml is required). The solution was then transferred to a 4 ℓ flask and the aqueous phase discarded. The organic phase was washed with 1000 ml increments of 2.4 N HCl, H_2O, 0.5 M Na HCO_3, H_2O and H_2O. $MgSO_4$ was then added to dry this organic phase. The volume of the resulting clear, golden solution was halved by vacuum evaporation and then, with the aid of a steam bath, taken to dryness. Average yeild at this point was 1050 g.

The residue was redissolved in CH_2Cl_2 (184 g in 1 ℓ), and sufficient acetone was added to clear the solution. The solution was stored in a dark glass, fired, N_2 oven dried bottle. Tightly sealed bottles of this solution have also been demonstrated to have shelf lives of at least one year, unrefrigerated, with no loss in reactivity or lowered molecular weight in the resulting block copolymer.

3. Block Copolymerization

As described previously, all solutions were prepared and stored in dark glass under N_2. Further, as recommended by Schnell, Bottenbruch, and Matzner [2, 3, 4], chloroform was replaced by methylenechloride in all polymerization reactions to avoid coloration in the product. All glass containers were washed thoroughly and rinsed with acetone, then dried at 110°C. A 12 liter three-neck flask was fitted with thermometer, dropping funnel, N_2/phosgene vent and supply (e.g., capillary tube to bottom of flask), and a paddle stirrer. This apparatus was flushed continually with N_2 for the duration of the process.

3800 ml of the CH_2Cl_2 solution of BPF (110.8 g/ℓ) was added to the flask. 3175 ml of the endcapped silicone solution was then added under a slow stream of N_2. The endcapped solution provides a theoretical stoichiometric ratio of 11.6 percent by weight of elemental silicon. 7.0 ml of triethylamine was then pipetted into the organic phase and the paddle stirrer was set at a moderate rate to mix the components into a clear, slightly yellow, homogenous liquid.

A aqueous phase solution was prepared by adding 0.9 g sodium gluconate per 1000 ml distilled H_2O, and 3175 ml of the solution was added to the flask. The N_2/phosgene vent/supply was switched to phosgene and vented to a NaOH/MeOH trap. The dropping funnel was charged with 950 ml of 16.55 M NaOH.

Phosgene was then bubbled through the mixture at a rate of 2.9 g/min (0.68 ℓ/min STP) and the NaOH solution added at a rate of 5.5

ml/min to maintain the pH at 10 ± 0.5. (Variation in pH was not found to be critical as long as the solution was kept at a pH > 9.7 to maintain alkaline phenoxides which hydrolyze phosgene at a greater rate than water [2, 3, 5, 6].) After 125 minutes the phosgene rate was cut back to 0.15 ℓ/min and the NaOH addition modified to maintain pH at 10 ± 0.5. The solution at this time was a milky-white, two-phase suspension which seemed to clear slightly with time.

After five hours at the lower phosgene addition rate and after approximately 950 ml of NaOH had been added, thin filaments of polymer were observed to form at the tip of the capillary gas tube. At this point the phosgene addition was terminated and N_2 was bubbled through the suspension to purge excess phosgene. The mixture was allowed to settle and the aqueous phase discarded. The organic layer was washed as described in the preliminary Statement of Work (dated April 3, 1978), dried over $MgSO_4$ and precipitated in acetone/methanol solution. The precipitate was filtered and vacuum dried at 80°C for 24 hours. Batches processed in this manner had an average yield of 89 percent.

Chloroform cast films exhibited a tendency to shrink after one or two days of storage in a warm, dry area. Average shrinkage along the side of any sheet was approximately 3-4 cm. As drying continues after release of the film from the plate, curling towards the glass side is also prevalent.

