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SYNTHESIS AND DEVELOPMENT OF LOW COST, HIGH TEMPERATURE N-ARYLENE POLYBENZIMIDAZOLE FOAM MATERIAL

by
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ANNUAL SUMMARY REPORT
Covering Period May 1974 to June 1975

June 1975

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by
WRD
A Division of WHITTAKER CORPORATION
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San Diego, California 92123

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California

FOREWORD

This is the final report on the work performed on Contract NAS2-8299, entitled" Synthesis and Development of Low Cost, High Temperature N-Arylene Polybenzimidazole Foam Material". The Technical Monitor was Mr. S. R. Riccitiello of the Ames Research Center, Moffett Field, California.

This program was conducted in the Polymer Research Department of WRD, a Division of Whittaker Corporation. Dr. Rex B. Gosnell, President of the Division, and Mr. Paul M. Hergenrother, Manager of the Polymer Research Department, shared the responsibility as program manager. Mr. Edward S. Harrison, Senior Chemist, was principal investigator and alternate program manager. At various times, Messrs. R. Rafter and R. Milligan, Chemists, and Messrs. M. McKee and R. Rothstein, Technicians, assisted in conducting the experimental work.

1.0 SUMMARY

Two candidates were selected as the most attractive from an initial listing of five poly-N-arylene benzimidazole (NABI) forming tetramines. Following the preparation of the tetramines, a series of polymers were prepared and partially characterized from the reaction of various aromatic dicarboxylic acid derivatives with the two tetramines, 4,4'-bis (o-aminoanilino)biphenyl and 4,4'-bis(o-aminoanilino)benzene.

Selection of 4,4'-bis(o-aminoanilino)biphenyl (BAB) as the most attractive tetramine was finalized. Polymer (and foam) studies followed two basic routes: 1) formation of high molecular weight uncyclized polyamide followed by subsequent fusion and cyclodehydration to yield NABI (foam) and 2) polymer and foam formation (in situ) by reaction of diphenyl esters (or anhydrides) with the tetramine. The latter route was found much more attractive since considerably versatility in both basic polymer structure and crosslinkability is achievable.

Preliminary studies on BAB, phthalic anhydride (PA), and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) as crosslinked polymer precursors were conducted. Nonmelting rigid char-forming foams with densities as low as 2.7 lb/ft^3 were achieved.

Stoichiometry studies on the BAB/PA/BTDA crosslinked NABI foam system were extended to include molar ratios to 100/50/25. Preliminary experiments yielded foams which were of relatively low densities (~3 lb/ft^3) but were apparently less thermally stable with increasing concentrations of the crosslinking BTDA reagent. Processing requirements for quality foam from this system were initiated. These studies included solvent content and type, various amounts of prepolymer, different prepolymer stoichiometries, and temperature profiles.

Preliminary experiments with the BAB/PA system using pyromellitic dianhydride (PMDA) as the crosslinking agent resulted in foamed polymer which failed to exhibit good toughness. The ranges evaluated included BAB/PA/PMDA molar ratios of 100/80/10 to 100/60/20 in 5% (PA) increments.

Alternate monomer systems studied included half acid-half ester analogs of PA and BTDA. Final parameter studies were carried out in a simple foaming fixture of novel design.

Four surfactants were evaluated in an attempt to control cell size and uniformity with negative results.

Foam billet diameters were increased in a stepwise manner from test tube scale through 7.5 cm. to a final 15 cm. diameter. Thicknesses varied from ~3 to ~6 cm.

The program was successfull in the preparation of a potentially low cost, low density, high char yield ($Y_C^{800°C} = >63\%$) high temperature foam material.

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2.0 OBJECTIVE

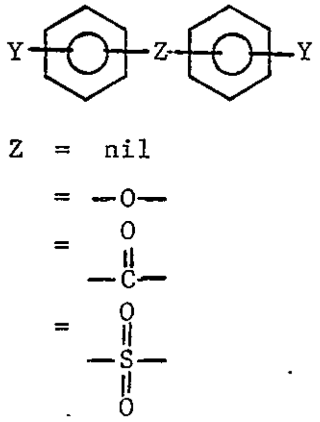
The objective of this program is to develop a low cost N-arylenebenzimidazole polymer into a low density flame resistant foam.

3.0 INTRODUCTION

Improved materials are drastically needed for high temperature insulation and fire survival systems in the space shuttle and commercial aircraft. An aromatic heterocyclic polymer, the polybenzimidazole (PBI), has exhibited a favorable combination of unique properties which enables a low density blown foam variation of PBI to perform well in these applications. Further improvements such as increased thermo-oxidative stability, better processability, and cost reductions are highly desirable. The work reported herein is directed towards these goals and involves a study on a similar polymer system, the poly-N-arylenebenzimidazoles.

