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SILICONE BLOCK POLYMERS: 1. BPF CARBONATE-SILICONE BLOCK POLYME--ETC(U)

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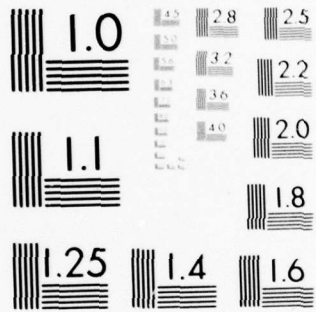
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**SILICONE BLOCK POLYMERS:  
1. BPF CARBONATE-SILICONE BLOCK POLYMERS:  
PRODUCTION OF OPTICAL GRADE EXTRUDATES  
2. FLAMMABILITY OF SILICONE BLOCK POLYMERS**

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develop a better understanding of the mechanism of the enhancement already known to exist in polycarbonate-silicone block polymers.

In the first effort, a continuation of previous work, a number of changes were made in materials and procedures that brought extrudate color intensity down to a level almost as low as that in the highest quality, natural-grade BPA polycarbonate extrudates. In order of importance these changes were a) use of acetonitrile in place of nitromethane as a BPF recrystallization solvent, b) removal of residual methanol from freshly made resin powder prior to drying, and c) the use of new extrusion equipment having smoother surfaces and tighter tolerances.

In the second effort the enhancement in limiting oxygen index (LOI) was found to vary considerably with composition and foreign block constitution. Maximum LOI enhancements varied by family in the order BPA polycarbonate = BPA polycarbonate  $\geq$  polydiphenyl phenylene oxide  $>$  polystyrene  $>$  polysulfone  $>$  polysilphenylene siloxane = polymethylmethacrylate, the first two being 20 points and the last two nil. Enhancement seemed to require a minimum level of melt viscosity and the formation of a residue having a carbon content. Broadly the mode of silicone incorporation (i.e., block, graft, or fine blend) appeared to have little effect on the synergism.

Mechanism studies concentrated on the BPA carbonate family revealed a strong correlation between resin LOI and pyrolytic char yield, the correlation encompassing all resins containing DMS but not BPA polycarbonate itself. However, the correlation was substantially different from that found by vanKrevelen for a wide variety of organic polymers including BPA polycarbonate, the block polymer chars being superior in raising LOI. Pyrolytic chars from the block polymers contained silicon dispersed on a submicroscopic to molecular scale, the degree of silicon retention correlating strongly with pyrolytic char yield. Inter-block products found in the pyrolysates suggested that the attack of phenolic degradation products on the carbon-silicon bond resulted in the formation of a crosslinked aromatic-silicate network. This network is thought to be an essential feature of these highly effective chars.

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SUMMARY

This report summarizes the results of two efforts dealing with silicone block polymers. The object of the first effort was to produce colorless transparent extrudates of bisphenol fluorenone carbonate-dimethylsiloxane (BPFC/DMS) block polymer elastoplastics suitable for use in aircraft transparencies. The objects of the second effort were to assess the extent to which silicone incorporation can enhance the flame resistance of organic polymers generally and to develop a better understanding of the mechanism of the enhancement already known to exist in polycarbonate-silicone block polymers.

In the first effort, a continuation of previous work, a number of changes were made in materials and procedures that brought extrudate color intensity down to a level almost as low as that in the highest quality, natural-grade BPA polycarbonate extrudates. In order of importance these changes were a) use of acetonitrile in place of nitromethane as a BPF recrystallization solvent, b) removal of residual methanol from freshly made resin powder prior to drying, and c) the use of new extrusion equipment having smoother surfaces and tighter tolerances.

From a laboratory development standpoint all problems in the way of using this resin in high grade transparencies have been solved. Further progress toward commercialization would require pilot plant scale synthesis and processing efforts. Some of the problems foreseen in such an effort are listed.

In the second effort the enhancement in limiting oxygen index (LOI) was found to vary considerably with composition and foreign block constitution. Maximum LOI enhancements varied by family in the order BPF polycarbonate = BPA

polycarbonate  $\geq$  polydiphenyl phenylene oxide  $>$  polystyrene  $\geq$  polysulfone  $>$  polysilphenylene siloxane = polymethylmethacrylate, the first two being 20 points and the last two nil. Enhancement seemed to require a minimum level of melt viscosity and the formation of a residue having a carbon content. Broadly the mode of silicone incorporation (i.e. block, graft, or fine blend) appeared to have little effect on the synergism.

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## 1. BPF CARBONATE-SILICONE BLOCK POLYMERS: PRODUCTION OF OPTICAL GRADE EXTRUDATES

The synthesis, processing and physical properties of bisphenol fluorenone carbonate-dimethyl siloxane block polymers (BPFC-DMS) have been systematically explored here in previous contracts with an eye to producing a high temperature aircraft transparency material.<sup>[1-3]</sup> Until recently the routine production of optical grade extrusions has been severely hampered by three major problems: haze, color and erratic molecular weights (and thus erratic melt rheology).

Elimination of haze and the control of molecular weight were achieved routinely in the previous contract leaving color reduction as the major goal for that part of the current contract focused on extrudate quality. As described below substantial reductions in extrudate color have now been achieved through changes in BPF monomer purification and polymer isolation procedures and the replacement of worn extrusion equipment.

The synthesis of the BPFC-DMS block polymers involves three steps: equilibration, endcapping and polymerization as shown in Figure 1 and described previously.<sup>[3]</sup>

### 1.1 BPF Monomer Purification

The influence of color in the BPF monomer on color in the resulting polymer was discussed in the previous report.<sup>[3]</sup> The best monomer in terms of low levels of both color and the undesirable o,p isomers of BPF was obtained by crystallization of the crude BPF product from a methanol-water mixture followed by repeated crystallization from nitromethane.

In the current contract two multi-pound batches of BPF monomer were produced. Effects of hot nitromethane filtration on color production in the first batch were noticed. Auxiliary spectroscopic studies showed conclusively that hot filtration of the nitromethane solution always caused an increase in color (Table 1). By contrast prolonged contact with methanol/water mixtures or acetonitrile caused no increases in BPF color. In retrospect the nitromethane color problem appears to have been made more severe by the long times required for filtration of the scale-up batches and the unavoidable contact with air

during these filtrations. Presumably oxidation of some species is directly responsible for the color.

The second large batch of BPF was synthesized by the standard procedure and isolated from the reaction mixture by crystallization from methanol/water. However, the crude product was dissolved in methanol at room temperature, filtered to remove any suspended particulates and crystallized by suitable dilution with water (Table 1, entry 6). The isolated product was quite low in color but had an unacceptably high o,p-isomer content. A further recrystallization of the monomer from acetonitrile reduced the o,p-isomer to an acceptable level (0.2%) and resulted in a further decrease in color. Six pounds of BPF (Table 1, entry 7), with extremely low color resulted. This material was used for all the subsequent polymerizations in work aimed at color reduction in extruded resins.

TABLE I  
Analytical Data for Purified BPF Monomer

Entry	Crude BPF	Recrystallization	Color Number x 10 <sup>3</sup> <sup>ⓐ</sup>		% o,p (II)
			Unfiltered	Filtered	
1	Sample 1	None	5.1	0.76	5
2	Sample 1	Nitromethane (1X)	6.02	0.83	0.4
3	Sample 1	Nitromethane (2X)	2.0	1.8	0.04
4	Sample 1	Nitromethane (3X)	1.8	1.5	0
5	Sample 2	None	1.4	0.6	5
6	Sample 2	Methanol/Water(1X)	0.6	0.5	3.8
7	Entry 6	Acetonitrile (1X)	0.34	0.34	0.2

<sup>ⓐ</sup> Color Number = Absorbance of 2.5 g BPF in 50 ml of MeOH at 400 nm divided by concentration in g/l.

## 1.2 Resin Synthesis and Isolation Modifications

The monomer having very low color described above was first used to prepare small quantities of block polymer that yielded powders, cast films and compression moldings all having low color levels. However, extrudates from these resins all exhibited unacceptably high color levels (e.g. No. 12, Table 2). Two changes were then made that resulted in a substantial reduction in extrudate color. The first, resulting from the discovery of non-uniform color distribution in extrudates, involved replacement of worn extruder parts (See Section 1.5).

The second change, one in the polymer isolation and drying procedure, came as a result of the observation that color in other bisphenol polycarbonate extrudates arises from the use of methanol during polymer isolation.<sup>[4]</sup> Thus 270 g. of resin were prepared by the standard method (See Section 1.4) and precipitated into a methanol/acetone solution (30/70). The isolated polymer was chopped into powder and divided into two equal parts. One powder sample (see Table 2, No. 13) was vacuum dried and served as a control. The other powder sample (see Table 2, No. 15) was thoroughly washed by slurring in water and then vacuum dried; the extrudate from this resin exhibited the lowest color of any BPFC-DMS extrudate produced in any of our work with these resins. However, the color of the extruded control was in the same range as the color of most of the previous extrudates. These results indicate that the removal of methanol was of greater importance in reducing color than was the replacement of extruder parts.

The intrinsic viscosity of the water-treated resin powder was lower than that of the control (0.44 vs. 0.65 dl./g.). This reduction was thought to result from hydrolytic degradation during the drying stage. A subsequent change in the drying procedure (see Section 1.3) minimized this effect.

TABLE 2

Extinction Coefficients of Dissolved BPFC-DMS Extrudates  
Produced in This and Previous Contracts

No.	Contract	Resin Code	[ $\eta$ ] <sup>20</sup> (dl./g.)	Remarks	Extrusion Conditions			Color Specimen Location in Extrudate	Extinction Coefficient			
					Equipment	Temperature (°C)	Atmosphere		Before Filtration T=250m $\mu$	Before Filtration T=400m $\mu$	After Filtration T=250m $\mu$	After Filtration T=400m $\mu$
1	2nd	10053-132C	0.68	Lowest color 1-lb. resin of 2nd contract	bar die	-325	air		.022	.0066	.016	.0022
2	3rd	10563-36C	0.44	Good monomer; old polymerization methods thorough water wash	1/8" rod die	330	air		.017	.0047	.012	.0014
3	3rd	7-22-76	0.58	Pyridine-catalyzed polym., thorough water wash	1/8" rod die	-330	air		.025	.0094	.016	.0024
4	3rd	10-7-76	0.48	Very light monomer; lowest color resin in 3rd contract	1/8" rod die	-330	air		.0096	.0026	.0072	.00080
5	3rd	11-24-76	0.46	1-lb run with new large batch monomer; very long time in solution	1/8" rod die		air		.24	.028	.200	.024
6	3rd	11-24-76	0.46	"	1/8" rod die		argon		.08	.0090	.070	.0077
7	3rd	11-24-76	0.46	Portion of batch sublet extracted with dimethoxy methane	1/8" rod die		argon		.050	.0092	.042	.0046
8	3rd	1-5-77	0.60	First use of sequestering agent for iron	1/8" rod die		argon		.050	.0053	.045	
9	3rd	1-25-77	0.61	0.1% polycarbonate heat stabilizer added	1/8" rod die		argon		.14	.0106	.106	.0069
10	3rd	1-25-77	0.61	Re-dissolved and re-precipitated	1/8" rod die		argon		.13	.0079	.12	.0054
11	3rd	2-2-77	0.62	Repeat of 10-7-77 polymer using monomer from same lot to re-check methods	1/8" rod die		argon		.021	.0068	.011	.0013
12	4th	9-14-77	0.75	Low color comp. molding; color in extrudate found conc. in surface and core regions	1/8" rod die	320	argon		.030	.0071	.040	.0033
13	4th	10-20-77A	0.65	Control portion--no extraction of methanol before drying	New screw, 1/8 rod die		argon	after 1 ft.	.035	.012	.019	.0046
14	4th	10-20-77A	0.65	"	"		argon	after 3 ft.	.031	.011	.028	.0053
15	4th	10-20-77B	0.44	Water extraction before drying	"		argon	after 3 ft.	.0080	.0027	.0062	.00060
16	4th	10-20-77B	0.44	Water extraction before drying	"		argon	after 35 ft.	.013	.0042	.0062	.00066
17	4th	10-27-77	0.58	Isolation without use of methanol	"		argon	after 1 ft.	.022	.011	.0066	.0014
18	4th	12-27-77	0.57	Scale-up of 10-20-77B to 270g.	New screw, old 1/8 x 3/4" bar die	320	argon	13th min.	.0078	.0033	.0042	.00050
19	4th	12-27-77	0.57	"	"	320-330°	argon	70th min.	.0074	.0027	.0045	.00063
20	4th	12-28-77	0.57	"	"	320-335°	argon	45th min.	.0076	.0027	.0052	.00082
21	4th	1-30-78	0.59	Ditto except different silicone fluid used	New screw, old 1/8 x 3/4" bar die	320-355°	argon	85th min.	.0107	.0036	.0067	.0014
22	4th	1-31-78	0.95	Ditto except lower chain stopper concentration used	"	340-355°	argon	13th min.	.0242	.0117	.0070	.0010
23	4th	1-31-78	0.95	"	"	350-370°	argon	22nd min.	.0105	.0037	.0058	.00078

<sup>1</sup> Absorbance in 10 cm pathlength cell divided by concentration in g/l at wavelength indicated

<sup>2</sup> 2nd ref. 2, 3rd ref. 3, 4th - current

<sup>3</sup> Left hand no. = barrel, right hand no. = die

<sup>4</sup> Chloroform solution at 25°C

Subsequently the effect of total exclusion of methanol from the polymer preparation was explored. Resin (Table 2, No. 17) was prepared by the standard method (Section 1.4). However rather than being precipitated in methanol/acetone solution the washed and dried polymer solution was evaporated to give a polymer film. Since the film was hazy it was then subjected to soxhlet extraction with dimethoxy methane<sup>[1]</sup> to remove the cyclic BPF carbonates thought to be the cause of the haze. The resin was then chopped in a Waring blender while still wet with extraction solvent (which makes comminution much easier). After drying the resin was extruded as before. The color of the extrudate was slightly greater than the color of the resin slurried in water to remove methanol before drying.

Thus these experiments show clearly that methanol in the resin at the time of drying results in substantial extrudate color. The water slurring method appears to remove all traces of methanol, at least to the extent that extrudate color is an indicator of such removal.

### 1.3 Block Polymer Synthesis Scale-up

For a large scale extrusion through a bar die (Section 1.5) in which production of optical quality flat stock was the goal; 2-1/2 lbs. of resin were produced. Because of equipment limitations and the necessity for continuous non-stop polymerization and workup to preserve the molecular weight of the polymer, 270 gm was selected as the maximum single batch size. A master batch of equilibrated dichlorosilicone fluid was prepared and used to make two separate but identically formulated batches of BPF-endcapped silicone fluid which in turn were used in four independent polymerizations.

Each polymerization was conducted using the previously developed procedure (See Section 1.4) and each isolated polymer was extracted with water to remove residual methanol before drying. These preparations incorporated all the technology developed to insure molecular weight integrity and provide polymer with the lowest possible color. The polymer drying procedure was modified compared to previous work to minimize molecular weight degradation: Drying was carried out under vacuum in three stages for 24 hours each at 25°, 40° and 85°C.

The first three polymerizations done in this scale-up used the same quantity of chainstopper (0.73 mole %) and provided block polymers with virtually identical intrinsic viscosities (Table 2, Nos. 18-21). In the fourth the chainstopper level was decreased to raise molecular weight in order to assess effects of increased melt viscosity on extrudate color.

#### 1.4 Experimental

##### 1.4.1 Synthesis of Bisphenol Fluorenone

Into a 12-ℓ round-bottom flask fitted with paddle stirrer, thermometer, gas inlet tube, reflux condenser, and nitrogen bypass was placed 2720 g. of 9-fluorenone (15.094 moles), 5684 g. of phenol (60.40 moles), and 20.60 g. of 3-mercaptopropionic acid (0.1943 mole).

While kept under a nitrogen atmosphere, the reaction mixture was heated to 85.8°C to effect complete solution. Forty-four (44.0) grams (1.096 mole) of hydrogen chloride was bubbled into the solution and external heating was stopped. The attendant mild exotherm carried the solution temperature to 98°C over the next 40 minutes. The reaction was heated at 90°C for 8 hours and cooled to room temperature. BPF crystallized from solution at 90°C.

The reaction mixture was dissolved in 8-ℓ of methyl alcohol and filtered. The filtrate was placed in a 22-ℓ round-bottom flask and 7.5 ℓ of water was added with stirring. The reaction mixture was heated to reflux

(84°C), to effect a clear solution, and allowed to cool slowly with seeding. The white crystals which formed were isolated by filtration, washed on the filter with 800 ml methanol/water (1:1 by volume) and dried 40 hours at 60°C and 10 mm Hg, to give 3745 gm (70.9%) of crude product. The methanol-water filtrate was highly colored. Recrystallization of this solid from methanol-water gave 3404 gm or (64.4%) of white crystals with low color but an unacceptably high o,p isomer level (3.8%). An additional recrystallization of this solid from acetonitrile (1 g. BPF/4.3 ml acetonitrile) provided 2998 g. (56.8%) of very pure BPF monomer with low color and low o,p isomer content. Isolation of second crops of product was not attempted in any of the above recrystallizations.

#### 1.4.2 Synthesis of Equilibrated Silicone Fluid

All glassware was flame dried, placed in a nitrogen-swept drying oven at 100°C for four hours and stored in the inner chamber of a nitrogen drybox for about 15 hours. All plastic equipment was treated in a similar fashion but with flame drying eliminated. The octamethylcyclotetrasiloxane ( $D_4$ ) and dichlorodimethylsilane were freshly distilled through a 2-foot Vigreux column, under nitrogen.

A solution of 0.32 g (0.02% by weight) of  $FeCl_3 \cdot 6H_2O$ , 1426.4 g (2.4 mol) of  $D_4$ , and 161.2 g (1.25 mol)\* of dichlorodimethylsilane was prepared by successive additions to a half-gallon bottle in a drybox and the bottle was then sealed with a polyseal cap. The bottle was removed from the drybox, covered with aluminum foil, and heated in a nitrogen-flushed drying oven for 24 hours at 48°C. The fluid was then placed back in the drybox for 24 hours and was now ready for use.

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\*NOTE: This weight of dichlorodimethyl silane was mistakenly entered as 80.65 gm (0.625 mole) in the previous contract report. The correct value should have been 161.2 g (1.25 mole) as recorded above.

### 1.4.3 Synthesis of Endcapped Silicone Fluid

Glassware and plastic equipment were dried and placed in the nitrogen drybox as described above. Dichloroethane was stirred over calcium hydride for at least two days, distilled through a 2-foot bubble cap column under nitrogen and placed in flame-dried round-bottom flasks. The BPF was dried for 48 hours at 75°C and 10 mm Hg, 24 hours in a nitrogen-flushed oven at 110°C, and placed in the nitrogen drybox while still hot.

Into a 5-ℓ round-bottom flask (in the nitrogen drybox) fitted with paddle stirrer, was placed 315.3 g (0.9 mole) BPF and 2.7 ℓ dichloroethane\* (freshly distilled as described above). All ground-glass joints were used without lubricant. The stoppered flask was removed from the drybox and fitted under nitrogen with a "y" gas inlet tube, thermometer, and nitrogen bypass. Ammonia (21.0 g, 1.24 mol) was bubbled into the slurry over a 10-minute period and a clear water/white solution obtained.

In the drybox an additional funnel with Teflon<sup>®</sup> stopcock, was charged with 361.4 g (0.31 mole) of equilibrated dichlorosilicone fluid (previously described) and 300 ml of dichloroethane. The addition funnel was then removed from the drybox; the gas inlet tube was removed from the flask (under slight nitrogen pressure) and replaced with the addition funnel. The dichlorosilicone fluid was added to the solution of BPF-ammonia complex over a 20-minute period during which time the temperature of the reaction rose from 23 to 41°C. A purple suspension was obtained after this addition was complete.† The reaction

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\* The BPF-ammonia complex tends to precipitate out if less solvent is used. Heterogeneity in this reaction leads to polymers whose cast films are hazy; homogeneous conditions provide polymers which give optically clear films.

† A resultant green color at this stage signifies that additional ammonia is needed. Additional ammonia was not required in any endcapped fluid preparation in the current contract work.

<sup>®</sup>Teflon is a registered Trademark of the E. I. DuPont DeNemours & Company

mixture was stirred at room temperature for one hour and then heated to reflux (81°C) for two hours after which time the suspension was white and the solution pH was 7.1.

The reaction mixture was cooled to room temperature and 1.5ℓ of H<sub>2</sub>O added. The resulting solution was acidified to pH = 3.8 by the addition of 10 drops of 12 N HCl to the well stirred solution. If a clear solution was not obtained at this point, then sufficient reagent grade acetone was added to achieve a homogeneous solution. The aqueous layer was removed by means of a 4-ℓ separatory funnel equipped with Teflon<sup>®</sup> stopcock, and discarded.

The solution was washed once more with acid at pH 3.5, five times with deionized water (pH = 6.5), once with dilute sodium bicarbonate, and finally with water. The solution was then dried over magnesium sulfate, filtered, and evaporated to dryness. The residue (666 g, 103% of theory) was then redissolved in a mixture of 3480 ml of ethanol-free chloroform and 50 ml of acetone and stored in an aluminum-foil-wrapped bottle in the nitrogen drybox. (Acetone was added at this point to dissolve the BPF.) The concentrations of polymerizable (i.e. free) BPF and BPF end-stopped silicone in solution were 0.0298 g/ml and 0.1574 g/ml, respectively.

#### 1.4.4 Synthesis of BPF Carbonate-Dimethylsiloxane Block Copolymer

The glassware was thoroughly washed with acetone and dried one hour in a nitrogen-flushed oven at 110°C.