C. FILM MANUFACTURE

Films have been cast giving clear colorless sheets 0.05 to 0.12 mm thickness. Five percent solutions were made up by dissolving the thourougly dried polymer in chloroform and stirring the solution over $MgSO_4$. The solutions were then filtered through coarse glass and stored until ready to use. If cloudiness persisted after filtering, it was cleared by heating to a low boil (with high agitation). If cloudiness and difficulty in filtering occur, unacceptably high amounts of unpolymerized silicone segments are present and the solution must be reprecipitated in a 50:50 heptane acetone mixture, filtered and dried as previously described.

The casting apparatus is similar to that described in the preliminary report, consisting of a 63.5 X 63.5 cm^2 glass sheet (1/8" glazing) bounded on the sides by a wooden frame 6 cm high. A 500-550 ml portion of the casting solution was slowly poured on the center of the casting plate and a glass cover slid over to shield the solution from convective currents. After 1-1 1/2 hours the films were noted to undergo unassisted release from the glass. This release, complicated by static buildup and inhomogeneity in drying, caused splitting in the films. This problem is aggravated for films of increased thickness.

Accordingly the procedure was modified to include surface treatment of the casting plate. 400 ml of a 1 percent solution of $Si(CH_3)_2Cl_2$ in acetone was poured onto the plate and evaporated dry. The plate was then flushed with water. This treatment proved to be effective in minimizing the splitting and produced a more even distribution of the casting fluid.

D. PROPERTIES OF BPFC-DMS FILMS

Samples of four groups were selected and designated as samples MB1-4. Molecular weight determination by gel permeation chromatography (GPC) show a range of $\overline{M}w$ from 32,000 to 36,000 with dispersities from 1.65 to 1.9. Figure 1-4 in Appendix A give G.P.C. charts and computer analysis of molecular weights and dispersities.

Intrinsic viscosities for the four groups and for the NASA-furnished sample appear in Appendix B. The viscosities vary from 0.13 to 0.29 dl/g with the NASA sample at 0.27 dl/g. These values were obtained employing chloroform as the solvent and a standard size 50 Cannon-Fenske viscometer.

Solubilities were determined by immersion of 1 g of both the film and the dried granular powder in 20 ml of test solvent. The polymer and film were found to be soluble up to at least 60 percent (by weight) in $CHCl_3$ and Chlorobenzene. The product is soluble up to 10-20 percent (by weight) in dichloromethane, THF and ethylenedichloride. The film clouds and swells considerably when placed in these solvents. The film forms a cloudy surface layer in diethylether, hexane and heptum but does not swell appreciably. Water and aliphatic alcohols have no short term effect. Long term effects in the later solvents has not been tested.

IR data for the four films are reported in Appendix C.

APPENDIX A

GPC DATA FOR FILMS MB-1, MB-2, MB-3 AND MB-4

Instrument: Waters Model

Solvent: Toluene

Sample Pressure: 85 K P sig

Oven Temp.; 35°C

Refract. Temp.: 37°C

Flowrate: 5.2 ml/count

Calibration: Polyscience - Styrene polymer series

Polymer: 100 k - 2,900 $\overline{M}w$

Columns:

1. TI 6040 50. 80A X 450 PFT
2. TI 6197 700-2000A X 700 PFT
3. TI 6600 5 X 10/3 1.5 X 10/4 X 750 PFT
4. TI 6488 100-350 A X 750 PFT

APPENDIX B

INTRINSIC VISCOSITIES OF NASA SUPPLIED BPC-DMS COPOLYMER AND POLYMER FILM SAMPLES MB-1, MB-2, MB-3 and MB-4.

B.1. INTRINSIC VISCOSITY OF NASA SUPPLIED SAMPLE BPC-DMS BLOCK COPOLYMER.