High temperature polymer research has classically evaluated various "bridging linkages" interposed between arylene groups as means of obtaining better processability, cost reductions, and polymerization reaction rate variations, with minimal sacrifice to thermo-oxidative resistance and thermo-mechanical performance.

The requisite tetramines for preparation of the N-arylene polybenzimidazoles are not unique in their adaptability to such modification by appropriate synthetic methods. Four such modifications are readily apparent and have been routinely evaluated in most high temperature (particularly aromatic heterocyclic) polymer studies.



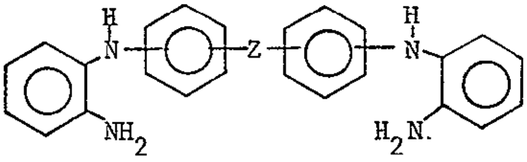
Z = nil

$= -O-$

$= -\overset{\overset{\displaystyle O}{\|}}{C}-$

$= -\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$

The "Y" species will of course vary with the particular polymer forming reaction under study. In N-arylenebenzimidazole (NABI) polymer, this grouping is, of course, the *o*-aminoanilino moiety, i.e.:



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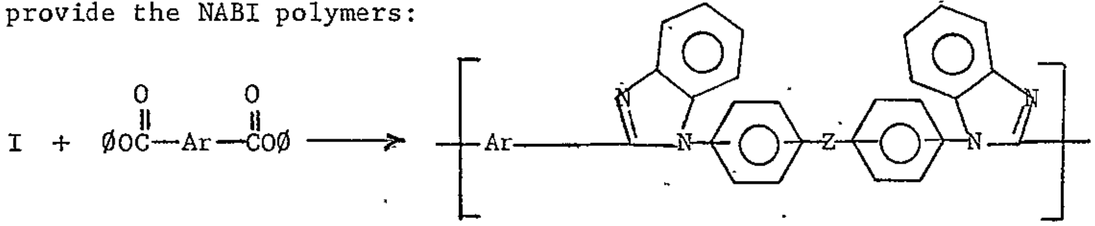
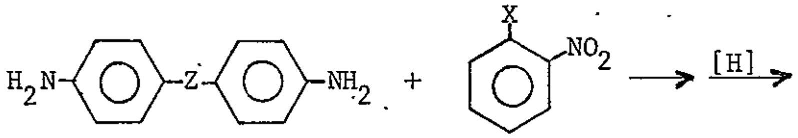
so that subsequent reaction with appropriate diphenyl esters (or anhydrides) will provide the NABI polymers:



3.1 TETRAMINE SYNTHESIS CONSIDERATIONS

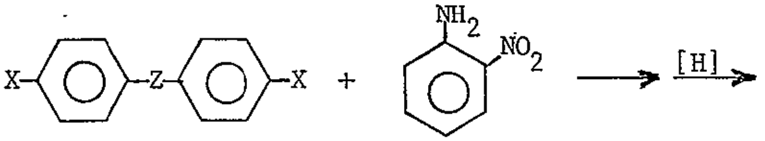
Two complementary synthetic modes are available for NABI tetramines; both are based on high temperature (copper catalyzed) nucleophilic substitution reactions.

Route A



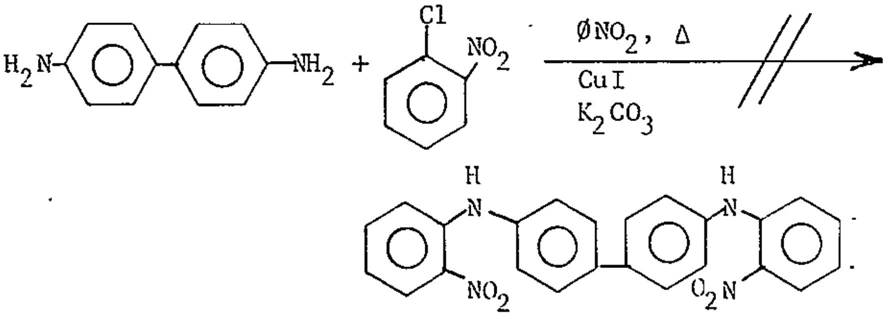
I (above)