Into a 5-ℓ, 5-neck, round-bottom vessel was placed 150.0 g of BPF (0.429 mole), 994 ml of endcapped[silicone]fluid solution [containing 29.6 g (0.0846 mol) of BPF and 156.4 g (0.0873 mol) D<sub>15</sub> endcapped fluid], 1150 ml CHCl<sub>3</sub> (B&J<sup>†</sup> ethanol-free), 0.400 g (0.00426 mole)\* phenol, 0.50 g (0.00229 mole)

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\* The weight of phenol constituted a chain stopper level of 0.71 mole % based on moles of reactive BPF.

† Burdick & Jackson Co.

sodium gluconate dissolved in 1.00 H<sub>2</sub>O, and 2.00 ml (0.0143 mole) triethylamine. The stoichiometry of this polymerization reaction was designed to provide a block polymer containing 27.3 wt. % silicone. (Found: 26.7 wt.% silicone.)

The 5-ℓ reactor was equipped with a paddle stirrer, nitrogen bypass, pH electrode, gas inlet tube, and an addition funnel containing a solution of 240 g of sodium hydroxide in 500 ml of water. This quantity of base corresponded to 250% of the theoretical amount required to effect neutralization of the polymerization reaction. A portion of the base solution was added to the reaction mixture to obtain a pH of 11, and phosgene addition was initiated at a rate of 3.5 g/h. Shortly after the addition was started, a considerable amount of white solid precipitated from the mixture, and stirring became difficult. After approximately 20% of the total aqueous sodium hydroxide had been added, stirring was considerably improved, and a homogeneous solution was observed when 50% of the total aqueous base was introduced. Aqueous sodium hydroxide and phosgene were added simultaneously to maintain a pH of 11.0 ± 0.2.

After 60% of the total base was consumed (elapsed time of 27 min.) the phosgene rate was reduced to 1.0 g/min. and continued until the entire amount of base was consumed; this corresponded to a total reaction time of 111 minutes. Nitrogen was bubbled through the water-white two-phase system (pH 11) for 5 minutes to remove any residual phosgene. The reaction mixture was diluted with an equal volume of CHCl<sub>3</sub>; the aqueous layer was separated and discarded. The organic layer was washed with deionized water (pH = 6.7), with aqueous HCl at pH = 2.0, and four times with deionized water. The last water wash was tested for pH and with silver nitrate for chloride ion. If chloride was present or pH was less than 6.5, water washing was continued.

The organic layer was dried over magnesium sulfate and filtered. The resulting clear, colorless solution was added over a period of 60 minutes to a well-stirred mixture of 7 l acetone and 3.5 l methanol to effect precipitation of the polymer. Prior to the precipitation of the filtered solution, 25 ml. were sampled, from which two films were cast by allowing the solvent to evaporate. The solution cast films were water-white and optically clear. Following precipitation, the fibrous polymer was filtered, chopped up in a Henschel mill, washed with 7 l of water and refiltered. The filter cake was vacuum dried in three 24 hour increments; at room temperature, 40°C and 80°C to give 26.71 g. (78.3%) of polymer. The entire operation consisting of polymerization, washing, precipitation and drying was done in a continuous non-stop fashion to minimize molecular weight reduction. (See page 9 of the previous contract report. [3])

#### 1.5 Extrusions

As in the previous contracts all extrusions were carried out with a Brabender extruder and a 2:1 compression screw. The small scale resins were extruded through a 1/8" rod die as before. The four 270 g batches were extruded through the 1/8 x 3/4 in. bar die used before with large scale extrusions. Barrel and die temperatures were 310 - 350°C for the most part.

The K-Tron feeder was used to control feed rates to the extruder hopper. As before feeding was set at a starvation level until extrudate appeared at which point the feed rate was raised gradually to the flood level.

Most of the resins were powdery or fibrous and somewhat caked. The feeding of these was often difficult due to bridging in the extruder hopper. Continuous stuffing was often required to pack enough resin into the extruder throat to prevent starvation conditions and a consequent increase in residence time inside the barrel.

Argon blanketing of resin from the K-Tron hopper to the extruder throat was effected as before with various make-shift fabrications of aluminum sheet, polyethylene film and funnels, tape, etc.

The extrudate of 9-14-77 (Table 2, No. 12) exhibited substantially more color than did a compression molding made from the same powder. Two quarter inch lengths of extrudate were thus ground and polished to produce optically flat cylinders that could be inspected in the axial direction by transmission light microscopy. In each piece the color was found to be concentrated in two regions: a surface region 5 or 10 mils thick and an axial core roughly 30 mils in diameter (Fig. 2). These color concentrations and an inspection of the equipment suggested that the surfaces of the extruder screw and die were responsible for most of the color. It seemed likely that worn and rough surfaces caused excessive residence times of small portions of resin allowing color-producing reactions therein to accelerate.

These extruder parts were replaced with new ones resulting in a measurable color reduction (Resin 10-20-77A).

The first three of the 270 g. batches were extruded in tandem. Screw speed was 70 RPM and about 90 minutes were required to extrude these resins. Set temperatures in the barrel were 320°C (first stage) and 330 to 340°C (second stage). Die temperature was set at 340°C initially but gradually raised to 360°C to improve extrudate surface smoothness.

Color levels increased slightly toward the end of the run due to the higher set temperatures, a gradual accumulation of degradation products in the extruder or perhaps to a small intrinsic difference between the second and third resin.

The matt finish on the extrudate surface disappeared on raising the die temperature to 350°C. Die lines and faint chatter markings persisted throughout the run however.

A two-inch piece of 12-28-78 extrudate produced at a die temperature of 355° was ground flat polished to an optical smoothness on both surfaces. Photographs at long and short range focus taken through this piece as a window (Figs. 3a and b respectively) demonstrate the low levels of haze and absence of the fine grain optical distortion discussed in the previous report.<sup>[3]</sup> A few tiny bubbles and black specks are the most noticeable defects. Optimized very large scale extrusions should be free of these defects.

The extrusion of the last of the 270 g batches 1-31-78 was unsuccessful due to the excessive molecular weight of this resin. Temperatures of barrel and die were raised gradually to 400° and 415°C without producing a smooth extrudate. Interestingly only modest color increases were observed at the higher temperatures, however; e.g., Section 21.5 extruded at 350 to 370°C exhibited extinctions only 50% greater than those of the best sections of the previous three resins. This result seems to attest to the improvements in resin quality mentioned earlier and to the intrinsic lack of color forming tendencies in highly pure BPF carbonate resins.

#### 1.6 Summary of Resin Quality Work

BPFC-DMS block polymers of a quality necessary for optical-grade extrusions have been reproducibly synthesized at the half pound scale. Specifically their molecular weights are reproducible, and the extrudates produced from them are low in haze,<sup>[1]</sup> free of optical distortion and are essentially colorless. More specifically perceived color in the extrudates is reproducibly nearly as low as that of extruded high quality natural-grade Lexan<sup>®</sup> polycarbonate (i.e. on the log intensity scale--to which the eye responds linearly--their color is about one half unit greater).

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<sup>®</sup> Lexan is a registered trademark of the General Electric Company

Haze reduction and molecular weight control were achieved in the previous contract. The reductions in color achieved reproducibly during the current contract result chiefly from

- Use of acetonitrile instead of nitromethane for monomer recrystallization.
- Removal of residual methanol before extrusion.
- New extrusion equipment having smoother surfaces and tighter tolerances.

### 1.7 Future Developmental Work

It is felt that a temporary limit has now been reached in extrudate optical quality. This limit has been set by several factors that would have to be addressed if a further effort were to be made to produce high quality sheet for aircraft transparencies. These factors are:

#### 1. Extrudate Finishing

As with other commercially extruded optical quality sheet products, polishing and take-up equipment of appropriate size will be necessary to develop the capability to produce flat smooth sheets uniformly.

#### 2. Extruder Equipment

Further extrusion scale-up and optimization will require extrusion equipment that is larger and more sophisticated than the Brabender extruder with its limited temperature profile capabilities and simple screw configurations. It is desirable that future work include assessment of various sheet die and screw designs and temperature profiles.

3. Resin Feed

Large continuous well-controlled extrusions will require elimination of the resin feed problems associated with the use of powdery and/or fibrous resins. Three alternative means for solving this problem appear to exist: a) use of resin granules produced by steam precipitation, a method previously found practical with quantities of resin larger than those processed in this contract; b) compaction of powdery or fibrous resins into tablets or "pills" of 1/8 in. dia. roughly using a commercially available tablet producing machine; c) use of an auxiliary solids extruder connected tightly to the feed section of the melt extruder.

4. Resin Volume

Reproducible batches of resin at the 20, 100 and 500 lb. scale will be required eventually for development work. (Commercial extruders producing 4 ft. wide polycarbonate sheet require roughly 300 lbs. of resin during start-up before the extrusion line variables are all optimized.) These volumes of resin will require the dedication of resin production equipment of pilot plant scale.

5. BPF Monomer Scale-up

BPF monomer is easily synthesized in large quantities. Serious problems however exist in purification and subsequent handling of this material. These problems arise from the intrinsic dermatological effects of BPF coupled with the powdery nature of the purified solid produced to date. [3]

Scale-up would require one of three alternatives to current procedures: a) remote handling of the dry solid in a separate building;

b) a change in crystallization media and/or temperatures that would result in the production of much coarser crystals; c) development of the ability to use wetted solid. Though wetting obviates the production of dust (which is responsible for much of the dermatological problems experienced), the presence of the liquid complicates the control of stoichiometry in subsequent reactions.

None of the problems outlined above is technically formidable. All are similar to difficulties faced in the scale-up of other sheet resins to commercial levels. Further progress requires simply a need great enough to justify the necessary commitment of people and investment capital.

## 2. FLAMMABILITY OF SILICONE BLOCK POLYMERS

A synergism in the Fennimore-Martin limiting oxygen index has been found previously in the BPF carbonate-silicone block polymer family.<sup>[2]</sup> Auxiliary investigations suggested that the enhancement in LOI brought about by silicone incorporation in BPFC resins resulted from the production of continuous layers of silica that retarded oxidation of the char.<sup>[3]</sup>

In the current contract the silicone dependence of LOI has been surveyed in each of several families of silicone copolymers in order to assess the generality of the LOI synergism. An added motive in this survey has been to help develop an understanding of the role of the non-silicone portion of the resin in the synergism. In addition to block polymers a number of graft polymers and polymer blends have been tested to aid in assessing the importance of component dispersity.

Auxiliary studies have been focused principally on the BPA polycarbonate-silicone block polymer family in order to explore the mechanism of LOI enhancement in depth.

Each family of resins, defined by the "hard" polymeric species involved together with types of subfamilies tested (blocks, grafts, blends), is listed below in approximate order of importance in this study.

1. Bisphenol fluorenone polycarbonate: Block polymers; blends of homopolymers with blocks, with silicone gum and with silica gel.
2. Bisphenol-A polycarbonate: Block polymers.
3. Polystyrene: Block polymers.
4. Polymethyl methacrylate: Block and graft polymers.
5. Poly(2,6-diphenyl phenylene oxide): Block polymers; blends of homopolymer with block polymers and with silicone gum.

6. Miscellaneous: One or two block polymers of the following:  
polysilphenylene siloxane, copolyether from dichlorodiphenyl sulfone and bisphenol-A, 50/50 copolycarbonate from bisphenol-A and tetrabromo bisphenol-A.

All of the materials, except the sulfone materials were made within the General Electric Company, mostly in various programs prior to the contract. A few block polymers and all of the blends were made under this contract specifically for this flammability study.

### 2.1 Synthesis of Block Polymers for Flammability Studies

A number of BPF carbonate-and BPA carbonate-silicone block polymers were prepared in 100 g quantities specifically for flammability studies in order to complete a composition-block length grid for each family. The procedures used were those described in Section 1.4 with the following exceptions:

1. Equilibration: The ratio of  $D_4$  to dichlorodimethyl silane was varied to give the desired silicone oligomer length.
2. Endcapping: For the BPAC-DMS resins bisphenol acetone was used in place of BPF in fluid endcapping.
3. Polymerization: a) BPA was used in all BPAC-DMS resins. These resins and all BPFC-DMS resins of silicone content greater than 20% were precipitated in methanol rather than acetone-methanol mixtures (the latter result in gummy precipitates). b) The ratio of endcapped silicone fluid to bisphenol was varied as necessary to produce a polymer of the desired silicone content.

The products are listed in Table 3. (Intrinsic viscosity variations in each series of resins resulted from the fact that in each series a number of

TABLE 3  
Polycarbonate-Silicone Block Polymers Synthesized for Flammability Studies

<u>Entry</u>	<u>Polymer</u>	<u>Bisphenol</u>	<u>Silicone Design D.P.<sub>n</sub></u>	<u>Wt % DMS (Design)</u>	<u>[<math>\eta</math>](dl./g.)</u>	<u>Wt % DMS (Found)</u>	<u>Yield(%)</u>
1	12-16-77	BPF	7	45	1.85	41.0	80.0
2	12-15-77	BPF	7	20	0.49	17.4	88.2
3	11-9-77	BPF	30	43	0.96	42.3	74.8
4	11-11-77	BPF	30	20	0.82	19.3	75.2
5	2-22-78	BPA	2	17.8	—	20.1	87.2
6	3-23-78	BPA	40	81	—	79.8	77.4
7	4-13-78	BPA	15	65	—	62.4	73.3
8	4-14-78	BPA	2	24.1	1.11	31.7	88.3
9	4-21-78	BPA	2	15	0.86	15.3	89.7
10	4-25-78	BPA	40	40	1.06	36.5	90.1
11	5-1-78	BPA	40	25	0.94	22.9	95.5

endcapped silicone fluids were required--one for each silicone block length. For none of these fluids were polymer intrinsic viscosity-chain stopper relationships determined.)

## 2.2 Limiting Oxygen Indices

The tables below list all the materials tested, their compositions and molecular characteristics, molding temperatures and limiting oxygen indices.

### 2.2.1 Bisphenol Fluorenone Polycarbonate (BPFC) Family

Table 4 summarizes all the materials and test results for this family obtained in this and previous contracts.

Several blends of BPF polycarbonate with silicone-rich BPFC/DMS block polymer and with SE-30 silicone gum were made by dissolving the two components in chloroform (~7% wt./vol.) and coprecipitating by pouring in a thin stream into 3 to 5 volumes of stirred methanol. Following filtration, trituration in fresh methanol and washing with water, these blends were dried in vacuum first at room temperature and then at temperatures up to 130°C. The blend of BPF polycarbonate with Cabosil silica gel was prepared by adding the latter to a chloroform solution of the former and casting a film from this solution. The film was vacuum dried at temperatures up to 200°C and comminuted dry in a Waring blender in preparation for molding.

All LOI's are plotted vs. elemental silicone content in Fig. 4. A maximum in LOI is reached at roughly 8% silicone. With the exception of one block polymer, maximum LOI's were 46 to 51 as before. This level was achieved over the range 4% to 12% elemental silicon for all materials containing silicone regardless of the details of its incorporation (i.e. DMS block length; pure block polymer vs. blend of homopolymer with block polymer or silicone gum).

TABLE 4

BPF Carbonate Family: Resins, Molding Temperatures  
and Limiting Oxygen Indices

<u>Code</u>	<u>Type</u>	<u>Wt. % DMS</u>	<u>Design D.P.n</u>	<u>Molding* Method</u>	<u>Molding T(°C)</u>	<u>LOI</u>
BPFPC <sup>†</sup>	Homopolymer	0	—	c	350	39±1
9824-97B-X <sup>†</sup>	Block	7.5	10	c	310	45.3±.3
9824-101A-X <sup>†</sup>	Block	8.7	10	c	~320	50.3
10053-129B <sup>†</sup>	Block	23	19	i	~325	48.5±.5
10053-129B	Block	23	19	c	310	48.4
10053-132C <sup>†</sup>	Block	24	19	i	~325	49.6±.5
1053-132C	Block	24	19	c	310	48.4
10053-136C <sup>†</sup>	Block	21.5	19	i	310	50±.2
10053-136C	Block	21.5	19	c	310	52.3±.7
10053-151 <sup>†</sup>	Block	16	19	i	~325	50.7±.4
10053-135	Block	46.7	20	c	260	42
11-9-77	Block	42.3	30	c	~260	43
11-11-77	Block	19.3	30	c	~330	49
12-15-77	Block	17.4	7	c	~270	58.5±1.5
12-16-77	Block	41	7	c	300	46±.5
4-13-78	Block	62.4	15	c	—	38
10846-124-A	Blend w/ 4-13-78	20	15	c	370	50.4±1.3
10846-124-B	Blend w/ 4-13-78	10	15	c	400	48.4±.7
10846-124-C	Blend w/ 4-13-78	30	15	c	400	40.7
10846-131-A	Blend with PDMS gum	25	∞	c	300	47.0±.6
10846-126	Homopolymer + SiO <sub>2</sub> (16.7 wt.%)	0	—	c	370	36.8±.8

<sup>†</sup> tested in previous contracts

\* c = compression, i = injection

Beyond about 12% elemental silicon a roughly linear drop in LOI with increasing silicon occurs.

One resin (12-15-77) exhibited a significantly higher LOI (57-60) in repeated testing than the LOI's of other resins of similar silicone content and higher DMS block lengths. No resins of DMS block  $\overline{D.P.}_n < 7$  were made in this silicone content range so that conclusions about block length effects are hazardous.

Finally, the mixture containing  $SiO_2$  exhibited a LOI equal to or lower than that expected of the homopolymer.

The character of the burning and of the residue produced changes substantially with silicone content. Rather loud decrepitation occurred with all resins. The residue changed from a fine black friable char with the homopolymer (Fig. 5a) to a more voluminous, very strong, largely black char at moderate amounts of silicone (Fig. 5b) to a gray coarse weak residue at high silicone contents (Fig. 5c).

By contrast the  $SiO_2$ -filled homopolymer burned quietly and slowly with little or no swelling of the residue. In fact burning of a thin surface layer only seemed to occur. The burnt layer peeled off leaving a white-surfaced core.

Overall, these results suggested that for the LOI synergism to exist the silicon must be present in a volatile, reactive form. That is the presence of  $SiO_2$  a priori is ineffective. However, the details of silicone incorporation (e.g. block length) were apparently not important as long as the dispersion was not heterogeneous on a gross scale. In addition, it was clear that an optimum silicone content exists.

### 2.2.2 BPA Polycarbonate Family

A large number of block polymers covering a wide range of silicone content and block length in the BPA carbonate family were assembled and tested (Table 5). The LOI's obtained are plotted vs. silicone content in Fig. 6.

TABLE 5

BPA Carbonate Family: Multisequence Block Polymers,  
Molding Temperatures and Limiting Oxygen Indices

<u>Reference Code</u>	<u>Figure Code</u>	<u>Wt. % DMS</u>	<u>Design <math>\overline{D.P}_n</math></u>	<u>Molding T(°C)</u>	<u>LOI</u>
9627-X	a	5.8	10	—	32.3-32.6
10846-133-1156	b	11	40	—	32.3
10846-133-1141	c	12.4	11	200-220	40-47
10846-133-1150	d	14	20	260	36.8
4-21-78	e	15.3	2	130	37.8-40.2
10846-133-2505	f	18	5	155	47.7-49.1
2-22-78	g	20	2	130	36.4
5-1-78	h	22.8	40	200	31.7
10846-133-9	i	24	20	230	35-38
10846-133-11	j	25	20	260	38.3
10846-133-5102	k	25	10	210	37.8
4-14-78	l	25.1	2	85	39.1-40.2
1048-74	m	25.9	5	210	37.8
1048-84	n	25.9	5	210	33.8
4-25-78	o	36.5	40	150	36.5
10846-133-0303	p	40	20	210	33.8
10846-133-3302	q	43	10	155	36.3
10846-133-0402	r	50	10	130	36.5
10846-133-945	s	51	40	205	30.5
10845-133-7	t	53	20	205	35.2
10846-133-3403	u	57	20	205	30.8-32.3
10846-133-944	v	60	40	205	33.8
10846-133-1	w	63.7	20	130	30.8
3-23-78	x	81.4	40	130	32.3

The LOI dependence on silicone in this family was very much like that in the BPF family in every respect once allowance was made for the fact that BPA polycarbonate's LOI is 25 vs. 39 for BPF polycarbonate. The LOI increased 13 points again, reaching a broad maximum in this family at LOI=38 to 40 and 15 to 30% silicone. However two resins (10846-133-1141) and (10846-133-2505) exhibited much higher LOI's than did other resins of similar silicone contents and block lengths. The value of 50 for the latter resin was reproducible. It is the largest LOI relative to that of the corresponding "hard" homopolymer, of any resin tested in this work.

No clear dependence of LOI on block length at fixed silicone content is evident in these results. Nor can any marked effects of polymer molecular weight be seen: For example 10846-133-11 is an injection molding grade resin ( $[\eta]=0.6$  dl./g.) while 10846-133-9 is casting grade resin ( $[\eta]=1.2$  dl./g.). The viscosity of latter is higher only because the total number of blocks per macromolecule is greater. Of course none of the resins tested were low enough in molecular weight to exhibit "runny" melt behavior.

However, BPA polycarbonate tends to drip somewhat on burning in contrast to BPF polycarbonate (Fig. 7a). The burning characteristics and the chars produced from the BPAC/DMS block polymers (Figs. 7b and c) were much like those in the BPF carbonate family: an increase in amount of char produced with silicone incorporation, a coarsening and weakening of the residue beyond the LOI maximum and the residue become progressively lighter in color. Other characterizations of the chars produced in this system are described in Section 2.3.