Cannon-fenske Size 50 Normal Viscometer
Serial No. B677
Constant = 0.000389 at 100°F

Temp. = 26.8°C CHCl$_3$ Solvent

Concentration C	Efflux Time t (sec.)	$N_r = \frac{t}{t_s}$	$N_{sp} = \frac{(N_r - 1)}{C}$	$\frac{(\ln Nr)}{C\ (dl/g)}$
0.0 g/dl	107.4 (.3)	-	-	-
0.125	111.6 (.2)	1.0382	0.03816	0.299
0.063	109.5 (.3)	1.01738	0.01738	0.273
0.249	115.9 (.3)	1.07850	0.07850	0.304
0.496	127.3 (.6)	1.1846	0.1846	0.342

From graphical extrapolation of above data $[\eta]$ = 0.27 dl/g.

B. 2. INTRINSIC VISCOSITY OF SAMPLE MB-1

Cannon-Fenske Size 50 Viscometer
Serial No. B677
Constant - 0.000389 at 100°F

Temp. = 26°C $CHCl_3$ Solvent

Concentration C	Efflux Time t (sec.)	$N_r=\frac{t}{t_s}$	$N_{sp}=\frac{(N_r-1)}{C}$	$\frac{(\ln N_r)}{C\ (dl/g)}$
0.0 g/dl	97.4 (.4)	-	-	-
0.10	98.7 (.3)	1.0137	0.1370	0.1361
0.20	103.0 (.1)	1.0575	0.2875	0.2795
0.40	109.0 (.6)	1.1208	0.3020	0.2851

From graphical extrapolation of above data $[\eta] = 0.13 \pm .04$ dl/g.

B.3. INTRINSIC VISCOSITY OF SAMPLE MB-2.

Cannon-Fenske Size 50 Normal Viscometer
Serial No. B677
Constant = 0.000389 at 100°F

Temp. = 26°C Solvent $CHCl_3$

Concentration C	Efflux Time t (sec.)	$N_r=\frac{t}{ts}$	$N_{sp}=\frac{(N_r^{-1})}{C}$	$\frac{(\ln Nr)}{C\ (dl/g)}$
0.0 dl/g	96.4 (.2)	-	-	-
0.10	99.5 (.5)	1.0329	0.3290	0.3237
0.20	101.3 (.2)	1.0512	0.2560	0.2497
0.40	108.5 (.2)	1.1263	0.3158	0.2973

From graphical extrapolation of above data [η] = 0.29 ± .03 dl/g.

B.4. INTRINSIC VISCOSITY OF SAMPLE MB-3.

Cannon-Fenske Size 50 Normal Viscometer
Serial No. B677
Constant = 0.000389 at 100°F

Temp. = 26°F

Solvent $CHCl_3$

Concentration C	Efflux Time t (sec.)	$N_r=\frac{t}{ts}$	$N_{sp}=\frac{(N_r^{-1})}{C}$	$\frac{(\ln Nr)}{C\ (dl/g)}$
0.0 (g/dl)	95.7 (.1)	-	-	-
0.10	97.5 (.3)	1.0200	0.200	0.1980
0.20	101.2 (.3)	1.0575	0.2875	0.2795
0.40	105.2 (.3)	1.0997	0.2491	0.2376

From graphical extrapolation of above data $[\eta] = 0.21 \pm .03$ dl/g.

B.5. INTRINSIC VISCOSITY OF SAMPLE MB-4.

Cannon-Fenske Size 50 Normal Viscometer
Serial No. B677
Constant = 0.000389 at 100°F

Temp. = 26°F

Solvent $CHCl_3$

Concentration C	Efflux Time t	$N_r = \frac{t}{t_s}$	$N_{sp} = \frac{(N_r{}^{-1})}{C}$	$\frac{(\ln Nr)}{C}$ (dl/g)
0 (g/dl)	96.1 (.1)	-	-	-
0.10	97.9 (.1)	1.0181	0.1810	0.1794
0.20	99.5 (.2)	1.0347	0.1735	0.1706
0.40	103.7 (.4)	1.0785	0.1963	0.1889

E. BIBLIOGRAPHY

1. Sorenson, W. R. and Campbell, T. W., "Preparative Methods of Polymer Chemistry", 2nd Ed., Interscience Publ. N. Y. (1968).