### 2.2.3 Polystyrene Family

Several styrene/silicone block polymers varying in number of blocks per chain, block length and silicone content were tested. In some cases polymer molecular weights were low enough that the resins were like paraffin wax in consistency at room temperature. The materials, their base characteristics, LOI's obtained, and observations on burning are summarized in Table 6.

All LOI's are plotted vs. silicone content in Fig. 8. These fall within an envelope the lower bound of which is the interpolation line between the LOI's of the two homopolymers. The upper bound reaches a broad LOI maximum of 28 or so centered at 60% silicone roughly.

Homopolystyrene burns with no char formation. A "cap" of melted resin exists on top of the LOI specimen (Fig. 9a). Vapor bubbles are produced in the cap, the vapor presumably consisting of styrene monomer and low molecular weight oligomers.<sup>[5]</sup> (Polystyrene's ceiling temperature for depolymerization is well known to be ca. 300°C.) The volume of the "cap" under the flame increases very slowly and eventually molten resin runs slowly down the side of the specimen. A stream of fine black smoke is emitted from the top of the flame.

A dramatic visual change is brought about by the presence of silicone in the test specimen even in small amounts. A solid residue forms on the top (Fig. 9b and c). At low silicone contents the residue is black with minor areas of gray but becomes much whiter with increasing silicone content. The volume increase accompanying residue formation is much less than with either bisphenol carbonate-silicone family.

The two bounds of the envelope in Fig. 8 appear to result from differences in rheological behavior of the resin. Specimens of some resins became very fluid in regions close to the flame and the molten material tended to run down

TABLE 6

Polystyrene Family: Resins and  
Limiting Oxygen Indices

<u>Code No.</u>	<u>Design Formula*</u>	<u>Found Wt. % DMS</u>	<u>[<math>\eta</math>] (dl/g)</u>	<u>Mechanical Character</u>	<u>Melt Character</u>	<u>LOI</u>
DB-61-97	D <sub>200</sub> S <sub>100</sub> D <sub>200</sub>	74	0.34	soft, cheesy	runny	19.6
DC-37-97	(D <sub>25</sub> S <sub>50</sub> D <sub>25</sub> ) <sub>4</sub>	36	0.20	hard, v. brittle	runny	17.6
DB-80-97	D <sub>400</sub> S <sub>100</sub> D <sub>400</sub>	82	0.66	rubbery	viscous	24.5
PA-55	D <sub>173</sub> D <sub>31</sub>	11	0.27	hard, v. brittle	runny	17.0
DB-108-97	S <sub>100</sub> D <sub>100</sub>	61	0.24	leathery, cheesy	viscous	27.8
DC-143	(D <sub>100</sub> S <sub>100</sub> ) <sub>~4</sub>	42	0.31	hard, weak	viscous	26.5 $\pm$ .7
DC-97	(D <sub>25</sub> S <sub>50</sub> D <sub>25</sub> ) <sub>~3</sub>	38	0.125	hard, brittle	runny	21.6
DE-15	S <sub>940</sub> D <sub>500</sub>	13	0.66	v. hard, strong	viscous	22
9535-6-1	S <sub>875</sub> D <sub>920</sub> S <sub>875</sub>	17	0.75	v. hard, strong	viscous	22
(Koppers Dylene 8)	Polystyrene M <sub>n</sub> =125,000	0	—	v. hard, strong	intermediate	18
HA-54-97	S <sub>200</sub> D <sub>1000</sub> S <sub>200</sub>	68	0.40	soft, cheesy	intermediate	22.2 $\pm$ .2

\* D =  $-(\text{CH}_3)_2\text{SiO}-$ , S =  $-\text{C}_6\text{H}_5\text{CH}-\text{CH}_2-$

the sides of these specimens; the LOI's resulting from these tests fell on the lower bound. Specimens of the other resins showed no tendency to flow in this manner; LOI's for these materials fell on the upper bound.

Each material on the upper bound left a residue in the form of a roughly cylindrical shell the wall thickness of which was estimated by eye to be 0.02 in. approximately. The lower end of the shell covered the molten resin cap, the upper end was completely empty. The resins on the lower bound left residues that tended to be fragmented.

Thus if melt viscosity is high enough the incorporation of silicone in sufficient amount can produce a stable char that results in a substantial increase in the LOI of styrene resins. Fractionally the increment in LOI achieved is as great as with the polycarbonate families. The silicone content required, however, is about twice as great.

Under inert atmospheres at temperatures of 500°C and above styrene monomer and its oligomers are known to break down to small hydrocarbon fragments ( $C_1-C_6$ ).<sup>[5]</sup> Presumably the shell of silica residue acts as a red-hot screen beneath which the atmosphere is largely inert and through which the styrene vapors must pass. During passage the temperature of the vapor must be raised to the point that these small hydrocarbon fragments are produced and some of these are carbonized.

#### 2.2.4 Polymethylmethacrylate Family

The MMA-silicone resins tested included several graft resins in addition to a number of binary block polymers. Resins tested, compositions, other characteristics and LOI's are summarized in Table 7.

All LOI's from this family are plotted vs. silicone content in Fig. 10. Very little sign of LOI enhancement is seen.

TABLE 7

Methylmethacrylate/Silicone  
Block and Graft Polymers

<u>Code No.</u> <sup>*</sup>	<u>Design Type</u> <sup>**</sup>	<u>Found Wt. % Silicone</u>	<u>[<math>\eta</math>](dl/g)</u>	<u>LOI</u>
9459-4-4(HI)	b	5.1	N.R. <sup>†</sup>	19.2
9459-41-1(HI)	b	38.4	1.06	22.0
9459-54-4(HI)	b	21.7	0.66	20.8
9535-17-1(HI)	b	18.0	1.20	19.6
9535-32-1(HI)	b	21.9	N.R.	18.7
9535-38-1	b	44.6	N.R.	20.0
9535-38-3	b	58.1	N.R.	21.2
9535-63-2	PMMA	0	0.82	17.0
9538-142-1(HI)	g	7.1	N.R.	17.0
9749-2	g	7.4	N.R.	17.0

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\* HI = Hexane-insoluble fraction

\*\* b = binary block polymer; g = graft polymer

† No Record

PMMA itself burns with a smokeless flame and no char formation. A molten cap of resin exists on top of the LOI specimen (Fig. 11a). Bubbles of vapor believed to be pure MMA monomer originating from thermal depolymerization<sup>[5]</sup> form in the cap and feed the flame.

With the block and graft polymers the flame is also smokeless. However a gray to white solid residue forms slowly on top of the molten cap. The residue takes the shape of a hollow cylindrical shell with a thin convoluted wall. The shell is white to gray outside but usually darker inside (Fig. 11b). Its diameter and wall thickness both increase strongly with DMS content (Fig. 11b vs. 11c). The gross form of this shell is much like that on the styrene DMS resins.

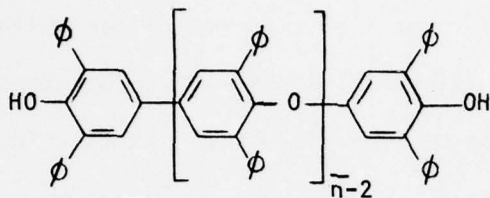
Of all the homopolymers tested in this study PMMA shows the least tendency to form char or smoke. Presumably this characteristic is related to the thermal depolymerization which occurs at low temperature and which yields only monomer, the monomer breaking down at higher temperature to smaller fragments.<sup>[5]</sup> In any case the evident lack of tendency to carbonize on burning is thought to be responsible for the lack of LOI enhancement by silicone in the block and graft polymers. However the fact that the inside surface of the residue shell is often black indicates that even MMA monomer can deposit a little carbon on a very hot substrate in an oxygen deficient atmosphere.

#### 2.2.5 Poly(2,6-diphenyl phenylene oxide) Family

High molecular weight poly(2,6 diphenyl phenylene oxide)(P<sub>3</sub>O) is a resin with a T<sub>g</sub> of 220°C and a T<sub>m</sub> of 490°C.<sup>[6]</sup> It can be cast from chloroform solution into films that are clear, amorphous and about as brittle as polystyrene. These films can be compression molded at temperatures up to 250°C into amorphous bars

that are nearly clear. At 260°C crystallization begins; once crystallized the polymer is intractable since degradation commences just above  $T_m$ . [7]

Multisequence  $P_3O/DMS$  block polymers have been previously made with a wide range of compositions and  $P_3O$  block lengths. [8,9] The making of these materials involved the use of the difunctional oligomers



where  $\bar{n}$  is two or greater. Microdomain formation occurs in all these materials with hard block domain  $T_g$ 's varying with block length as expected. [10] Crystallinity is not found in resins of  $\bar{n} \lesssim 20$ .

A small amount of each of five rubbery block polymers in this family was available. Compositions and block lengths along with molding temperatures, LOI's obtained and related observations are all summarized in Table 8.

Three blends of  $P_3O$  homopolymer with  $P_3O/DMS$  block polymer of 82% DMS and  $\bar{n} = 0$  were made by coprecipitation of chloroform solutions in methanol followed by vacuum drying at temperatures up to 190°C. Finally a blend of  $P_3O$  with SE-30 silicone gum was made in similar fashion. These blends were made in light of the behavior of the BPF polycarbonate/BPFC-DMS block polymer blends and in the hope that the blends would serve as substitutes for block polymers of high  $P_3O$  content as far as LOI testing was concerned. These blends are also listed in Table 8.

LOI's for this family are displayed vs. silicone content in Fig. 12. The block polymers showed a substantial synergism similar to that seen in the BPF carbonate family. The four blends however showed no LOI enhancement at all.

TABLE 8

Poly(2,6 diphenyl-1,4-phenylene oxide) Family of  
Block Polymers and Mixtures

<u>Code No.</u>	<u>Type</u> <sup>*</sup>	<u>Hard Block D.P.<sub>n</sub></u>	<u>Found Wt. % DMS</u>	<u>LOI</u>
—	h	"∞"	0	36.7±1.2
9665-81-1	b	2	66	39.8
9961-148E	b	40	74	32.3
9665-37-1	b	22	76	33.2
9665-52-1	b	2	78	37.8
9961-261	b	40	83	28.9±.3
10846-132B	h+h	∞	25	36.4±1.2
10873-33A	h+b	∞/20	19	33.8
10873-33B	h+b	∞/20	30	30.2±.3
10873-33C	h+b	∞/20	40	30

---

\* h = P<sub>3</sub>O homopolymer or SE-30 silicone gum; b = alternating block polymer;  
h+h = P<sub>3</sub>O homopolymer plus alternating block polymer of D.P.<sub>n</sub> ≈ 20

P<sub>3</sub>O homopolymer burns with substantial smoke and char formation (Fig. 13a). The char is slightly larger than the specimen in cross section and consists of a strong foamy core with a thin sooty surface covering. Thus the homopolymer behaves superficially rather like BPF polycarbonate. The LOI behavior of the block polymers and the appearance of their chars (Fig. 13b) are consistent with this fact. The behavior of the blends therefore seems inconsistent at first sight. A resolution to this paradox may lie in the thermal stability of the homopolymer and its blocks as affected by molecular weight. Thus it may be significant that the block polymers of  $\bar{n} = 2$  appear to have higher LOI's than those of  $\bar{n} = 20$  and 40. Pyrolysis results (Section 2.3.2) lend some support to this possibility. Lack of materials however has prevented a resolution to this inconsistency.

#### 2.2.6 Miscellaneous

A silicone block polymer from each of three other families was available in sufficient quantity for compression molding and LOI testing. These materials and the corresponding polymers with no silicone together with test results are listed in Table 9. Each "family" is discussed separately below.

a. Polysulfone Family. Polysulfone itself burns with substantial smoke and black char production. The char is foamy and about as strong and voluminous as the char from BPF polycarbonate. The 58% silicone block polymer produced char that was visually much like that from the polycarbonate-silicone block polymers of the same DMS content: a white flaky exterior, a dark more continuous, foamy interior. A 5% DMS block polymer previously was reported to have an LOI equal to that of polysulfone itself.<sup>[10a]</sup> The 58% DMS resin tested here yielded a LOI, at most, 4 units higher than the interpolation value (i.e. the

TABLE 9  
Miscellaneous Polymers Tested

<u>Code No. or Reference</u>	<u>Polymer</u>	<u>Found Wt. % DMS</u>	<u>D.P.<sub>n</sub></u>	<u>L01</u>
Thermalux	Polysulfone of BPA and dichlorodiphenyl sulfone	0	—	30.7±1.5
A. Noshay, Union Carbide	Sulfone/silicone block polymer		***	29.5
11014-100	Polytetramethylsilphenylene siloxane (PSPS)	0*	—	42.4
10674-119	SPS/silicone block polymer	59*	40	34.5
10846-133- 3302-Br	BPA/tetrabromo BPA carbonate-block-dimethyl siloxane**	43	10	53

---

\* Exclusive of DMS in SPS

\*\* Copolycarbonate block contains 26 wt. % bromine

\*\*\* Not known to us

value predicted from the LOI vs. % DMS interpolation line). By contrast both polycarbonate families gave 10 to 12 units LOI enhancement over their interpolation lines at this DMS concentration. The source of this difference in behavior could not be sought owing again to limitations in time and material.

b. Polytetramethylsilphenylene siloxane (PSPS) Family. Small amounts of PSPS and one rubbery multisequence block polymer containing 59% DMS of  $D.P._n = 40$  were available. The homopolymer exhibits a  $T_m$  of  $150^\circ\text{C}$  and a  $T_g$  of  $-25^\circ\text{C}$ .<sup>[11]</sup> The block polymer tested exhibits a hard domain  $T_m$  of  $100^\circ\text{C}$ . Both homopolymer and block polymer are opaque.

The burning of PSPS yielded a substantial amount of a thick coarse, flaky, weak residue. Residue color was variegated--white in some places, gray in others, black in still others. A thick zone of clear melt existed below the burn front on the 01 specimen. The melt zone tended to flow and the "char" plus underlying melt tend to tip over, sag, and collapse on the lower, still solid section of bar. This collapse tended to fragment the residue and also to melt and ignite the lower bar section. The smoke also varied in character, being black, coarse and wispy most of the time but white periodically.

The block polymer burned in similar fashion in every respect except that the residue was somewhat lighter in color.

The LOI of PSPS is a very respectable 43 in spite of the unstable melt zone. The LOI of the block polymer is only 4 units higher than the value of 30 obtained from interpolation between the two homopolymers.

Several factors may underlie the lack of LOI enhancement in this family. The first, by analogy with behavior seen in part of the styrene family is low melt viscosity.

The second is the elemental silicon content--27 wt. % is PSPS and 33 wt. % in the block polymer. The Si levels are much higher than that at the LOI maximum of either polycarbonate family (7 to 8%). In fact the 27 wt. % silicon of PSPS is equivalent to 71% DMS in any of the silicone block polymers in which the "hard" block does not contain silicon. In none of these other systems does the LOI at 71% DMS exceed 34, a level almost 10 units below the LOI of PSPS.

A third factor is hard block chemical structure and its role in pyrolysis-- a subject dealt with at greater length in Section 2.3.

c. BPA/Tetrabromo BPA Copolycarbonate Family. Mixtures of tetrabromo BPA with BPA form random copolycarbonates having LOI's that rise linearly with bromine concentration.<sup>[12]</sup> Thus at 17 wt. % bromine the LOI is 44, an increase of 19 units over BPA polycarbonate.

A silicone-copolycarbonate multisequence block polymer of 43% DMS of  $\overline{D.P.}_n = 10$  and 15 wt. % bromine was available. The copolycarbonate block contains 26 wt. % bromine (28 mol % tetrabromo BPA carbonate). The LOI for this material was 53. The material burns much like a BPAC/DMS resin of similar DMS content except that the char is darker and much more voluminous.

There are two ways to compare the relative effects of bromine on the LOI's of polycarbonate vs. BPAC/DMS block polymer. In the first comparison the silicone content is fixed, in the second the mol fraction of polycarbonate is fixed.

First a BPAC/DMS resin of the same silicone content (43%) is expected to have a LOI of 35.5 (Fig. 5). Thus the bromine has raised the LOI by 17.5 units which is 1.17 units per percent bromine in the whole polymer or 0.67 units per percent bromine in the polycarbonate block.

Second replacement of the 15% bromine with the corresponding mol % of hydrogen results in a BPAC/DMS block polymer of 51% DMS. Such a block polymer

is expected to have a LOI of  $34 \pm 2$  (Fig. 6). Conversely the substitution of bromine for hydrogen in this block polymer has raised the LOI 19 units or 1.27 units for each part of bromine in the whole polymer.

In any case the increment in LOI per part of bromine is, if anything, slightly greater in the block polymer than in the homopolymer. This result suggests that the LOI enhancement mechanisms associated with silicone and with bromine are separate but additive.

### 2.3 Mechanism Studies

A previous study of LOI chars from BPFC/DMS resins of low silicone content reported that the silicon content of the chars increased in proportion to the DMS content of the resin approximately.<sup>[3]</sup> Furthermore an electron microscopy investigation of one of these chars revealed a hard, brittle, amorphous, electron-dense substance that appeared to line the pores of the char. On this basis principally, it was suggested that LOI enhancement by silicone occurred because this layer (thought to be silica) tended to protect the underlying carbonaceous char from oxidative attack. This protection was thought to allow the char to remain thicker and a more effective thermal insulator than it would otherwise have been. No quantitative data on char yields, densities, morphologies, etc. were available to support this contention, however.

Moreover, this mechanism has been afflicted from its conception by a major weakness when viewed in the framework of the generally-accepted scheme for burning of organic solids.<sup>[13]</sup> In this scheme the oxidation processes that produce the heat occur largely in the outer portions of the flame. The inner portion of the flame is considered to be deficient in oxygen. Essentially no external oxygen penetrates the solid: Here only pyrolysis occurs, the

pyrolysates simply diffusing and effusing out through the degrading solid to be burned in the flame (Fig. 14). Thus the contradiction: How can dimethyl siloxane be oxidized to silicone dioxide in the reducing atmosphere of the solid interior?

A somewhat different view of the LOI synergism in silicone-polycarbonate resins emerges from the recent company-funded studies described below. These studies were primarily focused on the chars produced from BPAC/DMS resins. The new view of the synergism still focuses on similar brittle, electron-dense layers. However, the understanding of their production mechanism, composition and function in raising LOI, has changed substantially.

In summary in the view provided by the following account these friable layers are currently thought 1) to be produced under pyrolytic conditions by rather specific chemical processes involving the hard block residue and dimethylsiloxane; 2) to produce the synergism by altering the structures of pyrolysates and/or their rates of transport to the flame; and 3) to exhibit morphologies and compositions that are optimum for this purpose only when the chemical composition of the resin is correct.

The experimental work underlying this new view deals with two subjects:

- a) LOI chars — their yield, composition density and resistance to further oxidation; the morphologies of these chars and the siliceous residues left by their complete oxidation.
- b) Pyrolysis Products, i.e., the chars and pyrolysates produced by vigorous pyrolysis under inert atmospheres — their compositions, structures and morphologies.

### 2.3.1 Experimental

#### 2.3.1.1 L01 Char Yields

For purposes of determining the yield of char or residue per unit weight of polymer burned a modified L01 test procedure was devised as follows. A piece 3/8 to 1/2" long was cut off an L01 test specimen and a small hole drilled into the piece along the specimen long axis. The piece and a two inch diameter aluminum weighing cup were both weighed. The cup was impaled on a needle mounted in the L01 specimen clamp. The polymer piece was then slipped onto the tip of the needle. The mantle of the apparatus was put in place and the oxygen index set at the previously determined limiting value. The top of the piece was lighted with the torch in the standard way.

The flame progressed as usual down the sides of the piece and soon engulfed it completely. At the end of the burning process the char would usually be left sitting whole on the end of the needle. The cup was then carefully pulled off taking the char along, often completely intact. The cup and char were weighed once again and char yield calculated.

#### 2.3.1.2 L01 Char Oxidation at Fixed Oxygen Index

A further modification involved running the test described in Section 2.3.1.1 in the same way in all respects except that the oxygen index was fixed for all burnings at one level--a level high enough to insure combustion for all members of the resin family. In this modification glowing of the solid would often continue long after the flame went out. The length of this period of flameless combustion (the afterglow period) was recorded. The final solid residue was much whiter usually than the residue left after burning at the L01.

### 2.3.1.3 L01 Char Compositions

Residues from the char yield test just described were analyzed for elemental carbon, for hydrogen and for silicon. Occasional small bits of resinous material arising from tiny unburnt sections of resin were found on breaking the chars apart. These were discarded. Apart from these the remainder of each char was easily reduced to a powder with a mortar and pestle.

### 2.3.1.4 L01 Char Densities

As part of the effort to assess the insulating effectiveness of the chars their macroscopic densities were measured. The measurements were made using the chars from the modified OI test. Ottawa beach sand was used as a space-filling fluid in these tests. This material was used rather than a liquid for several reasons:

- a) The sand filled all the large holes but did not penetrate the channels of the chars.
- b) Chars would remain submerged in sand despite their very low densities.
- c) The sand could easily be removed from char pieces thus permitting their subsequent use in other tests.

Each measurement was made by breaking a char specimen in to two or three pieces, putting these in a small graduate cylinder and filling with sand to a known volume. Weighings were made after each step with an analytical balance. With light tapping to insure that the sand settled properly, polycarbonate char density could be determined reproducibly to a few percent. Density determinations were progressively more erratic with increasing resin DMS content. The chars from these resins included an increasing amount of loose,

whispy material deposited externally from the vapor phase. Inasmuch as this material was thought to be less important as an insulator than the underlying char produced in situ this deposit was broken away and discarded. What portion to choose to breakaway and discard became increasingly difficult to decide upon since with increasing resin DMS content the in situ char itself had progressively less integrity.