2. Schnell, H., Chemistry and Physics of Polycarbonates, Interscience, John Wiley & Sons, N.Y. (1964).

3. Bottenbruch, L., "Polycarbonates," Encyl. of Polymer Science and Technology, N. M. Bikales Eds., John Wiley & Sons, N. Y., 10, 710 (1969).

4. Matzner, M., Kurkjg, R. P. and Cotter, R. J., *J. Appl. Polymer Science, 9,* 3295 (1965).

5. Kambour, R. P., Corn, J. E., Miller, S. and Nizhik, G. E., "Tough Transparent Heat- and Flame-Resistant Thermoplastics Via Silicon Block-Modified Bidphenols Fluorenone Polycarbonate," *J. Appl. Polymer Sci., 20,* 3275 (1976).

6. Morgan, P. W., *Macromolecules, 3,* 536 (1970).

7. *Angew. Chem., 68,* 688 (1956).

APPENDIX C

IR DATA FOR THE CAST FILMS MB-1, MB-2, MB-3 and MB-4.

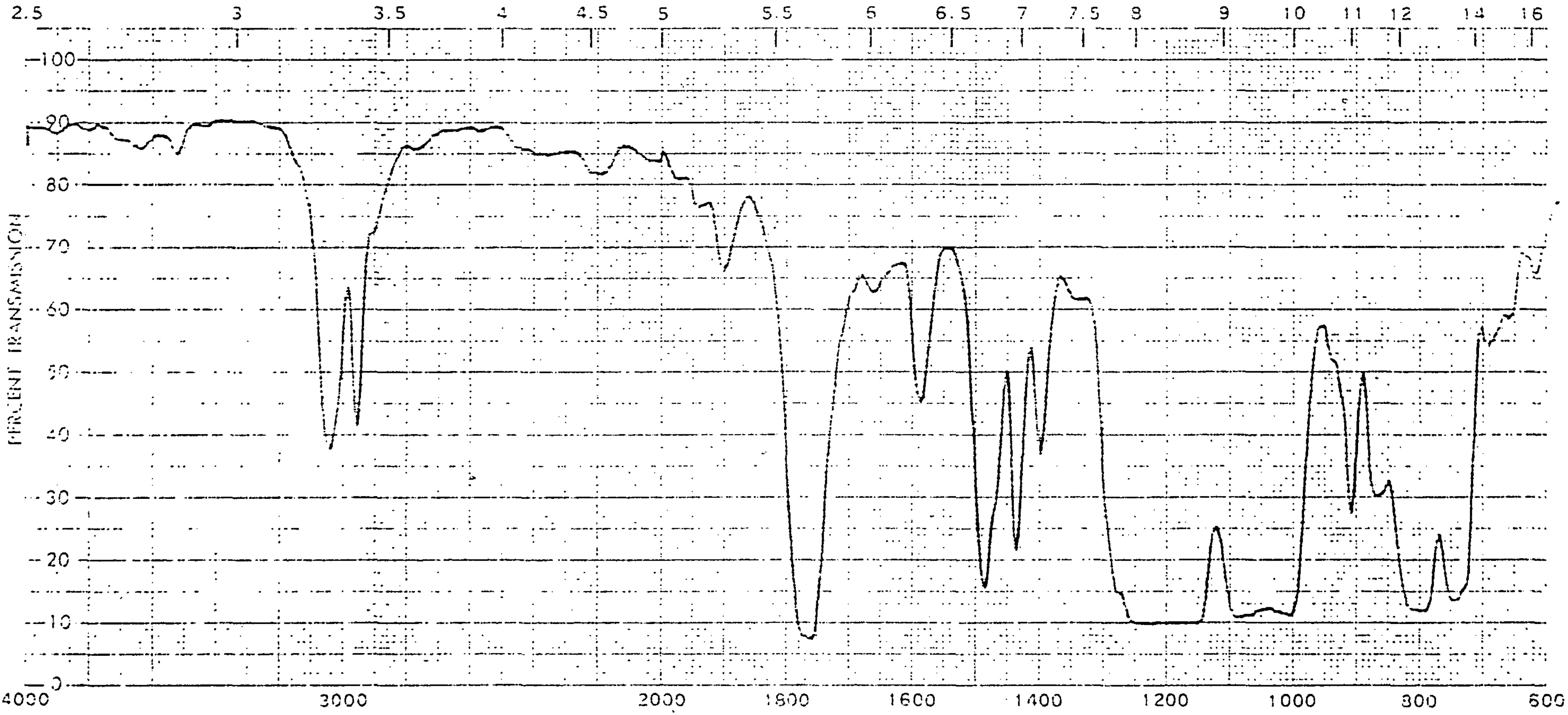
Beckman

INFRARED SPECTROPHOTOMETER

SPECTRUM NO. 1 DATE ______ SAMPLE MB1 - 7ILM SOURCE BPF-5

PATH ______ mm ______ SOLVENT CHCl$_3$ CONCENTRATION ______ PHASE SOLID

ANALYST ______



WHEN REORDERING SPECIFY CHART NO. 579315 78

BECKMAN INSTRUMENTS, INC., FULLERTON, CALIFORNIA, PRINTED IN U.S.A.

INFRARED SPECTROPHOTOMETER

Beckman

SPECTRUM NO. 2 DATE

PATH mm

SOLVENT CHCl3

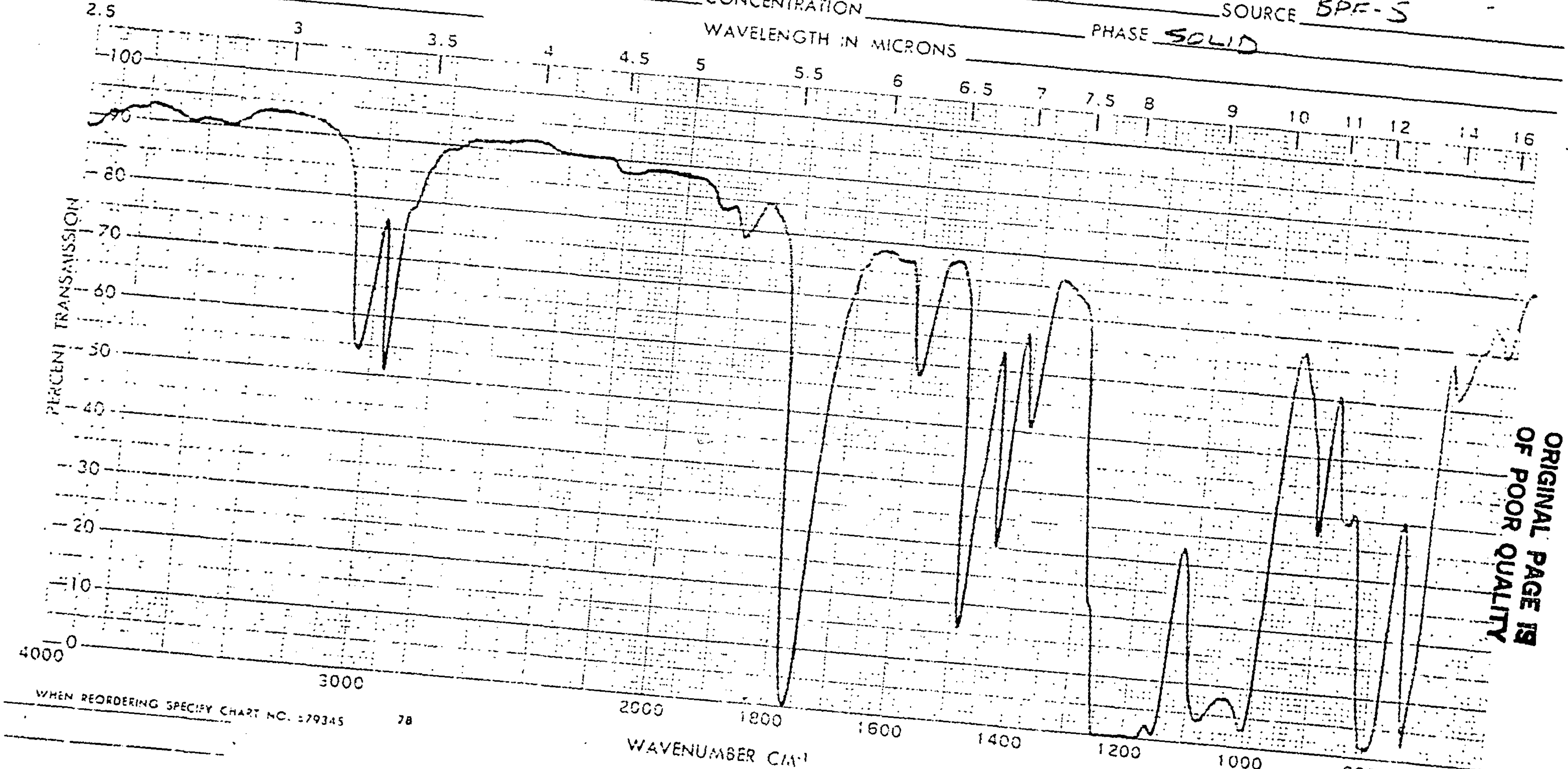
SAMPLE MBZ - [illegible]