#### 2.3.1.5 Pyrolyses and the Treatment and Analysis of Resulting Products

Pyrolyses of BPA polycarbonate and several of the BPAC-DMS block polymers have been carried out in nitrogen atmospheres under vigorous heating conditions until no more vapors were evolved. The pyrolyses were effected on small pieces of 1/8 in. thick moldings placed in the bottoms of pyrex tubes and round bottom flasks, which were then heated directly by a Meeker burner. While still red hot these containers were plunged into water; this treatment served to free and quench the solid residue from each pyrolysis, usually in one piece.

In a few cases the effluents were passed through water-cooled condensers in order to collect the less volatile pyrolysate products. One of these pyrolyses produced a small amount of foamy material outside the main body of char; the foamy material would swell substantially (but not dissolve) in chloroform.

Pyrolysates were analyzed by  $^1\text{H}/^{29}\text{Si}$  and  $^{13}\text{C}$  nuclear magnetic resonance and by tandem gas chromatography-mass spectroscopy. Pyrolysate chars were analyzed for silicon by heating them up gradually to  $300^\circ\text{C}$  in air in a muffle furnace and weighing the  $\text{SiO}_2$  residues.

Pyrolyses of mixtures of SE-30 silicone gum and a variety of small molecule organic compounds were also carried out. These compounds were all

related one way or another to the organic components of the block polymers described in Section 2.1 that exhibited foamy char formation and evidence of the polycarbonate-silicone type of LOI synergism.

#### 2.3.1.6 Microscopy of Chars

LOI test specimens, modified LOI chars and pyrolysis chars were inspected by light, transmission electron- and scanning electron-microscopy. A variety of techniques were used to prepare specimens for these inspections.

LOI test specimens were photographed whole and then vacuum impregnated with epoxy resin as before. [3] These specimens were then sawn in half down the long axis. Macrophotographs were taken of the ground and polished cross section, small blocks were then cut from selected regions; from these blocks ultrasections were microtomed for TEM. These sections were backed with evaporated carbon for stability during viewing.

Pyrolysis chars were prepared for TEM in a similar manner. In addition some ultrasections were treated with hydrofluoric acid in an attempt to etch away any hydrolyzable, silicon-containing components (e.g. silicon dioxide, organic silicates, silicones, etc.).

Chars from both the modified LOI tests and from the pyrolyses were broken open, metallized and inspected directly by scanning electron microscopy. In addition other pieces of these chars were inspected after muffle furnace oxidation up to 800°C had removed all remaining carbon and hydrogen. Still other pieces were inspected after digestion in aqueous hydrofluoric acid at temperatures up to 100°C to remove siliceous components.

## 2.3.2 Results

### 2.3.2.1 Modified LOI Chars and Their Oxidation Residues

Fig. 15 exhibits the char yields from the modified BPAC/DMS LOI test specimens each burned at its own LOI: yield is seen to increase in rough proportion to resin DMS content. This correlation does not extrapolate to the experimental yield of  $\text{SiO}_2$  obtained from the burning of silicone gum (0.65 g./g.) however, but to a much higher level.

When a duplicate set of specimens was burned at  $\text{OI}=41$  the residues obtained were all nearly white. Small amounts of wispy soot deposited on the tops of the specimens were the only black regions. The yields of these residues are displayed vs. resin DMS content in Fig. 16. Again a roughly linear dependence is seen, the yield rising from zero for BPA polycarbonate and extrapolating to 0.8 g./g. of resin (the theoretical maximum yield) at 100% DMS.

Finally specimens of three resins were burned at  $\text{OI}=41$  but quenched by changing to  $\text{OI}=0$  as soon as the flame died out. The weights of these chars are compared to those produced by burning at LOI in Fig. 15. The similarity in weights of char from the two procedures reinforces the belief that atmospheric oxygen level has little effect on char production during the flame stage of combustion as long as this level is great enough so that all of the pyrolyzable products are evolved.

The compositions of the modified LOI chars are displayed in Fig. 17 vs. Resin DMS content. In support of visual observations the silicon content rises steadily with DMS content. The slight break in this curve occurs at the same DMS content as the LOI maximum.

The fractional retention in the char of silicon originally present in a given resin is obtainable by combining total char yield with char silicon content.

This quantity is displayed vs. resin DMS content in Fig. 18 for several BPAC/DMS resins. A corresponding quantity for carbon is also displayed. Finally, since the aromatic carbons and hydrogens are undoubtedly much more stable than are their aliphatic counterparts or the carbonate carbon, the carbon and hydrogen contents of the chars are plotted in Fig. 19 as a fraction of aromatic carbon and hydrogen in the resin.

The macrodensities of several chars, determined by the sand method, are displayed vs. resin DMS content in Fig. 20. No density maximum or minimum at the DMS content of the LOI maximum is evident, though the scatter seen here would admittedly obscure any trends but the most pronounced.

#### 2.3.2.2 LOI Char Oxidation Kinetics

The length of the afterglow period is plotted vs. DMS content in Fig. 21 in contrast to the trends in Figs. 15-16 the shape of this plot mimics the shape of the LOI vs. DMS plot (Fig. 6).

Two other notable aspects of the afterglow process connected with the progress of this phase of burning should be described. First a distinct geometric difference between the burning up of the chars from polycarbonate and its silicone block polymers was apparent. During this process the polycarbonate char became steadily smaller in diameter and more porous as well. The whole remainder of the char at any point glowed uniformly. By contrast this process in the block polymers left the total residue diameter constant; rather the fuel in the outside regions was consumed first leaving a dead, white outer shell and at intermediate times a smaller core of glowing material in the center of the specimen.

The kinetics of weight loss during the afterglow period were explored with the BPA polycarbonate and two block polymers. In Fig. 22 weight loss

during this period is displayed vs. the quenching time (length of time from the start of afterglow to the point that the glow died out as a result of the switch to 100% nitrogen in the atmosphere). Unexpectedly the oxidation rate of the outer portions of the block polymer chars was seen to be little different from that of polycarbonate itself. Thus these results suggested that the long afterglow period of the block polymers arose from a much reduced rate of weight loss from the innermost portion of the char.

### 2.3.2.3 Pyrolysis Chars

The yields of pyrolysis char plotted vs. resin DMS content display a pronounced maximum at the DMS content of the LOI maximum (Fig. 23). In addition a minimum in yield at 5% DMS seems to be present.

On complete oxidation at 800°C these pyrolysis chars leave a white residue (presumably  $\text{SiO}_2$  at this point) having the same form as the original char. The yield of this residue expressed as fractional retention of resin silicon shows a very sharp maximum at the DMS content of the LOI maximum (Fig. 24). A subtraction of this material as retained  $\text{SiO}_2$ , allows the total yield of carbon, hydrogen and carbonate oxygen in the char to be plotted in the same graph.

The macrodensities of the pyrolysis chars from BPA polycarbonate and one block polymer of 25% silicone were found by the sand method to be 0.34 and 0.27 g/ml, respectively. The value for the homopolymer char is more than twice that of the char from the modified LOI test (Fig. 20). That of the block polymer is also higher than obtained from the LOI test, though the difference is not as great. In any case the two values for the pyrolysis chars are sufficiently similar that the calculated comparative effectiveness of these chars as thermal insulators needs little correction for density differences.

The weight losses from air oxidation at 580°C of the pyrolytic chars of BPA polycarbonate and of 108453-133-11 (25% DMS) are shown vs. time in Figs. 25a and b. Compared in terms of total residual weight vs. time a large difference in resistance seems to develop in the latter stages of oxidation. However in terms of residual consummable weight the oxidation kinetics are essentially indistinguishable.

In Table 10 the compounds that were mixed with SE-30 silicone gum are listed in order of their effectiveness in inducing silicon retention in their pyrolysis chars. Of the materials tested it appears that the most effective ones are those of high molecular weight having free aryl hydroxy or aryloxy groups. On this basis presumably diphenylcarbonate is slightly active because decomposition produces phenoxy intermediates. Those liquids which boiled without decomposition at relatively low temperatures (e.g.  $\beta$  naphthol and the phenylene ether tetramer) gave rise to no silicon retention because boiling removed them before the temperature became high enough for reaction.

Presumably pyrolysis of many of these mixtures under pressure would have given much greater silicon retention.

#### 2.3.2.4 Microscopy of BPAC/DMS Chars

Electron microscopy of the LOI chars of the BPAC/DMS resins revealed friable electron-dense, heat resistant layers (Fig. 26) similar to those seen in the BPFC/DMS resins previously. In addition rippled layers of density intermediate between those of undegraded resin and the friable layers were also found (Fig. 27). (Stereo pairs show that the ripples are a stick-slip effect on the cutting surfaces.) Electron microscopy of the pyrolysis char from the block polymer of greatest LOI showed the char structure to consist entirely of friable electron-dense layers (Fig. 28) similar to those in Fig. 26. On

TABLE 10

Silicon Retention in Chars from Pyrolysis  
of Silicone Gum Mixtures

<u>Compound</u>	<u>M</u>	<u>B.P. (°C)</u>	<u>Mixture Wt. % DMS</u>	<u>Retained Silicon (%)</u>
Bisphenol fluorenone	350	450-500ca.	25	12.2
tetraphenyl diphenquinone	488	400-500?	25	4.2
bisphenol acetone	228	410	20	1.5
2,6 diphenylphenol	245	400-500?	12	1.3
diphenyl carbonate	214	306	20	0.63
phenol-stopped phenylene ether tetramer	446	?	25	0.4
$\beta$ -naphthol	160	295	32	0
hydroquinone	108	286	40	0

this basis it seems evident that the friable layers are the end produce of pyrolysis while the less dense, more deformable layers are resin in an intermediate state of degradation.

With the LOI specimens the friable layers could usually be found in the thinnest part of the char, i.e. the char last produced by the advancing flame front, which suggests their importance in protecting underlying resin from the very start of combustion.

Scanning electron micrographs of the interior of modified LOI chars show that their morphology is highly dependent on resin DMS content. Thus BPA polycarbonate and block polymers up to about 20% DMS produce interior char morphologies comprised of curved membranes punctured frequently by holes (Figs. 29 & 30). The holes have lips that are clearly the remains of bubbles that formed, burst, collapsed, retracted and then became fixed in shape by the completion of pyrolysis. In one case a bubble was found that became fixed in shape just as (or perhaps before) it broke. (Fig. 31) Above 20% silicone or so the morphology of these chars becomes more and more similar to those of open cell foams. (Figs. 32 and 33)

All parts of the pyrolysis chars exhibit morphologies similar to those of the interiors of the counterpart LOI test chars (e.g. Fig. 34 vs. Fig. 30).

These char morphologies are preserved when either the silicon is removed by hydrofluoric acid treatment or the carbon and hydrogen are oxidized, either by burning as in the modified LOI test glow period or by 800°C air oxidation in the muffle furnace. (Figs. 35 and 36 vs. Figs. 32 and 30)

Moreover HF treatment of microtomed sections fails to produce holes detectable by transmission electron microscopy (i.e. holes larger than  $20\text{\AA}$ , the size of the grains of the carbon support film) suggesting that the silicon is distributed on a molecular scale.

The morphologies of the outermost regions of the LOI chars, regardless of resin composition, differ greatly from those shown in Figs. 29 to 36.

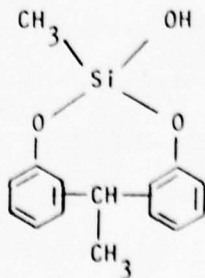
Whether black or white these exterior regions all consist of collections or

deposits of fine particles. The amount of deposit is small in the case of BPA polycarbonate (Fig. 37) but grows larger with resin DMS content. Occasionally these deposits show a markedly laminar form, the lamina conforming to the shape of the char surface (Fig. 38). These shapes suggest vapor flow directions.

### 2.3.2.5 Pyrolysate Constituents

The pyrolytic degradation of BPA polycarbonate produces a host of volatile products including water, methane, carbon dioxide, bisphenol-A, phenol, various alkyl phenols, and isopropenyl phenol.<sup>[14,15]</sup> The pyrolysis of polydimethyl siloxane at 600°C produces silicone cyclics; at higher temperatures hydrogen, methane and C<sub>2</sub> hydrocarbons are produced also.<sup>[16]</sup>

The analysis of the pyrolysates from BPAC/DMS polymers here is still in a rudimentary state. Several significant things are already clear however: a) The pyrolysate from the one block polymer pyrolyzed in quantity [10846-133-11 (25% DMS)] contains major products additional to those found in the pyrolysates of the counterpart homopolymers; b) Silicon-29 Fourier Transform NMR has revealed a methyl trioxy-silane compound and a larger quantity of a broad distribution of organosilicates; c) Gas chromatography up to 300°C has separated one component from the block polymer pyrolysate not present in that from BPA polycarbonate. Mass spectrometry indicated that this component is a trioxy silicon compound of mass 272 having a structure like that shown below.



### 2.3.3 Discussion

The experiments described above make it clear that L0I char has a two-fold nature: an in situ pyrolytic char and what might be termed soot or condensed smoke. The mature in situ pyrolytic char consists of homogeneous continuous membranes or strings of friable material. The soot consists of weak collections of carbonaceous and siliceous particles. Soot is found of course on the exterior (particularly the uppermost regions) of the burnt specimen, being deposited from the inner regions of the flame largely. Soot is also found in pockets of the in situ char, although in smaller amounts.

These experiments also suggest that the coupling between the characteristics of whole L0I chars and the L0I synergism is weak at best. Of all these characteristics only the afterglow period mimics L0I in its dependence on resin DMS content (Fig. 21). And this appears to be the case only because variations in the time for complete oxidation of the in situ portion of the L0I char.

#### 2.3.3.1 Relationship Between Pyrolytic Char Yield and L0I in the BPAC/DMS Family

L0I is correlated best with pyrolytic char yield; however, as seen in Fig. 39 the correlation is significantly different from that found by Van Krevelen<sup>[13]</sup> for a wide variety of organic polymers. Indeed all of the block polymers of the BPAC/DMS family fall on a line that includes silicone gum itself. Curiously BPA polycarbonate itself lies on Van Krevelen's line rather than the block polymer line.

Van Krevelen pointed out that charring results in a corresponding decrease in the yield of combustible vapors which in turn results in an increase in L0I. This effect was thought to be the basis of the general organic polymer correlation in Fig. 39. This effect may well contribute to the block polymer L0I-char yield

correlation. It is clear however that other effects leading to an additional 6 to 16 points in LOI enhancement must be involved. (Moreover if the yield of SiO<sub>2</sub> is subtracted from the yield of pyrolytic char (dotted line) the difference between the two correlations appears even greater.)

At present, it is not clear what effects are responsible for the difference in the LOI correlation lines in Fig. 39. Several possibilities for the BPAC/DMS resins are as follows:

- 1) Their pyrolytic residues are transport barriers (oxygen and/or heat in-, pyrolytic vapors out-).
- 2) An additional flame retardant mechanism separate from char formation exists that springs from the same underlying cause--a sister mechanism so to speak.
- 3) An additional separate property operates to enhance the effectiveness of the silicone resin chars, a property not found in BPA polycarbonate itself.

These possibilities are each discussed below.

First, it is questionable that the pyrolysis char functions additionally as an oxidation barrier as originally proposed.<sup>[3]</sup> Such a function contradicts the general view of the burning of organic solids, i.e., that the inner region of the flame is usually a reducing atmosphere and that pyrolysis only occurs in this solid. (This is not always the case, however.)<sup>[17]</sup>

Moreover, the intrinsic oxidation resistance of char appears to be independent of retained silicon content (Fig. 25). Therefore, the total time to oxidize completely the pyrolytic char resulting from a given quantity of resin should be proportional to the yield of that char (Fig. 24). In turn this conclusion would imply that the LOI vs. % DMS curve (Fig. 6) should reach a minimum at ~6% DMS before rising to a maximum at ~20% DMS. This does not seem to occur.

Second it is possible though not likely that the pyrolytic char functions primarily as a thermal barrier. The macrodensities of the pyrolytic chars (Fig. 20) plus their estimated microdensities (1.5 to 2.2 g/cm<sup>3</sup> based on the densities of amorphous carbon and silica) show that the chars contain 75 to 90% void. They are presumably good thermal insulators therefore. However the soot has an even greater void content and should thus contribute substantially to thermal insulation; this suggests that LOI would tend to correlate better with total LOI char yield, which is not the case. Moreover there is no evident reason that the BPAC/DMS pyrolytic residues should be superior in this regard to those of any of the non-silicone, char-forming polymers.

The third possibility, that the char may restrict the outward transport of pyrolysates was suggested originally by the occurrence of decrepitation during the burning of LOI specimens. An examination of notes taken during the LOI tests indicated that decrepitation occurred with all BPAC/DMS block polymers but tended to be most audible with resins of highest LOI. Thus the build-up of pyrolysate gas pressure seemed to correlate with char yield crudely.

This correlation was reinforced by the scanning electron micrographs showing widespread bubble formation in pyrolysis and in situ chars from resins of low silicone content (Figs. 30, 31 and 34). However, the same micromorphology is found in the char from BPA polycarbonate. Moreover the change in char morphology above 18% silicone to an open celled one seemingly incapable of restraining vapor efflux (Fig. 33) is not matched by a decrease in effectiveness in enhancing LOI when viewed in terms of yield of char. In other words, chars of open-cell morphology are just as effective on a yield basis as are those of closed-cell morphology in enhancing LOI.

Two conceivable sister mechanisms to char formation involve soot and smoke.

It is clear that the formation of carbonaceous soot removes fuel from the flame. It is also known that black soot and smoke particles are efficient at transferring energy out of flames by radiation.<sup>[18]</sup> Both effects would tend to raise LOI. BPA polycarbonate burned with relatively little soot or smoke production. However, all BPAC/DMS resins burned with the formation of moderate to copious quantities of soot, some of which re-deposited on the upper parts of the LOI char. Even 9627-X the block polymer with the lowest silicone content produced large quantities of black coarse smoke. With increasing silicone content the smoke and soot become increasingly white and, of course, the increasing LOI char yield (Fig. 15) implies that the amount of matter from which smoke can be formed decreases. Both changes should lead to a decrease in energy loss by radiation from the flame.

The fact that even the block polymer with the least silicone content, 9627-X, gave large amounts of coarse black soot suggests the possibility that volatile pyrolysis products containing fragments from both blocks are effective initiators of soot formation. In turn it would be likely that these interblock volatile fragments are formed by the same chemistry basically that leads to a maximum in pyrolytic char yield. The delay of the outward transport of pyrolysates by the closed cell char morphology seen at low DMS contents could be responsible for maximizing the yields from such chemistry. If so, pyrolysis under pressure should lead to a dramatic increase in pyrolytic char production from these resins.

Finally another separate property, melt viscoelasticity, may conceivably enhance the effectiveness of the pyrolytic chars of the block polymers. This thought springs from several observations. First the importance of melt viscosity to the formation of a stable residue shell on styrene-silicone LOI specimens was noted earlier. Second, the BPA polycarbonate exhibits a large

melt cap only part of which is covered by char. (Fig. 7a) By contrast all of the block polymers in this family and silicone gum itself are covered by char residue. The BPAC/DMS block polymers are known to have high melt viscosities and elasticities thought to be due to the resistance to deformation caused by the microdomain boundaries.

Moreover it seems likely that the rheological characteristics of the melt change, as pyrolysis proceeds, in ways that depend on composition: specifically the production of the rubbery and horny intermediate materials during pyrolysis implies a process of crosslinking involving both blocks. The concept of a degrading resin sustaining a high degree of deformability to very high temperatures and high degrees of conversion to final char product is appealing as a mechanism of retaining the pyrolysate products that are responsible for enhancing char and soot formation.

#### 2.3.3.2 Pyrolytic Char Yield Maximization

A question of equal importance to that of the role of char in LOI enhancement is that of the mechanism by which pyrolytic char yield is maximized at about 20% DMS. Though by no means clear this mechanism would appear to revolve about two coincidences. The first is that char morphology begins to become an open-cell one above 20% silicone. The second is that the mole ratio of BPA to DMS is 1 at 22% DMS.

Modeling the formation of pyrolytic char might well start by likening this char to a leaky chemical reactor inside which reactions go on under pressure that can, if contained long enough, lead to more of the reactor wall material. At intermediate stages of reaction the important products of the reactions are volatile however. Thus the leakier the reactor the less its ability to retain the very products that thicken its walls on further reaction.

In such a model the leakiness of the reactor (char) would be related to the degree to which the char has an open cell morphology. This morphology is set while the degrading resin still has a rubbery character. Presumably ultimate properties of this material depend, e.g, on gel content and crosslink density as with normal rubbers.

Crosslinking and chain scission reactions would compete and thus define the character of the network. Rates of crosslinking, thought to involve moieties of both blocks should be fastest where reactant stoichiometry is ideal, i.e., at a 1:1 BPA:DMS mole ratio. The rate of chain scission would rise with excess DMS since the latter would tend to be split out as volatile cyclics to an ever greater extent. This alteration in the ratio of crosslinking and scission reactions would limit network buildup and bring on the change to an open cell char morphology.

Although a drop in carbon retention below 20% resin DMS would be expected by this rationale, the observed drop to levels below that from homopolycarbonate is hard to rationalize. Harder yet to rationalize is the drop toward zero in silicon retention. One inference of this behavior is that the rate of the crosslinking reaction that leads to silicon retention involves DMS concentration to a power greater than one, while that of cyclic formation is first order in DMS content.