ANALYST

CONCENTRATION

SOURCE BPF-5

PHASE SOLID



WHEN REORDERING SPECIFY CHART NO. 179345 78

BECKMAN INSTRUMENTS, INC., FULLERTON, CALIFORNIA, PRINTED IN U.S.A.

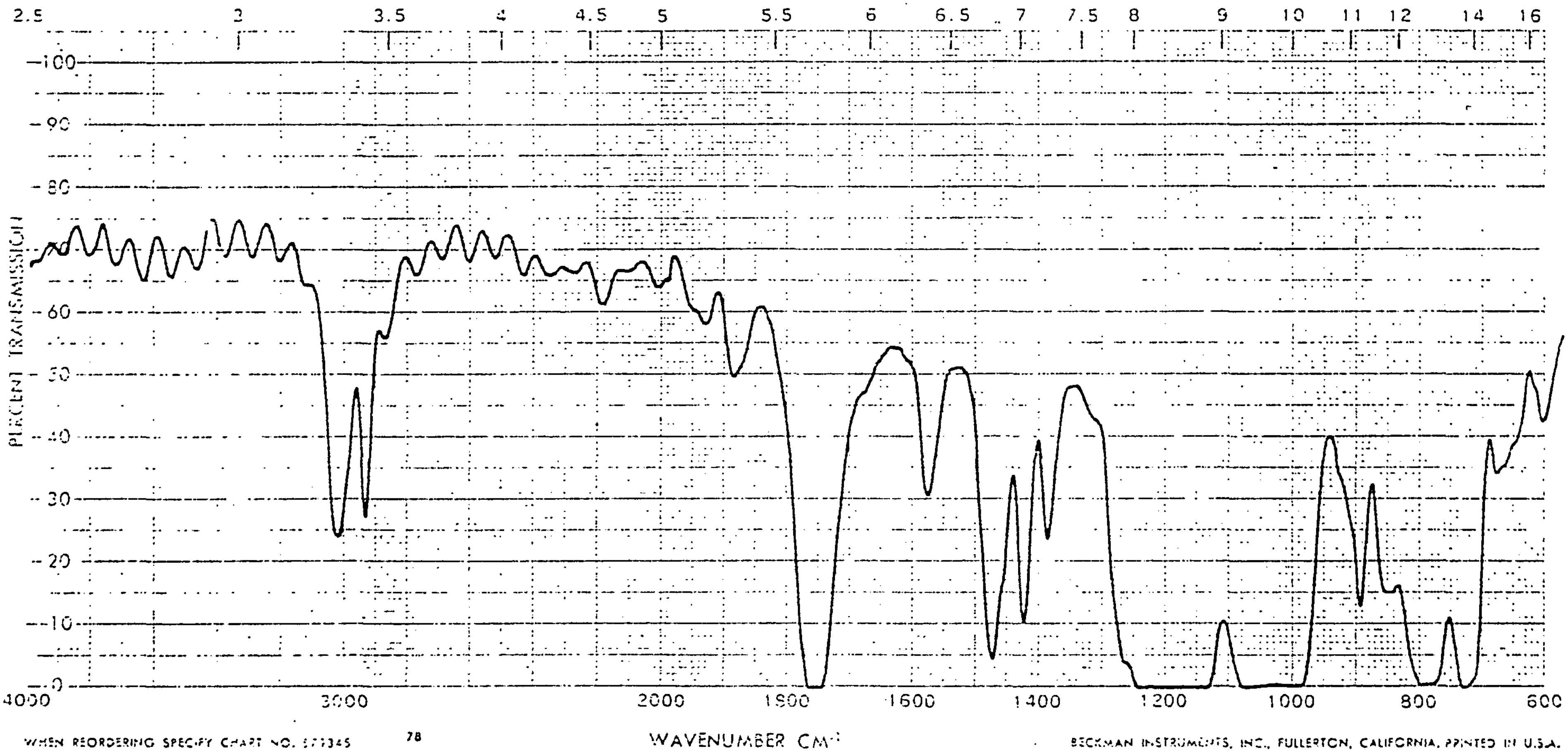
Beckman

INFRARED SPECTROPHOTOMETER

SPECTRUM NO. 3 DATE _____ SAMPLE MB-3-Film SOURCE 3X-S

PATH _____ mm _____ SOLVENT $CHCl_3$ CONCENTRATION _____ PHASE SOLID

ANALYST _____



WHEN REORDERING SPECIFY CHART NO. 577345 78

BECKMAN INSTRUMENTS, INC., FULLERTON, CALIFORNIA, PRINTED IN U.S.A.