#### 2.3.3.3 Chemistry Underlying Pyrolytic Char Yield Maximization

The exploration of the crosslinking chemistry peculiar to the BPAC/DMS resins has clearly just begun. The fact that trioxy and tetroxy silanes have been detected in the pyrolysate from one block polymer strongly suggests reactions between BPA, various phenols, their anions and/or their radicals (or polycarbonate chain fragments having these ends) with the methyl-

silicon bond resulting in the formation of a wide range of volatile products and a crosslinked network. The network, at least in an intermediate stage of maturation is pictured to have a variety of bridges between siloxane chains such as those in Fig. 40. The formation of these specific bridges is suggested by two sets of experimental evidence: 1) the yields of  $\text{SiO}_2$  from the pyrolyses of the mixtures of silicone gum and the bisphenols and related compounds (Table 10) and 2) previous observations of the susceptibility of the carbon-silicon bond to attack by strong bases at much lower temperatures. [19]

Since hydrogen abstraction reactions occur readily at high temperatures, it would not be surprising if carbon-carbon bond formation involving the silicon-methyl carbon and, e.g., the 4-carbon of the phenolic fragments of BPA decomposition occurred. (That some silicons may be tied into the pyrolytic char by carbon-carbon bonds is also suggested by the pyrolysis chemistry of polydimethyl siloxanes [16] and the fact that digestion of chars in hydrofluoric acid has so far removed only 2/3 of the silicon present.)

#### 2.3.3.4 Future Work

Many avenues of exploration in understanding and optimizing the BPAC/DMS flame synergism and extending it to other systems lie open. Probably the first priority is to elucidate the chemistry of pyrolytic char formation. Partial degradations, the effects of pressure on yield, chromatographic separations of char and pyrolysate products, and product analysis by a variety of techniques like the ones already described would lie at the core of this work.

Another avenue of work is focused on optimizing the LOI synergism in the BPAC/DMS system in terms of silicone composition and block length. Synthesizing small quantities of several block polymers of 14 to 22% DMS content and several DMS block lengths from  $\overline{D.P.n} \approx 5$  to 15 should aid considerably in defining the maximum LOI obtainable and assessing its reproducibility. Once this objective

is attained syntheses scale-up of a select resin should permit the fabrication and testing of large scale flame test specimens (e.g. for radiant panel and various flame spread tests.)

Still another important avenue of exploration concerns the mechanism(s) by which the BPAC/DMS pyrolytic chars are so efficient compared to chars from all-organic polymers in raising LOI. For this study a variety of measurements related to the LOI test might be implemented--measurements e.g. of flame spread rates, radiant energy losses, flame temperatures, soot and smoke yield and composition. Useful supplemental tests might include measurements of heats of combustion of each resin, its pyrolytic and LOI chars and its collected soot and smoke. Pyrolysis of thin films might allow experimental assessment of pyrolytic chars as transport barriers. Finally understanding the chemistry of BPAC/DMS pyrolytic char formation should lead to trials of other selected model mixtures in order to assess which other silicone-organic polymer combinations might exhibit LOI synergisms. Synthesis of appropriate block and graft polymers and/or formulation of the right polymer mixtures would provide the ultimate opportunity for testing this understanding and establishing the breadth of its significance. A millennial goal of this work would be to provide economical non-halogen flame retardant "packages" for the whole spectrum of organic plastics and for silicone rubbers.

### 3. ACKNOWLEDGMENTS

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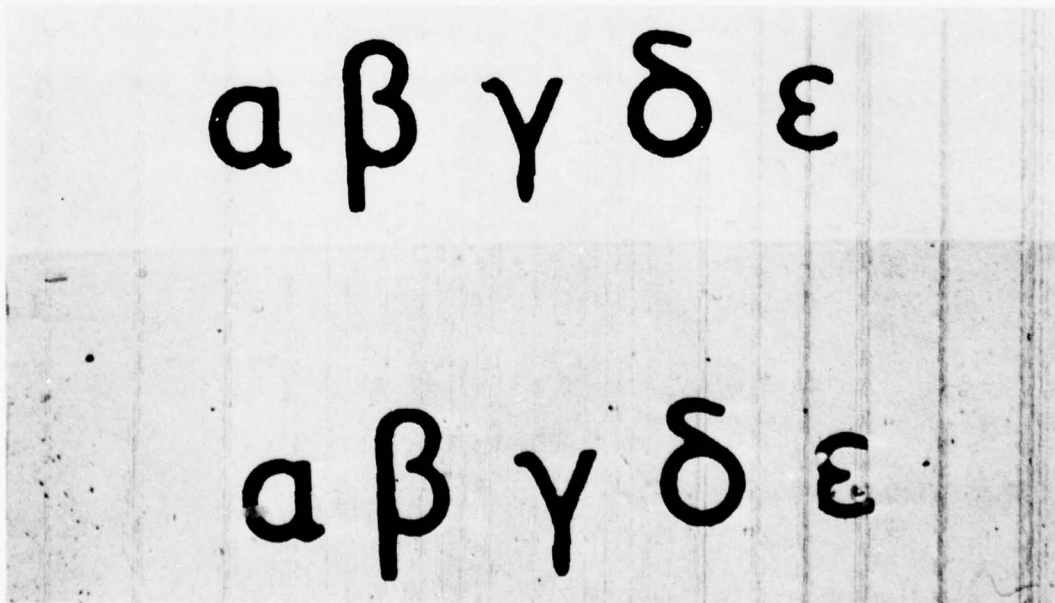
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a. Specimen 1-1/2 ft, Wall 45 ft from Camera



b. Same Specimen Lying on Typed White Paper

Figure 3. Photos Through Ground and Polished 1/8 x 3/4 x 1-1/2 in. Piece of Extrudate 12-28-78 Demonstrating Its Low Color Level and Its Freedom from Haze and Distortion. Specimen edge distortion due to rounding. Specks are air bubbles.

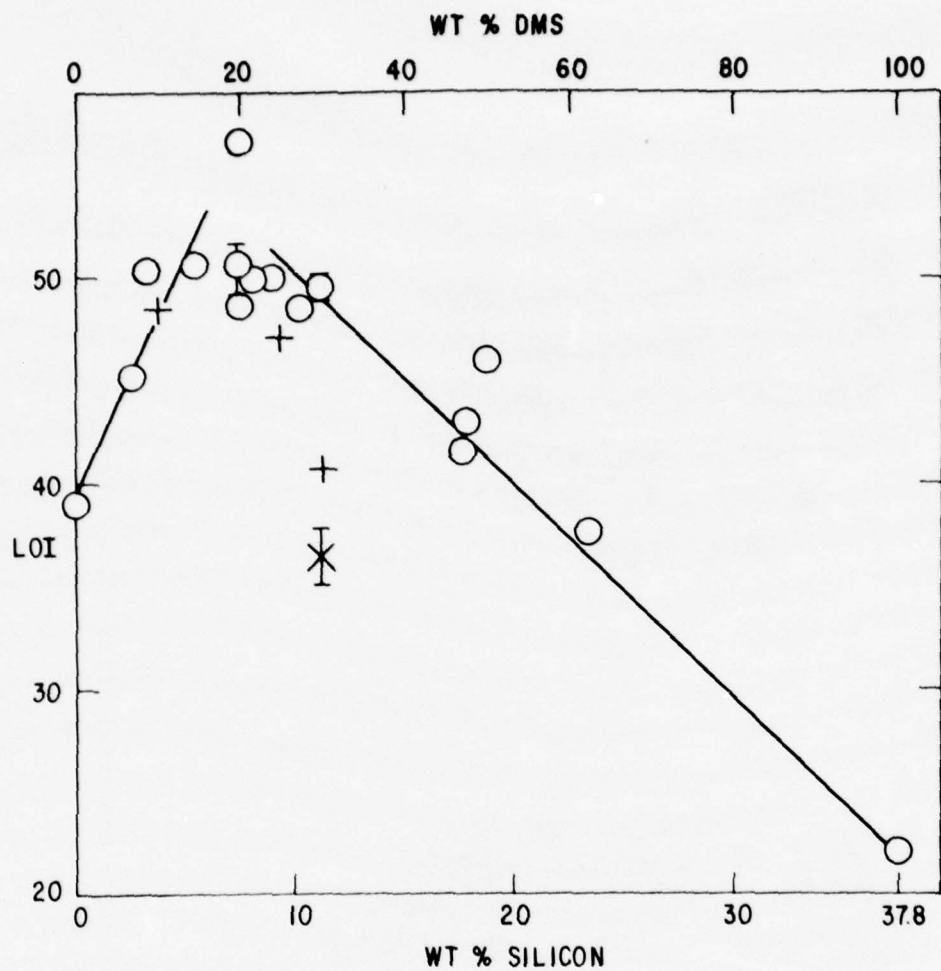


Figure 4. BPF Carbonate Family: Dependence of LOI on Silicon Content. [○ - block polymer, + BPFPC + block polymer blend, X - BPF PC + SiO<sub>2</sub> (upper scale for all materials except SiO<sub>2</sub> mixture)].

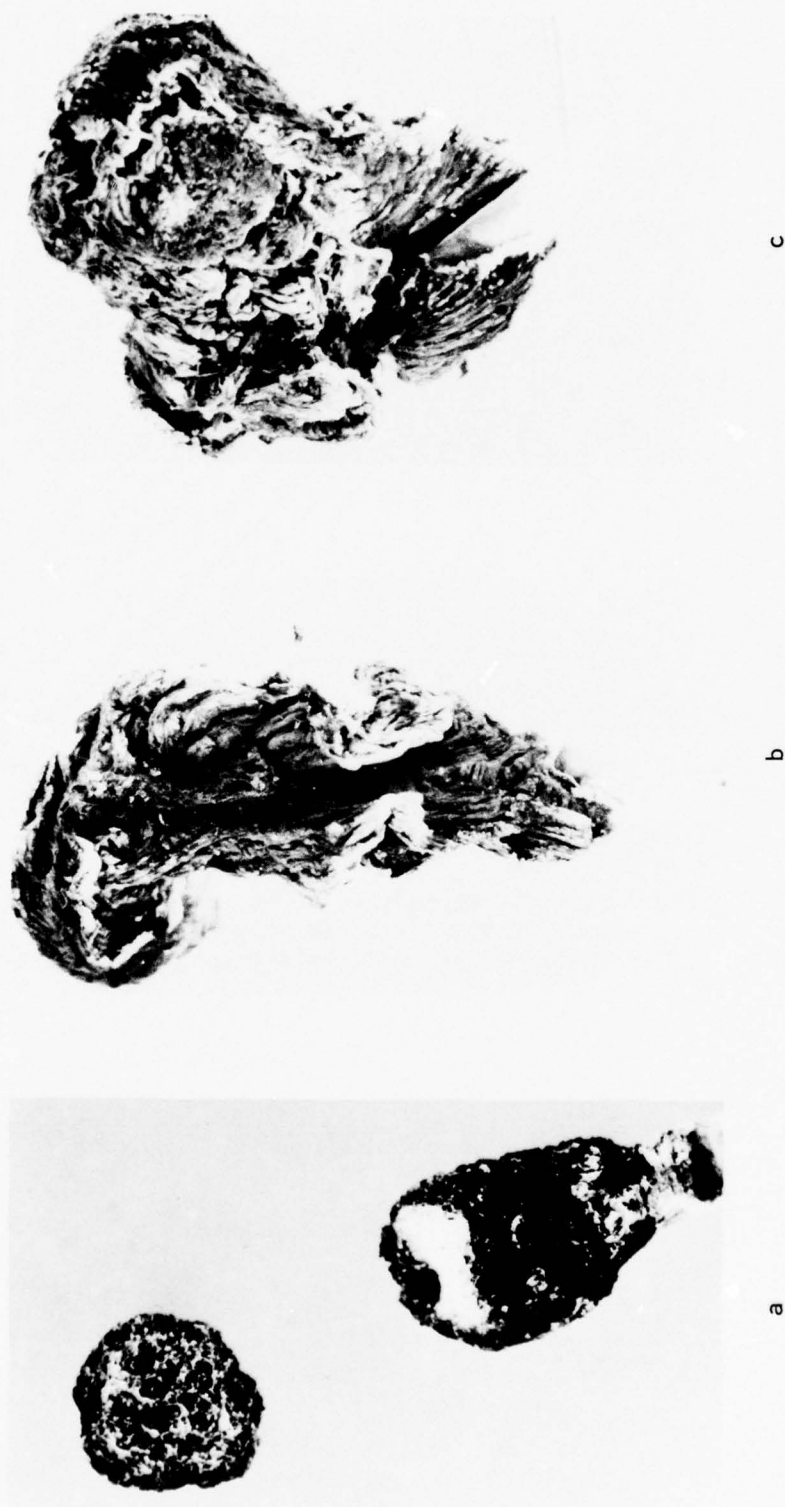


Figure 5. L01 Specimens of a) BPF Polycarbonate and Its Silicon Block Polymers, b) 12-15-77 (17% DMS), and c) 12-17-77 (45% DMS)



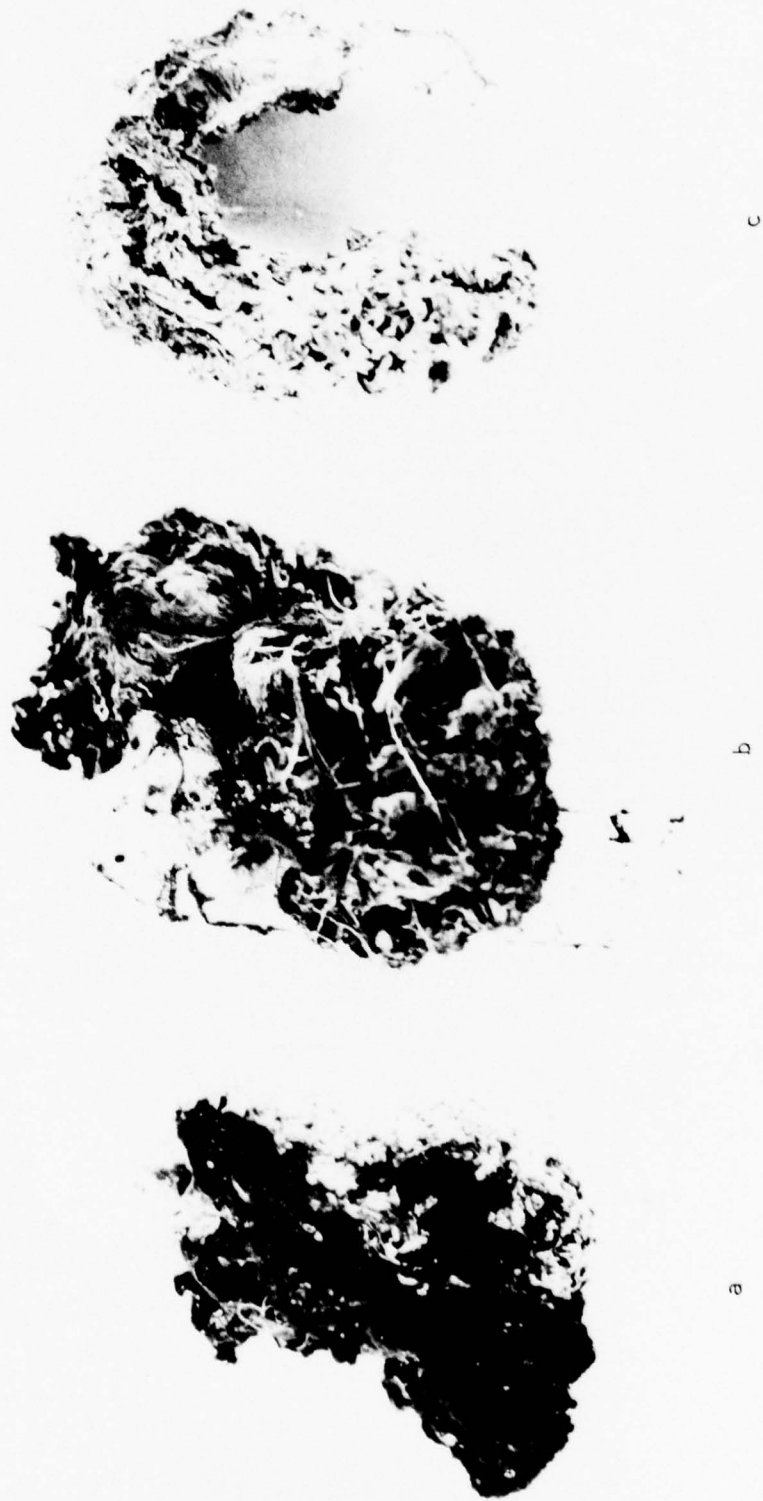


Figure 7. L01 Specimens of a) BPA Polycarbonate and Two of Its Block Polymers, b) 10846-133-25D5 (18% DMS), and c) 10846-133-0402 (50% DMS)

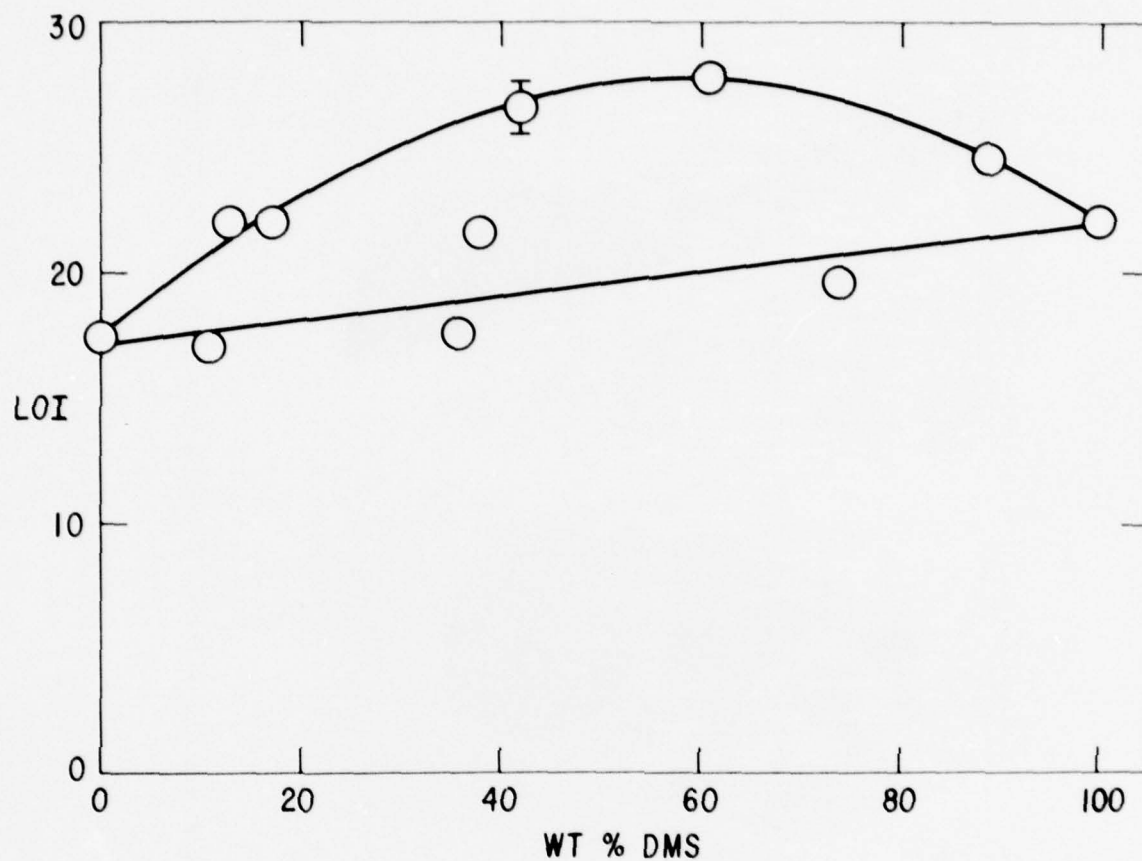


Figure 8. Styrene Family: Dependence of LOI on DMS Content. (Upper and lower bounds set by resin viscosities.)



a b c  
Figure 3. L01 Specimens of a) Polystyrene and Its Silicone Block Polymers, b) DE-15 (13% DMS), and c) DC-143 (42% DMS)

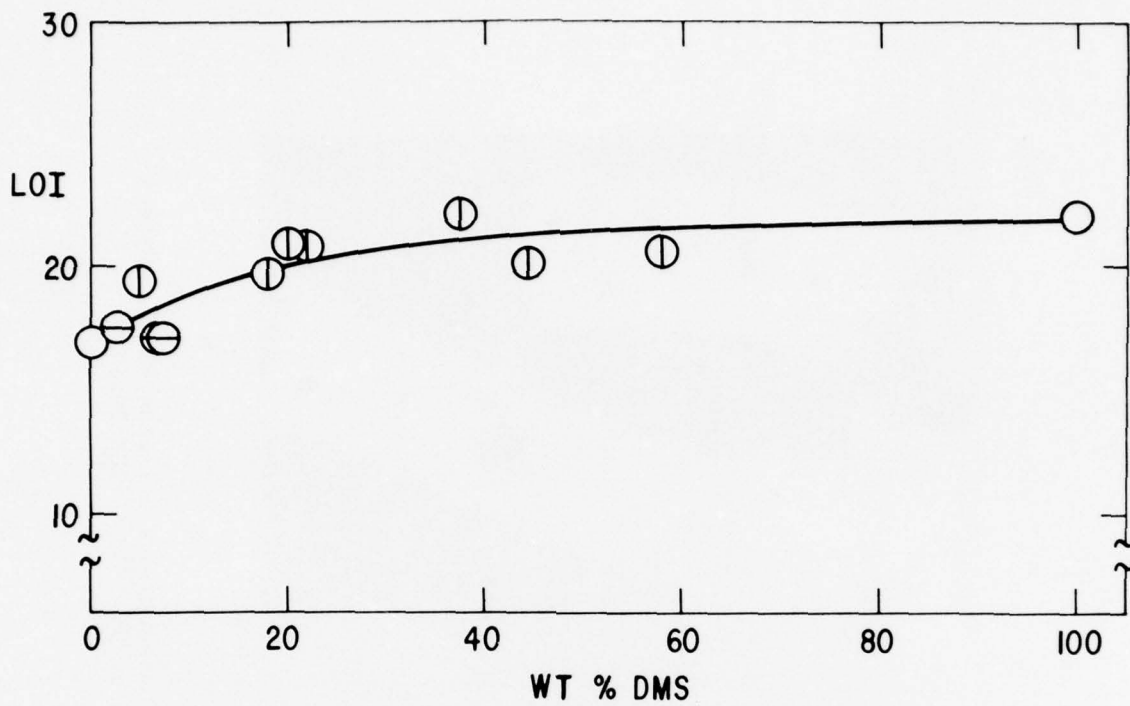
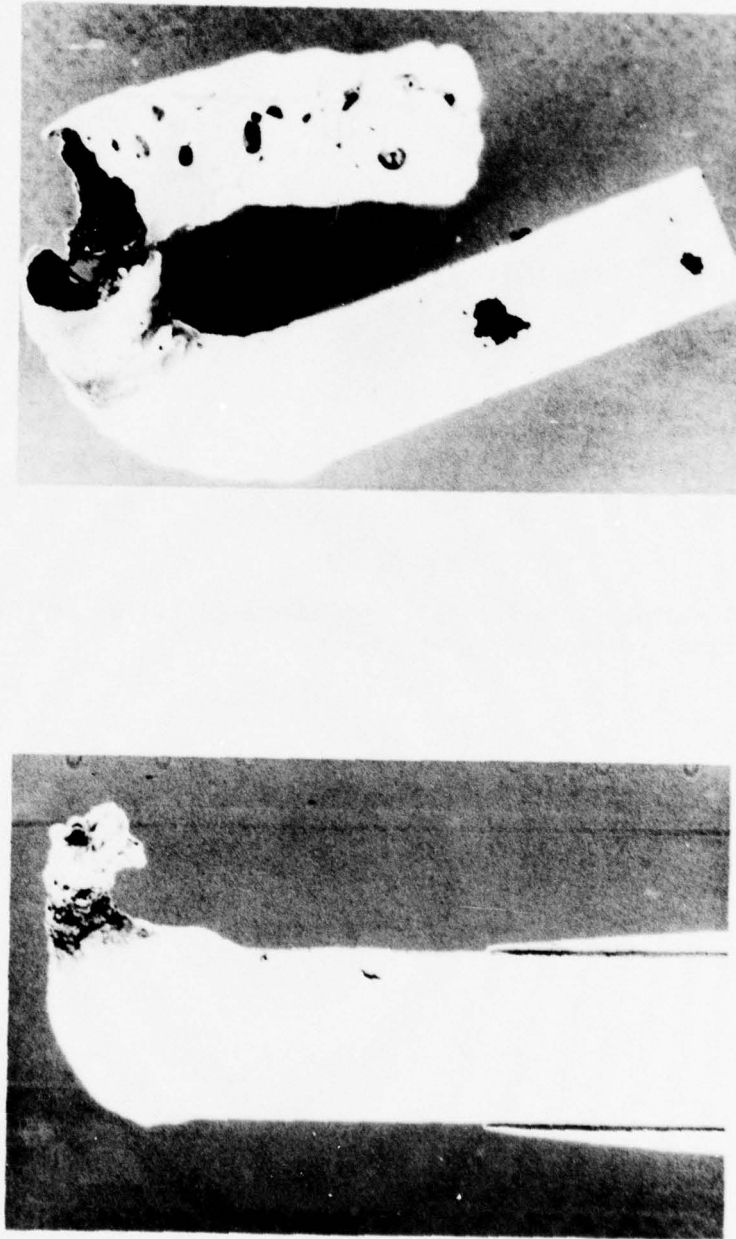


Figure 10. Methyl Methacrylate Family: Dependence of LOI on DMS Content. (⊖- block polymer, ⊕- graft polymer).



a b

Figure 11. L01 Specimens of Two Methyl Methacrylate/Silicone Block Polymers  
a) 9535-150-1 (2.6% DMS) and b) 9371-85-1 (20% DMS)

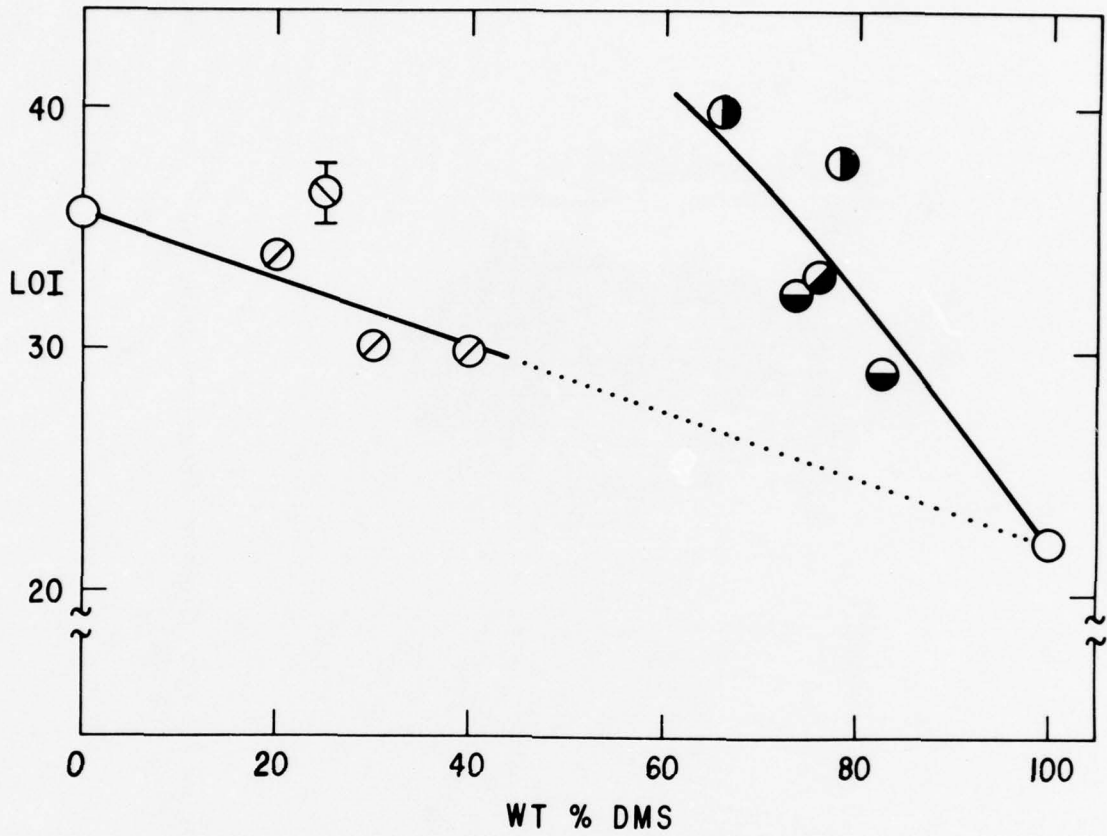
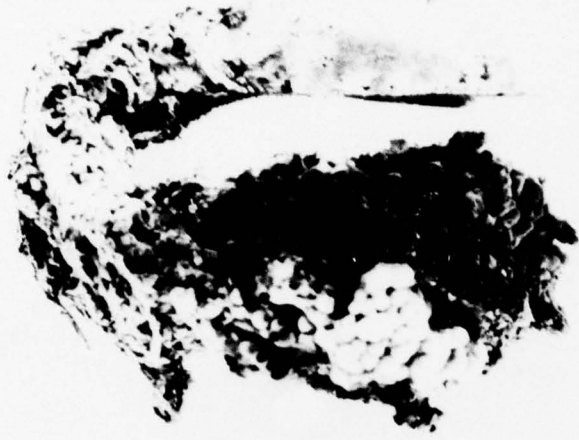
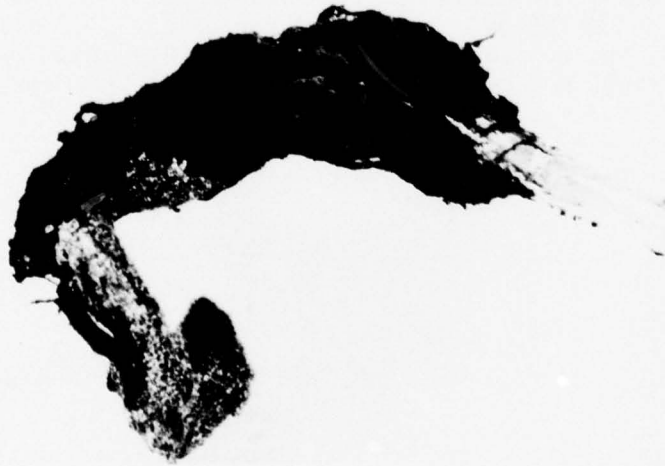


Figure 12. Diphenylphenylene Oxide Family: Dependence of LOI on Silicone Content. (●, ●, ●, - block polymer of  $\overline{D.P.}_n$  of DMS block equal to 2, 22, 40, respectively. ○ - blend of P<sub>30</sub> homopolymer with P<sub>30</sub>/DMS block polymer. ⊖ - blend of P<sub>30</sub> and silicone gum.)



b



a

Figure 13. L01 Specimens of a) Poly 2,6 Diphenyl Phenylene Oxide and  
b) 9665-81-1 ( $n = 2$ , 66% DMS)

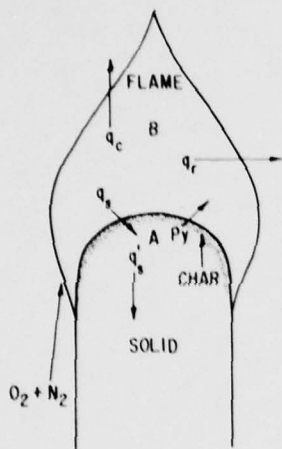


Figure 14. Conventional Schematic for Burning of Solids with Char Formation

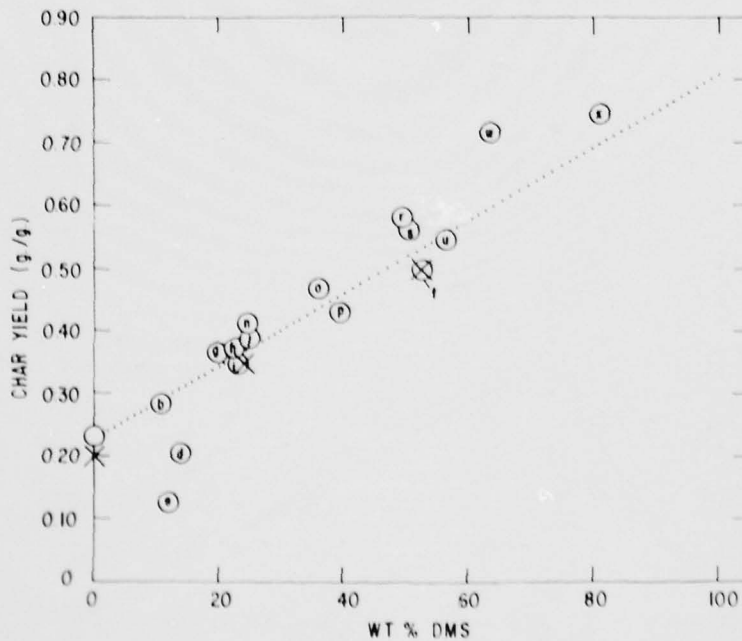
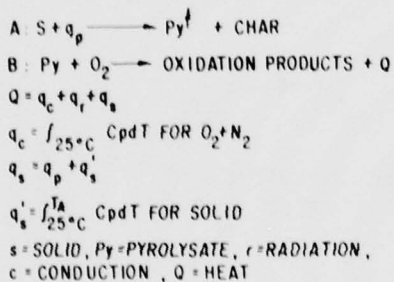


Figure 15. BPAC/DMS Char Yield from Modified LOI Test (O) vs. Resin Silicone Content. Also char yield from test at 0l = 4l followed by quenching in pure nitrogen at end of flame period of burning (x). (Dotted line theoretical: yield from BPAC fraction = 0.23 g/g., 100% DMS converted to SiO<sub>2</sub>. Letter code in Table 5.)

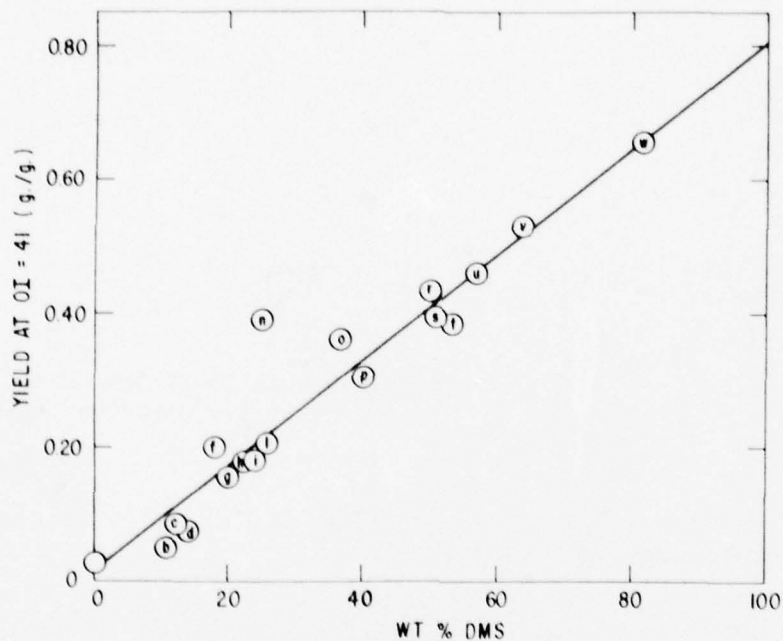


Figure 16. White Residue Yields from Complete Burning of BPAC/DMS Specimens at OI = 41. Letter code in Table 5.

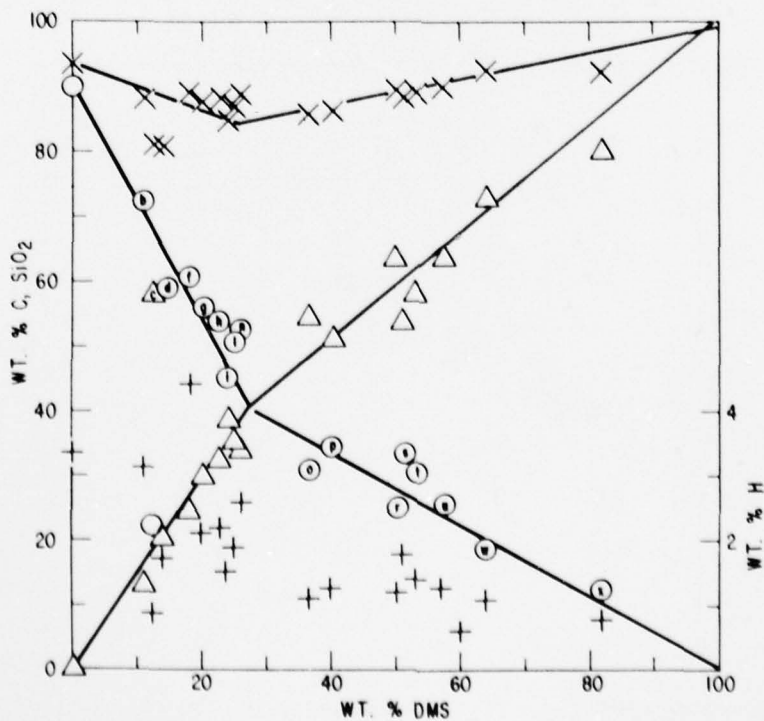


Figure 17. Compositions of BPAC/DMS Chars from Modified LOI Tests. (Left hand scale: carbon (O), SiO<sub>2</sub> yield on complete oxidation (Δ), total carbon, hydrogen + SiO<sub>2</sub> (X). Right hand scale: hydrogen (+). Letter code in Table 5.

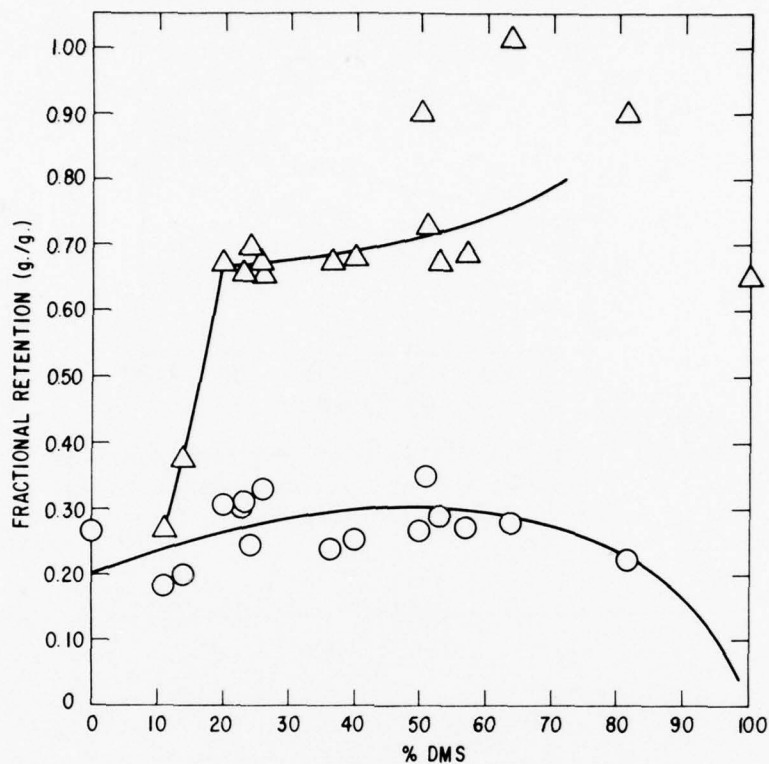


Figure 18. Fractional Retention of BPAC/DMS Resin Silicon ( $\Delta$ ) and Carbon (O) in Modified LOI Char

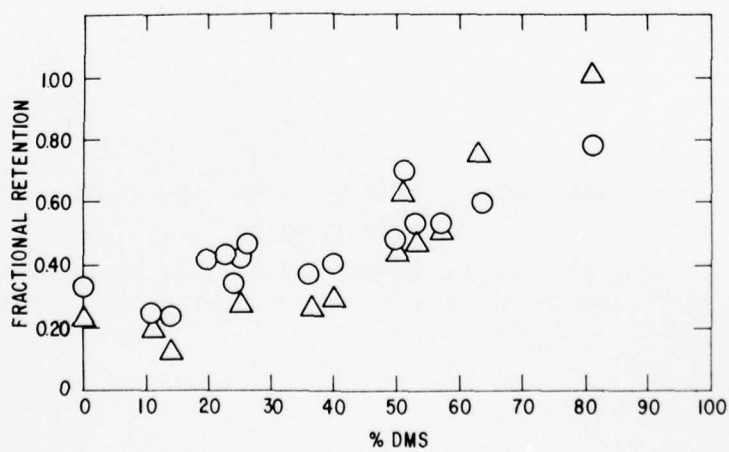


Figure 19. Carbon (O) and Hydrogen ( $\Delta$ ) Retention in Modified LOI Char as Fraction of Aromatic Carbon and Hydrogen Contents of Original BPAC/DMS Resins

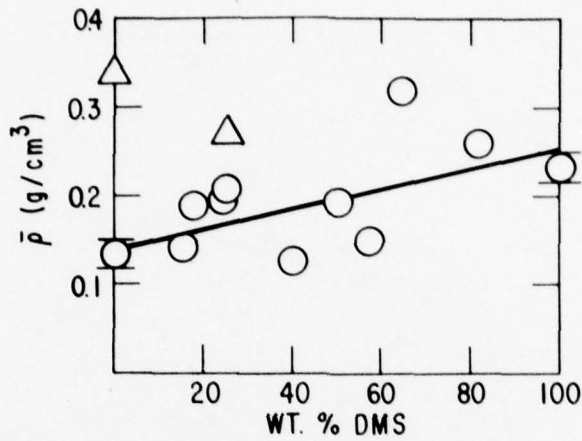


Figure 20. Macrodensities  $\bar{\rho}$  of BPAC/DMS Modified LOI Chars Freed of Loose Deposits (O) and of Two Pyrolysis Chars

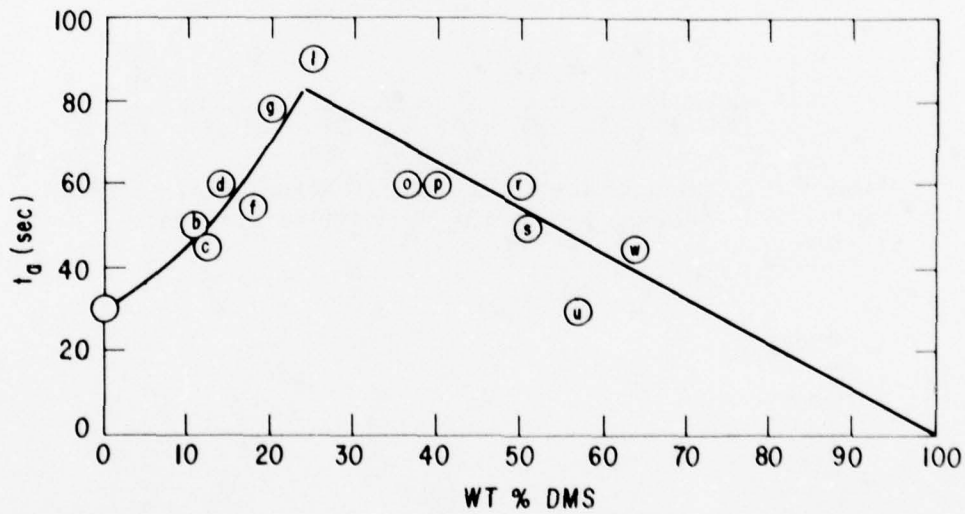


Figure 21. Afterglow Period in OI = 41 Test of BPAC/DMS Resins vs. Resin Silicone Content. (Letter code in Table 5.)