ORIGINAL PAGE IS
OF POOR QUALITY

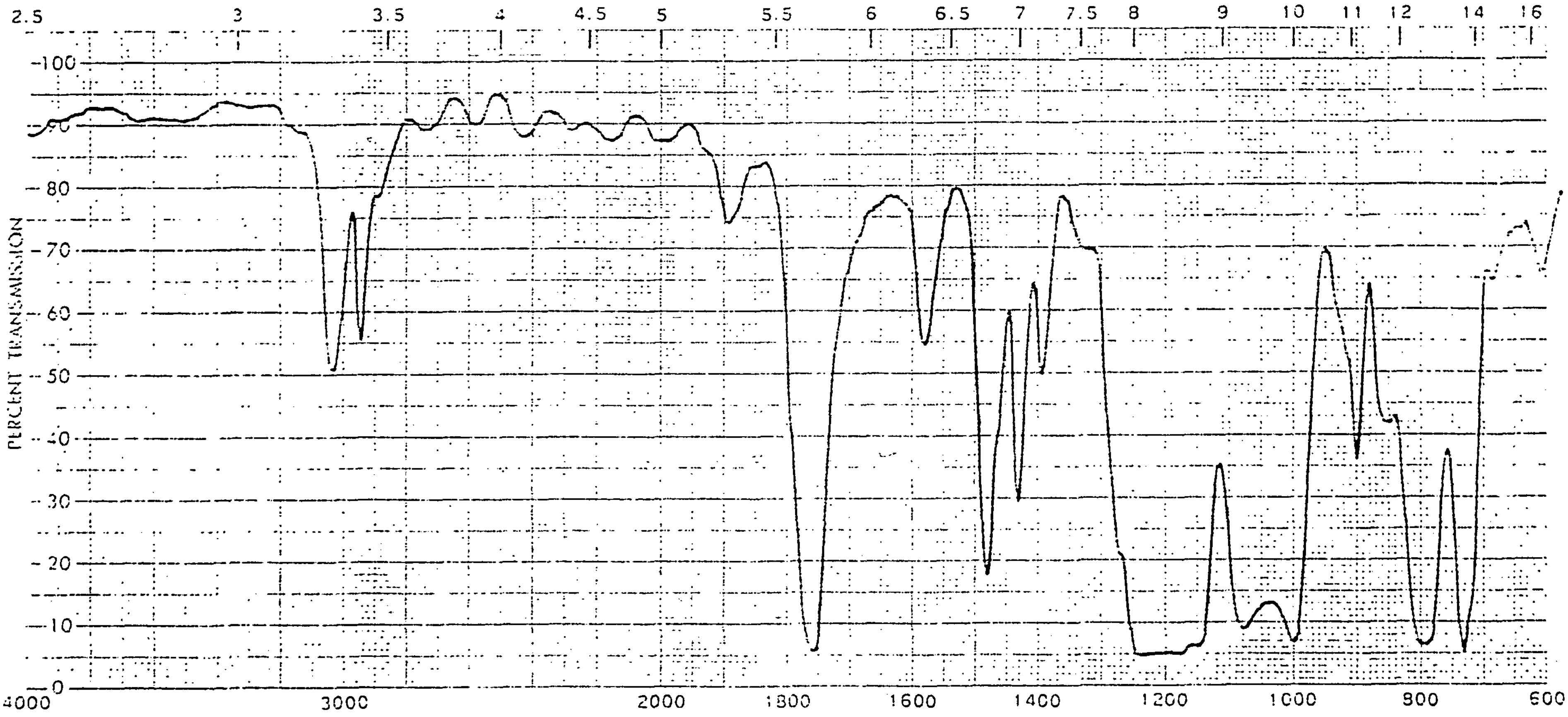
Beckman

INFRARED SPECTROPHOTOMETER

SPECTRUM NO. 4 DATE ____ SAMPLE M34 – FILM SOURCE BPF-S

PATH ____ mm ____ SOLVENT $CHCl_3$ CONCENTRATION ____ PHASE SOLID

ANALYST ____ WAVELENGTH IN MICRONS ____



WHEN REORDERING SPECIFY CHART NO. 573345 78 WAVENUMBER CM⁻¹ BECKMAN INSTRUMENTS, INC., FULLERTON, CALIFORNIA, PRINTED IN U.S.A.

1. Report No. NASA CR- 166276	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle
Manufacture of DPFC-DMS Polymer in the SKG Range

5. Report Date
1979

6. Performing Organization Code

7. Author(s) B. Mason Hughes, Donald R. Owen, Jean H. Futrell

8. Performing Organization Report No.

10. Work Unit No.
505-44-21

9. Performing Organization Name and Address
University of Utah
Flammability Research Center
Salt Lake City, Utah 84108

11. Contract or Grant No.
NAS2-10064

13. Type of Report and Period Covered
Final Report

12. Sponsoring Agency Name and Address
NASA-Ames Research Center
Moffett Field, California 94035

14. Sponsoring Agency Code

15. Supplementary Notes
Technial Monitor, D. A. Kourtides
NASA, Ames Research Center, Moffett Field, California 94035

16. Abstract

BPFC-DMS block copolymers have been synthesized on a pre-pilot scale (i.e., to 5 Kg lots) and subsequently fabricated into clear, colorless films. Details of the synthesis procedures, property determinations, and film casting techniques are presented. Solubility, viscosity and molecular weight characteristics of the resulting product are reported.

17. Key Words (Suggested by Author(s))

Polycarbonates

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 22	22. Price*

[redacted]