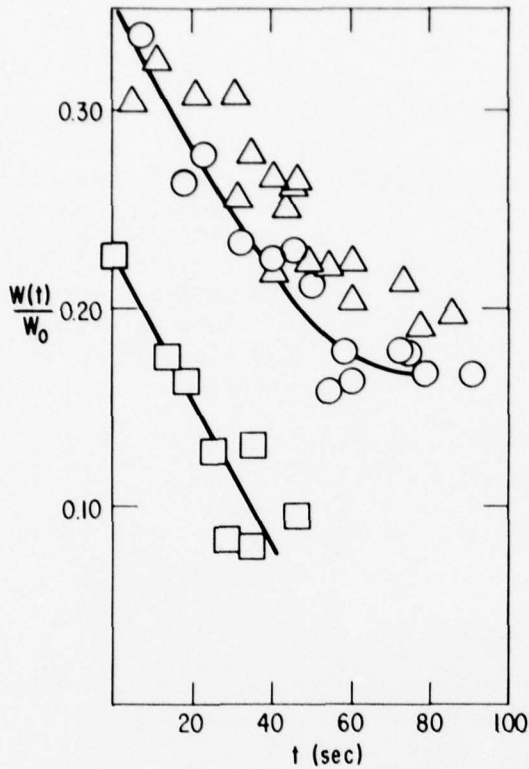


Figure 22. Specimen Weight  $W(t)$  During Afterglow Period for BPA Polycarbonate ( $\square$ ) and BPAC/DMS Resins of 25 and 53% Silicone. ( $W_0$  = resin specimen weight.)

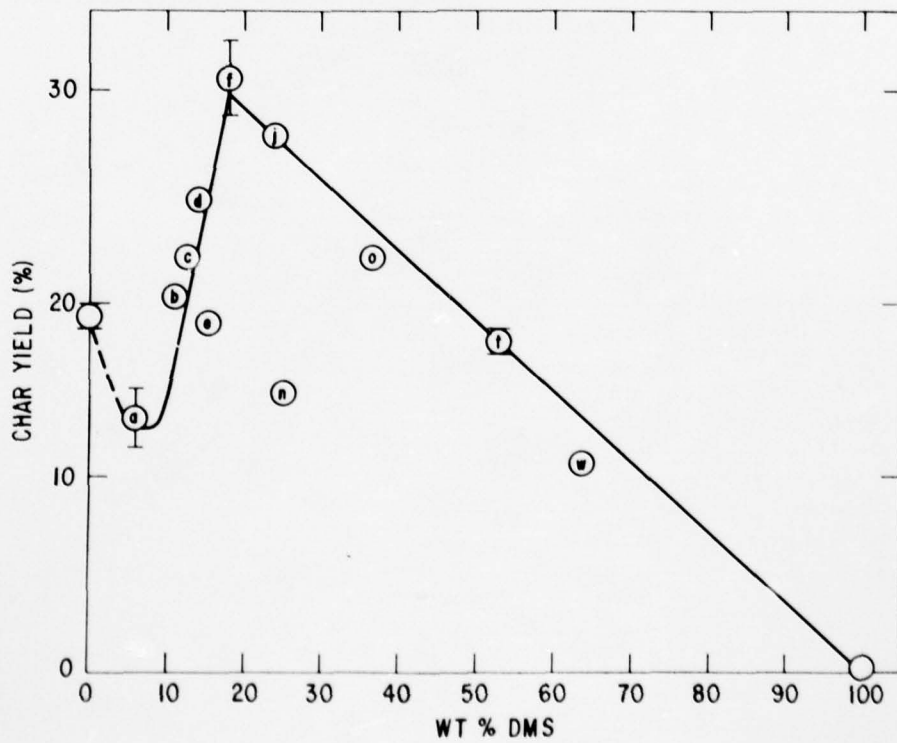


Figure 23. Yields of Pyrolysis Chars from BPAC/DMS Resins vs. Resin Silicone Content. (Letter code in Table 5.)

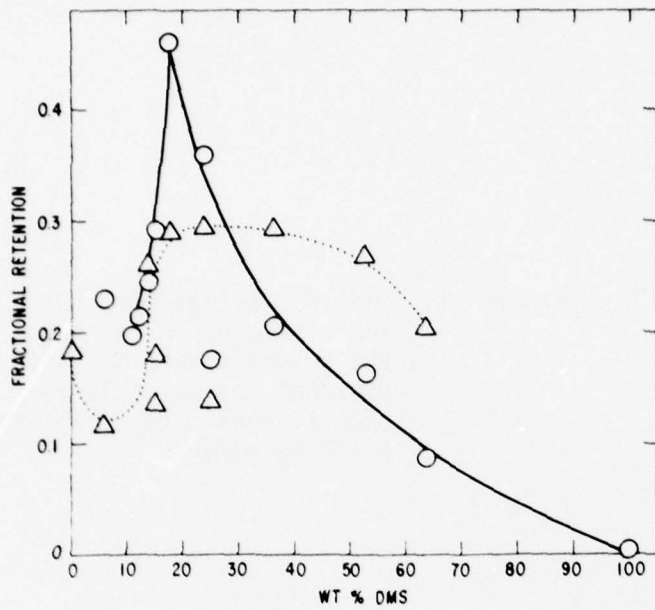
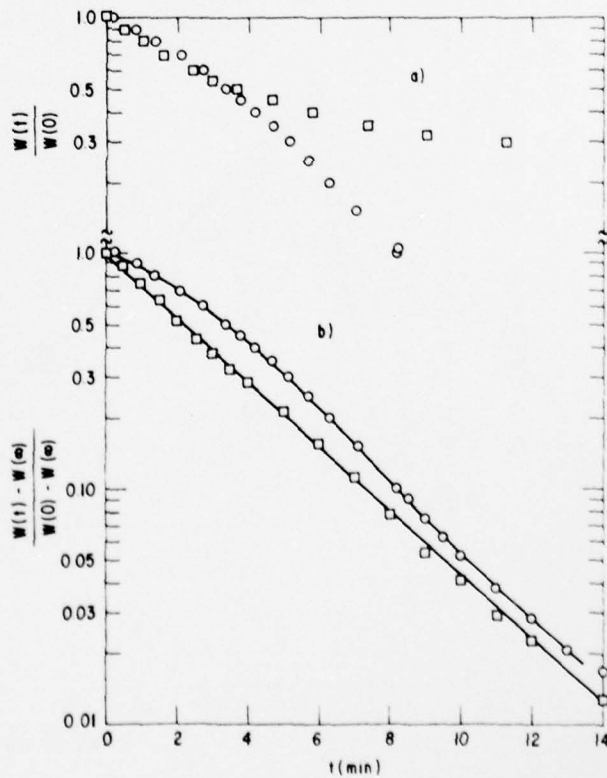


Figure 24. Fractional Retentions in Pyrolysis Chars from BPAC/DMS Resins (○ - silicon yield/DMS weight fraction; △ - (char yield - SiO yield)/BPAC wt. fraction)

Figure 25. Thermogravimetry of Chunk of Pyrolytic Char of Each of Two Polymers (○) BPA Polycarbonate and (□) 108453-133-11 (25% DMS), in Air at 580°C; a) Fractional Total Weight ( $W(t)/W(o)$ ) vs. Time; b) Fractional Consumable Weight ( $[W(t) - W(\infty)]/[W_o - W_{\infty}]$ ) vs. Time



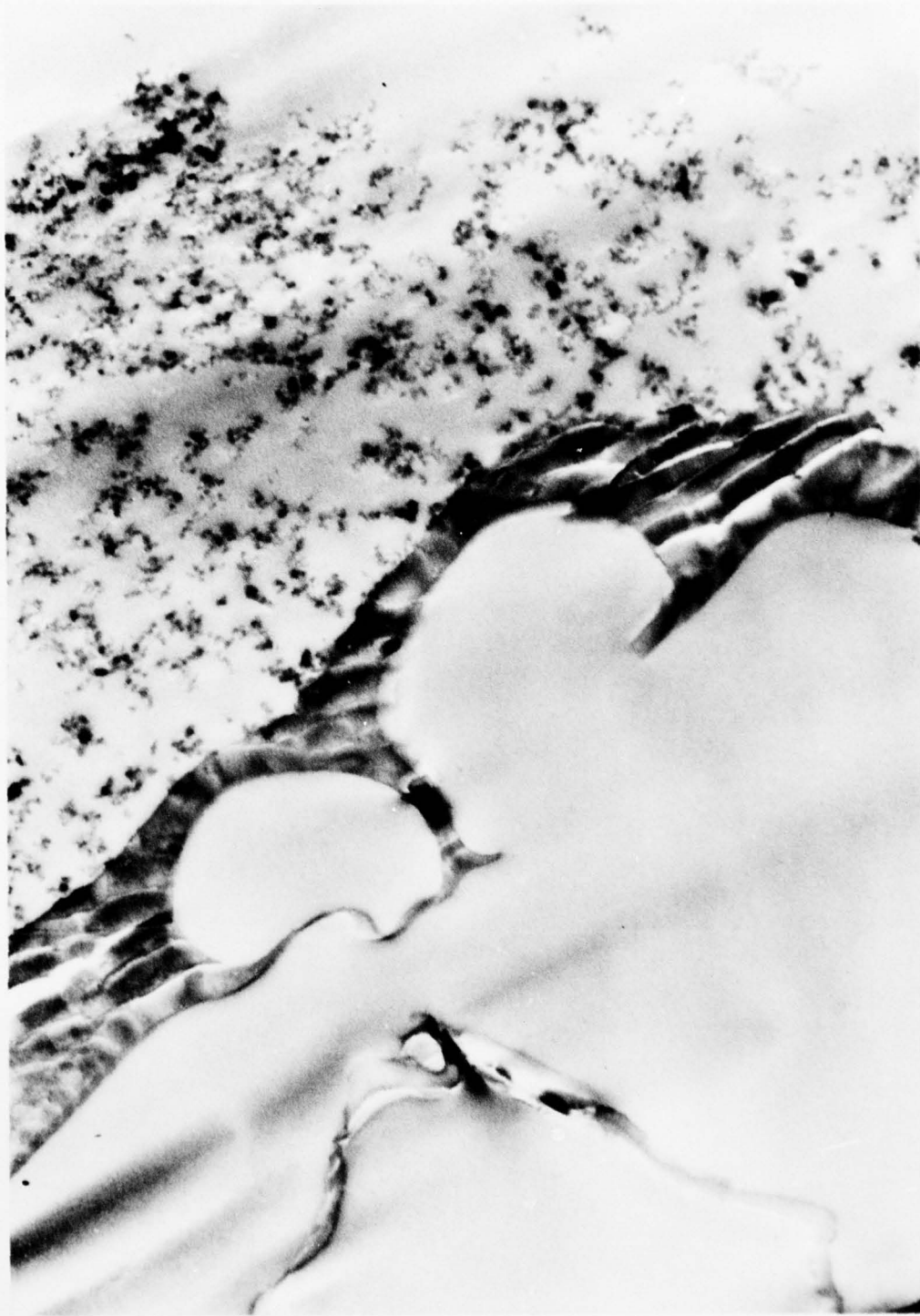


Figure 26. Transmission Electron Micrograph of Ultrasection of Epoxy-Impregnated LOI Char from 10846-133-1141 (12% DMS) Showing Friable Electron-Dense Layers

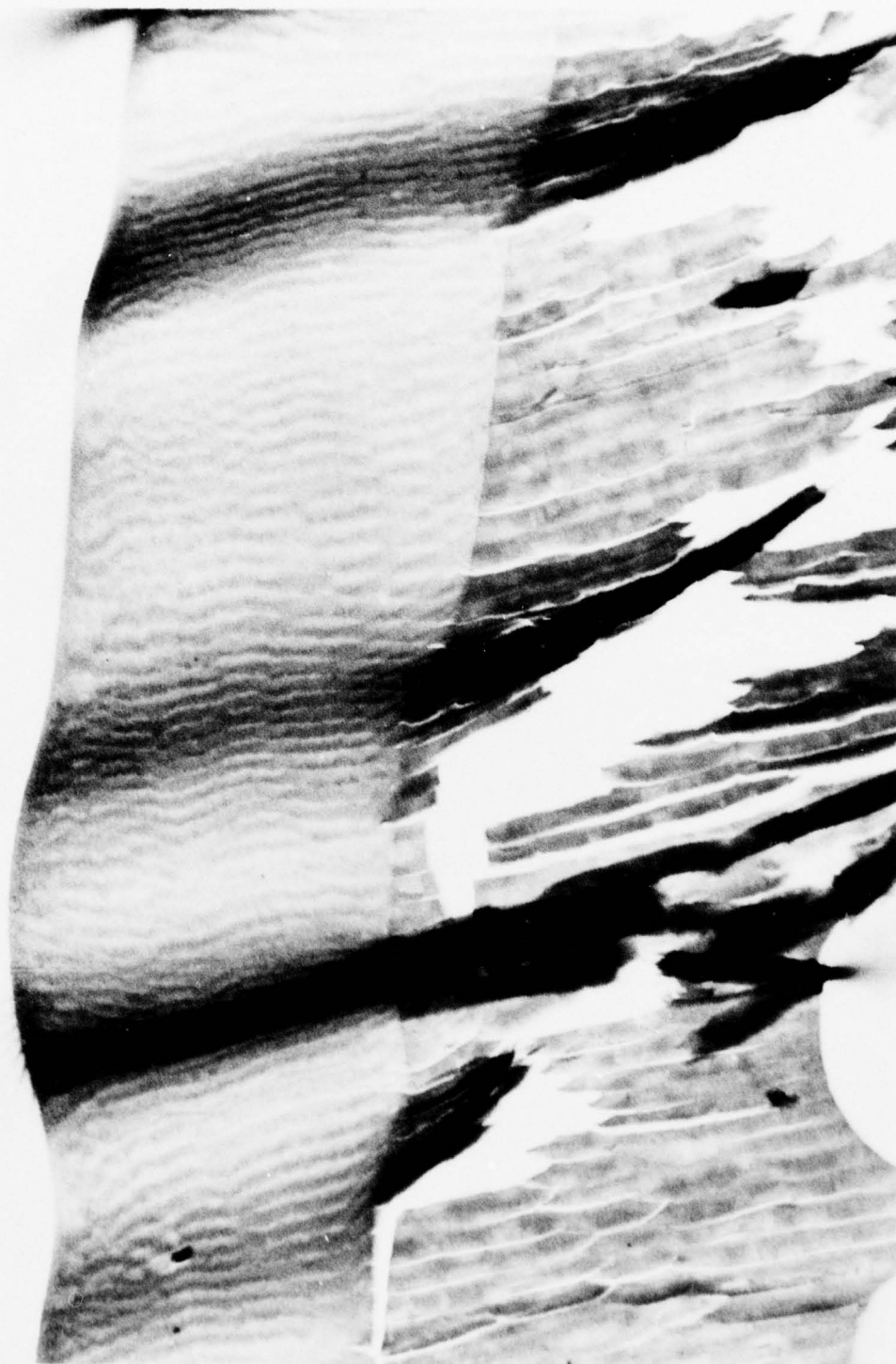


Figure 27. Ultrasecton of Epoxy-Impregnated L01 Char from 2-22-78 (20% DMS) Showing Additional Layer of Intermediate Electron Density and Greater Toughness (rippled regions)



Figure 28. Ultrasession of Pyrolysis Char from 10846-133-25D5 (18% DMS) Showing Char Wall of Same Character as Friable Layers in Figure 26

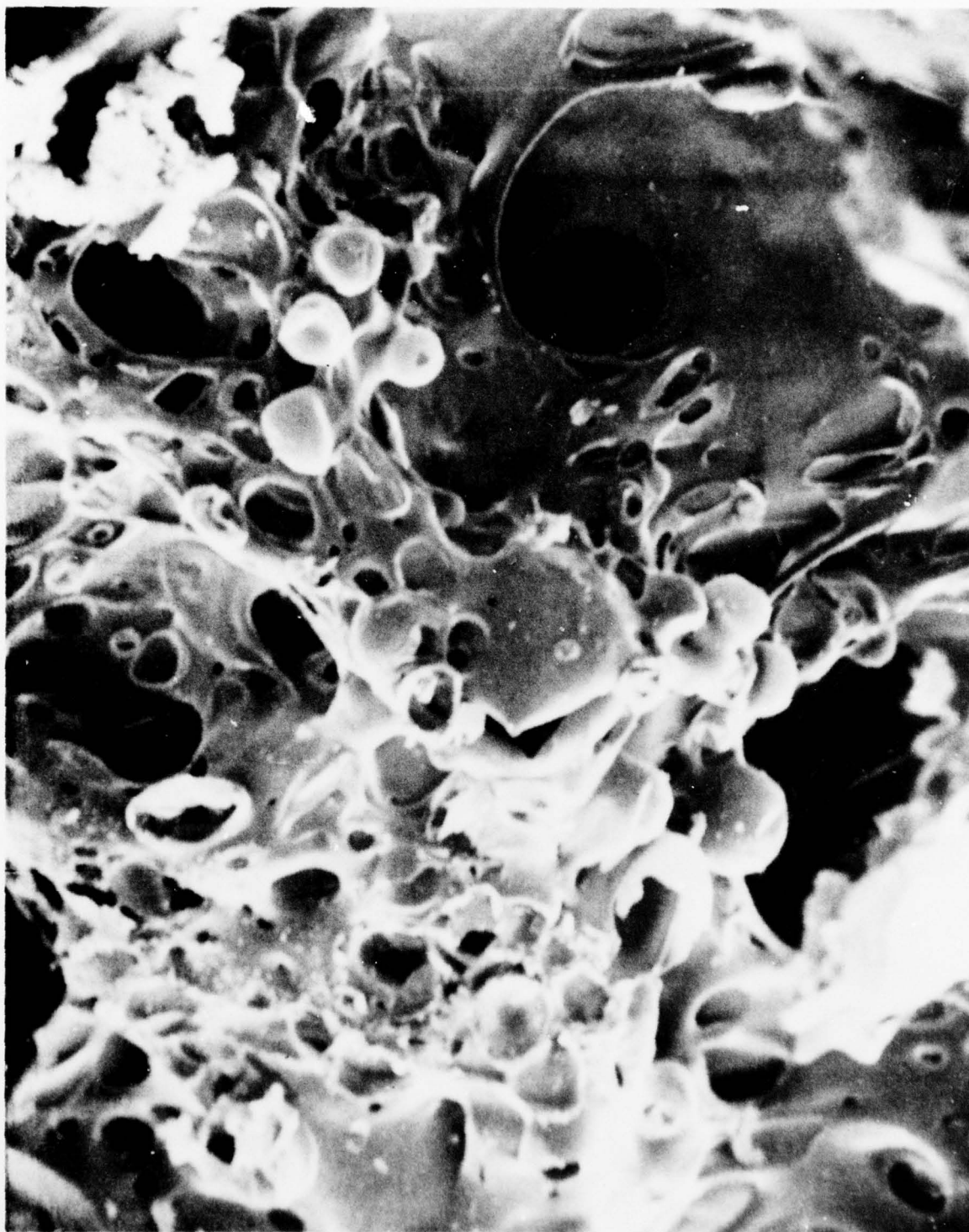


Figure 29. Interior of Modified LOI Test Char from BPA Polycarbonate (scanning electron micrograph)



Figure 30. Interior of L01 Test Char of 108453-133-25D5 (18% DMS)  
(SEM)

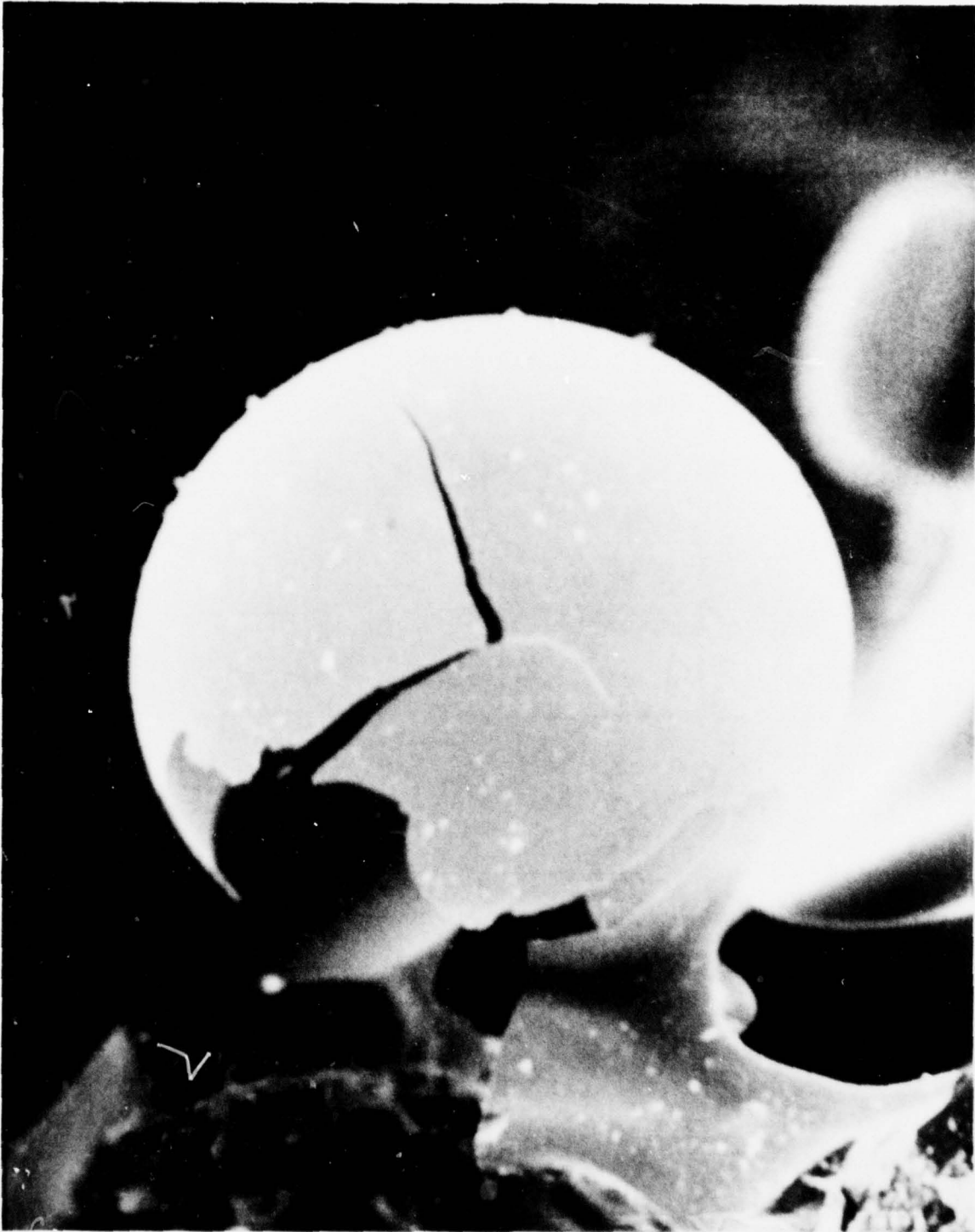


Figure 31. Interior of L01 Test Char of 108453-133-25D5 (18% DMS)  
(SEM)



Figure 32. Interior of LOI Test Char of 108453-133-9 (24% DMS) (SEM)

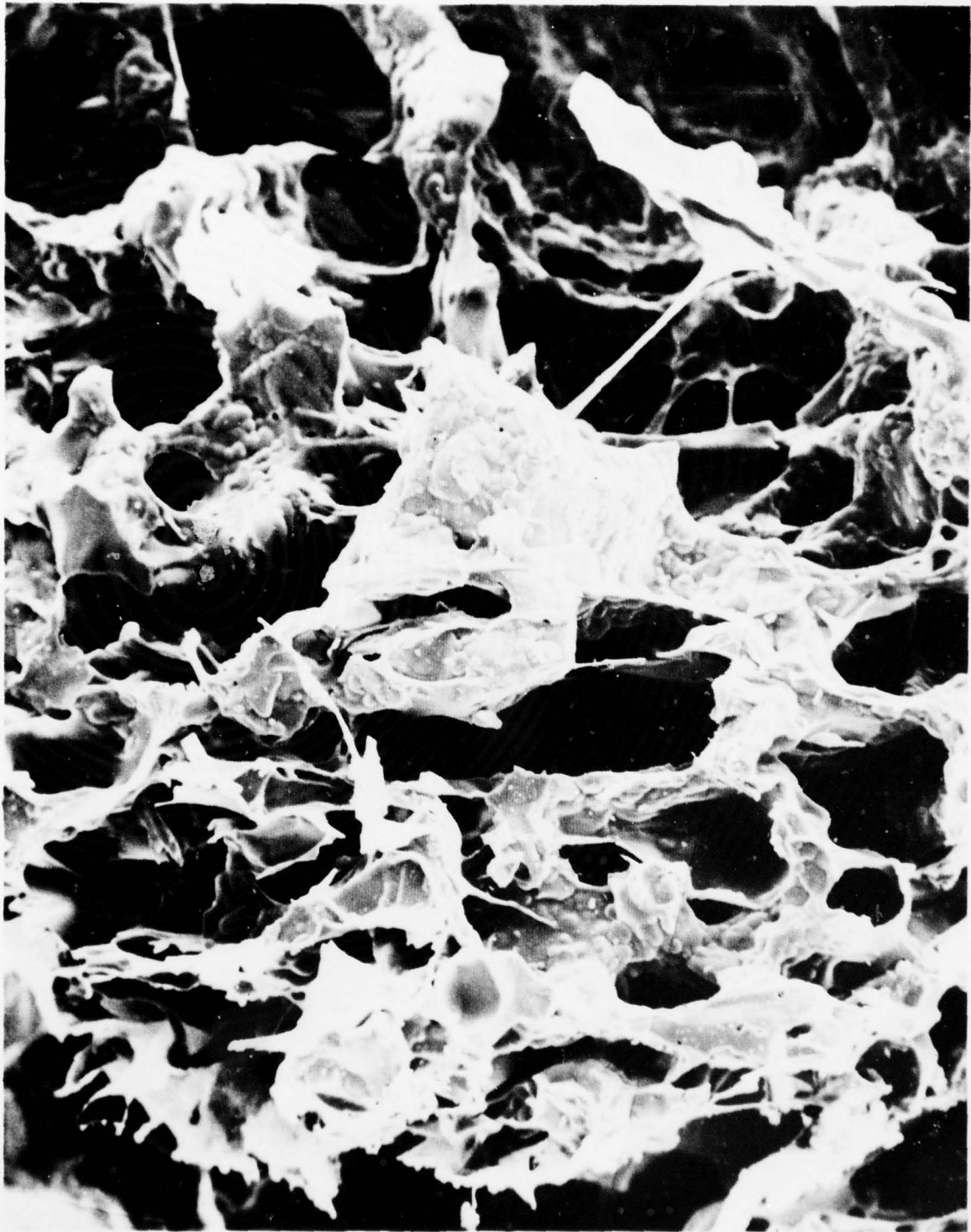


Figure 33. Interior of L01 Test Char of 4-25-78 (36.5% DMS) (SEM)

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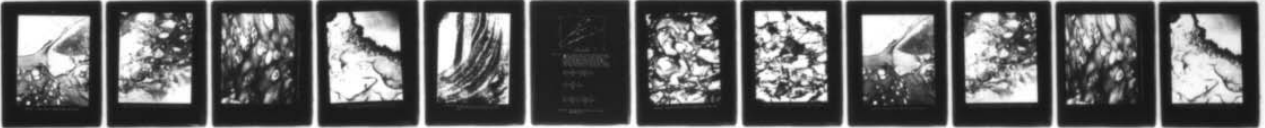
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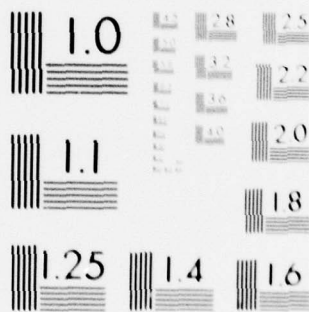
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Figure 34. Pyrolysis Char of 108453-133-25D5 (18% DMS) (SEM)



Figure 35. HF-Treated Pyrolytic Char of 108453-133-11 (25% DMS) (SEM)



Figure 36. Residue from 800°C Oxidation of 108453-133-25D5 (18% DMS) (SEM)



Figure 37. Cross Section of BPA Polycarbonate LOI Char Showing Surface Deposit of Fine Black Particles (soot) (SEM)



Figure 38. Laminar Deposits of Silica Particles in Surface of 108453-133-25D5 Char Burned Out at 01 = 41 (SEM)

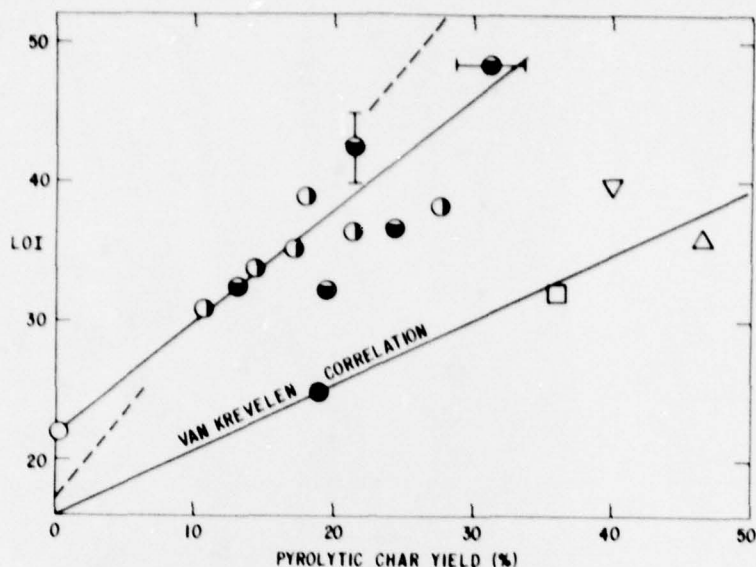


Figure 39. LOI vs. Pyrolytic Char Yield for BPA Polycarbonate (●) Polydimethylsiloxane (○) and Several of Their Block Polymers of Silicone Contents Equal to or Less than 18% (◐) and Greater than 18% (◑). Pyrolytic char yields (this work) for polysulfone (□), BPF polycarbonate (▽) and P<sub>3</sub>O (△). Dotted line: best line for LOI vs. char yield - SiO<sub>2</sub> yield.

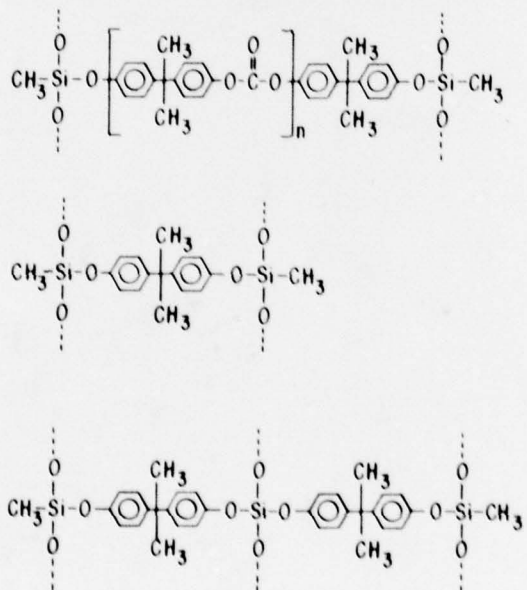


Figure 40. Some Possible Crosslinks in Pyrolyzed BPAC/DMS Resins



Figure 32. Interior of L01 Test Char of 108453-133-9 (24% DMS) (SEM)

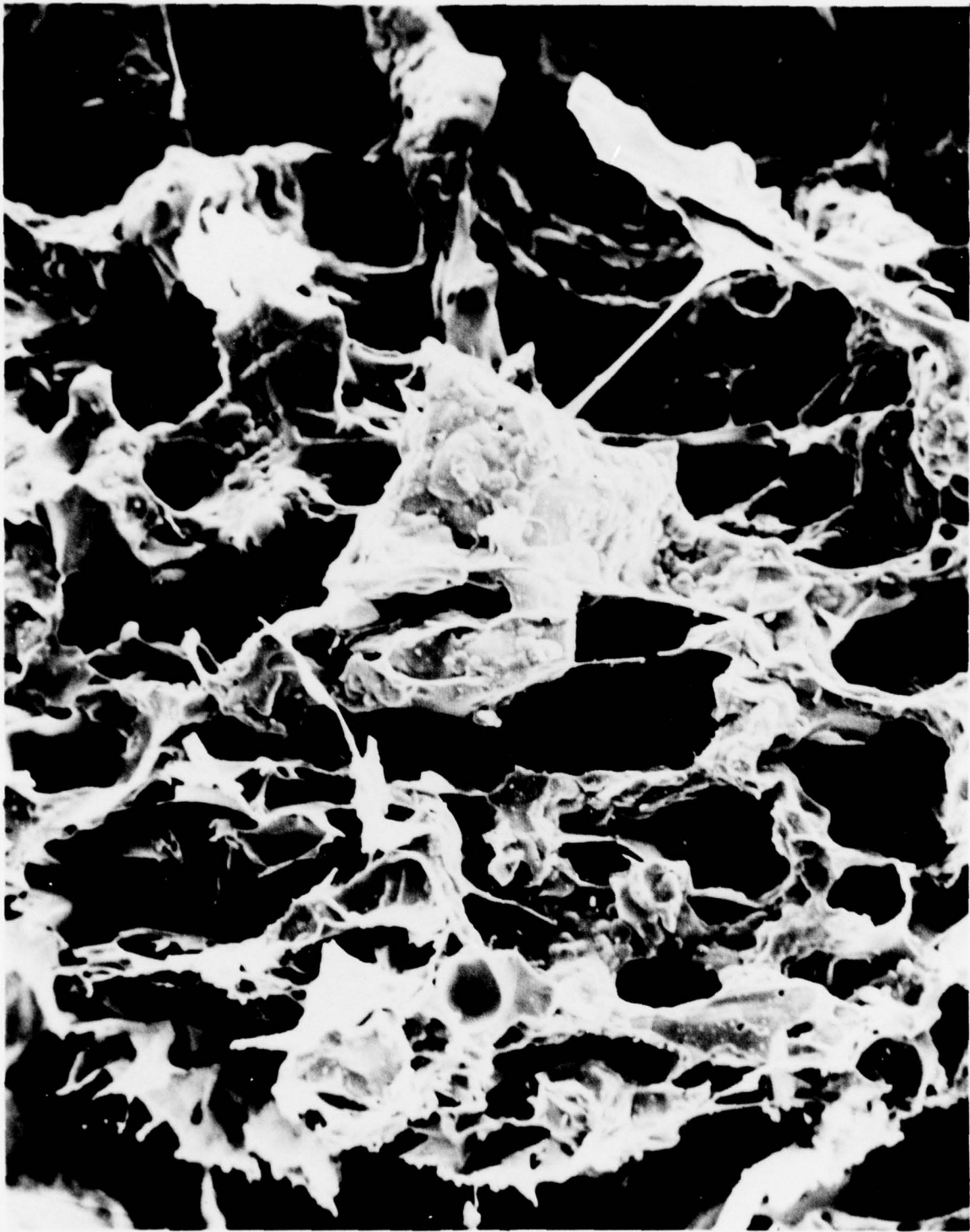


Figure 33. Interior of L01 Test Char of 4-25-78 (36.5% DMS) (SEM)



Figure 34. Pyrolysis Char of 108453-133-25D5 (18% DMS) (SEM)



Figure 35. HF-Treated Pyrolytic Char of 108453-133-11 (25% DMS) (SEM)



Figure 36. Residue from 800°C Oxidation of 108453-133-25D5 (18% DMS) (SEM)

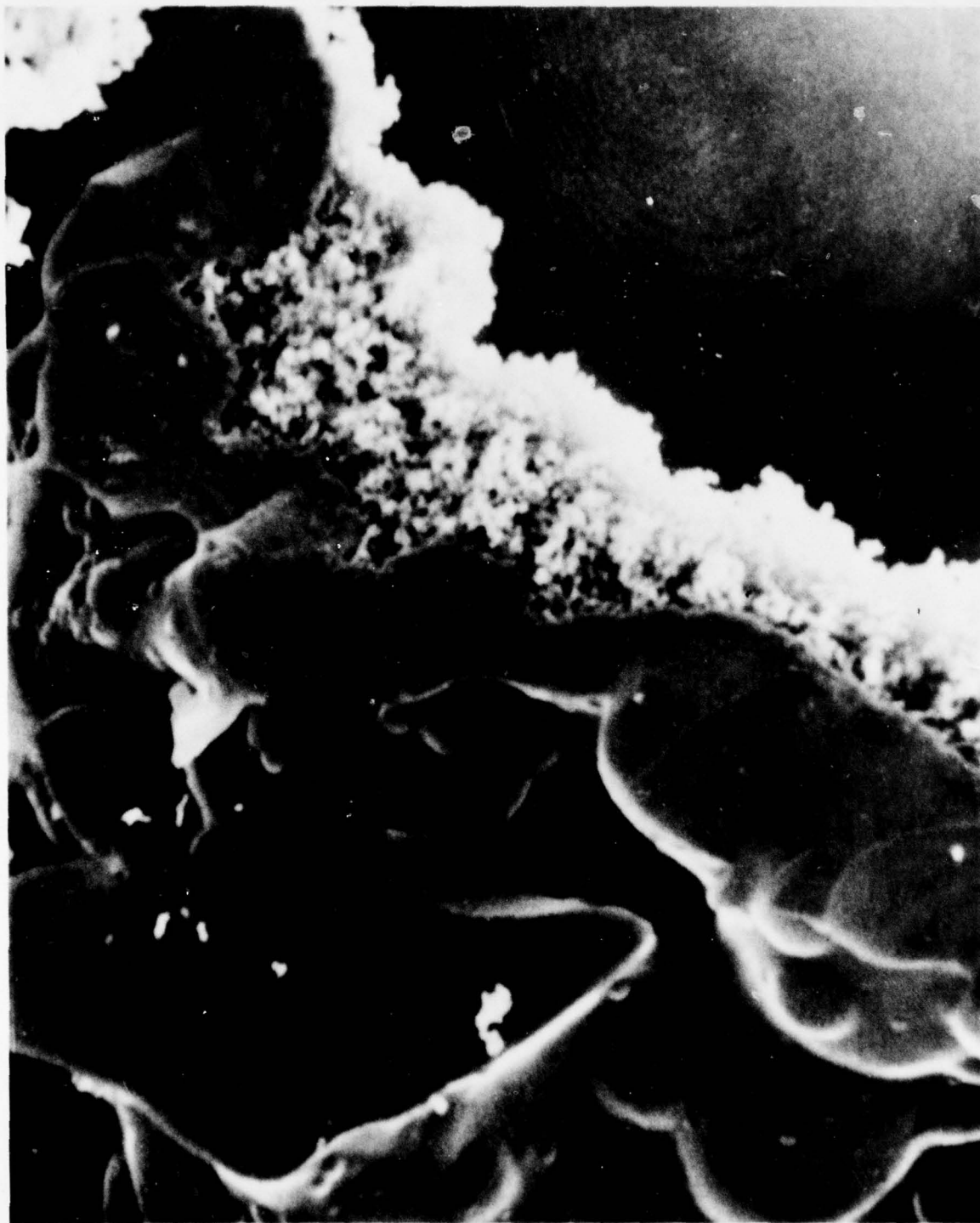


Figure 37. Cross Section of BPA Polycarbonate LOI Char Showing Surface Deposit of Fine Black Particles (soot) (SEM)



Figure 38. *Laminar Deposits of Silica Particles in Surface of 108453-133-25D5 Char Burned Out at 01 = 41 (SEM)*

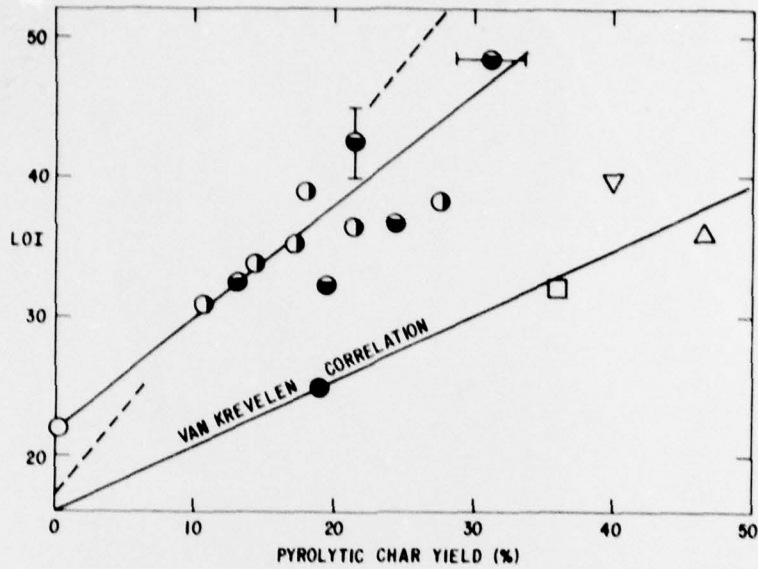


Figure 39. LOI vs. Pyrolytic Char Yield for BPA Polycarbonate (●) Polydimethylsiloxane (○) and Several of Their Block Polymers of Silicone Contents. Equal to or less than 18% (◐) and greater than 18% (◑). Pyrolytic char yields (this work) for polysulfone (□), BPF polycarbonate (▽) and P<sub>3</sub>O (▲). Dotted line: best line for LOI vs. char yield - SiO<sub>2</sub> yield.

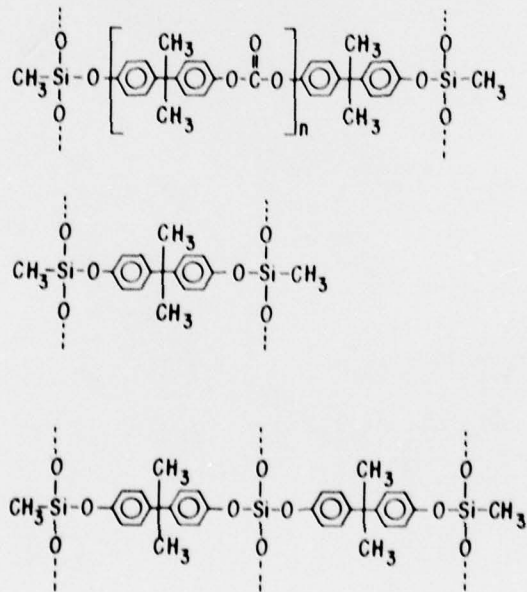


Figure 40. Some Possible Crosslinks in Pyrolyzed BPAC/DMS Resins

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