Route B

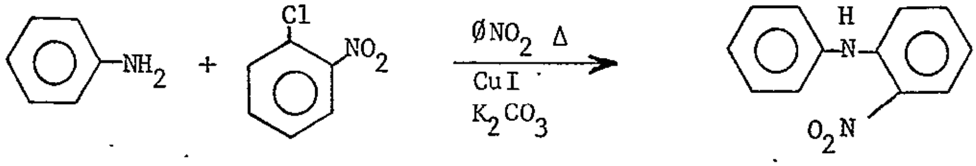


I (above)
X = halogen

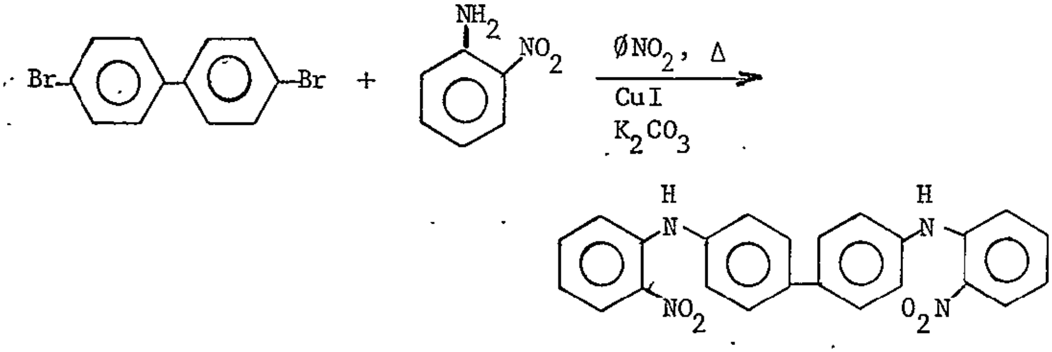
In Route A, the nucleophilicity of the parent diamine is of utmost importance. Basicity, as it relates to nucleophilicity has been shown to be strongly dependent on the bridging group (Z).(1-6) Electron withdrawing moieties (e.g., $-\overset{\overset{O}{\|}}{C}-$ and $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$) are expected to reduce the relative nucleophilicity to an unacceptably low level. Conversely, groups which are electron donators (e.g., -O-) would be expected to impart enhanced nucleophilicity. This rationale has been further substantiated in our work in the preparation of the tetramine where Z = nil. The reaction between benzidine and o-chloronitrobenzene fails



in contrast to the high yield synthesis of 2-nitrodiphenylamine:



Perhaps surprisingly, the reverse route B proceeds in high yield.



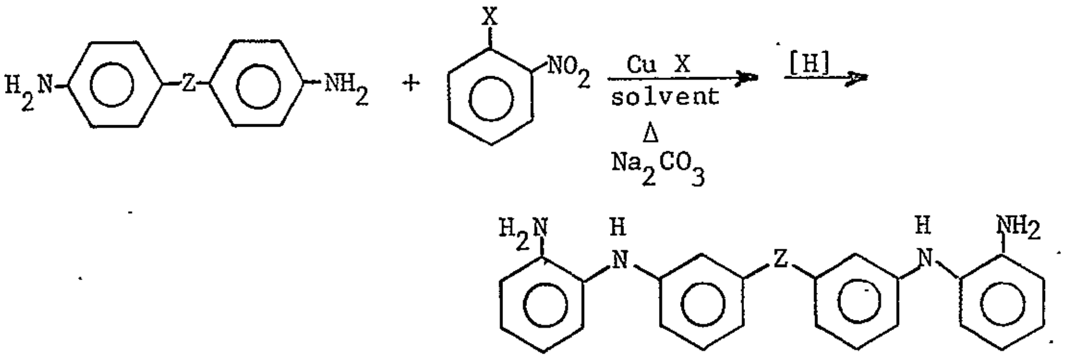
Here the contribution of electron withdrawing Z groups would be beneficial in that nucleophilic substitution will be enhanced.(7-9)

3.2 LITERATURE SEARCH AND COST CONSIDERATIONS

The initial efforts were primarily directed toward uncovering pertinent references to the proposed compounds and, similarly, to analogous polymer systems. A recent U.S. patent(10) describes the preparation of NABI tetramines by reaction of the corresponding diamines with fluoronitrobenzene.

Four potentially useful tetramines were cited previously. Inquiries were sent to several suppliers and custom synthesis firms regarding availability of pertinent intermediates. Replies from only a few manufacturers and custom synthesis houses were received with discouraging estimates. These estimates generally indicated only partial or negative response to the request for quotes on a 10,000 lb/year basis. The general consensus was that until preliminary reactions were run, costing would necessarily be ill-defined. The following compounds were requested:

I. PRECURSOR AROMATIC DIAMINES



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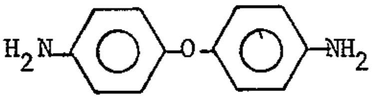
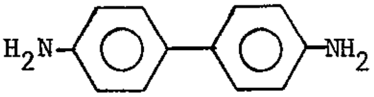
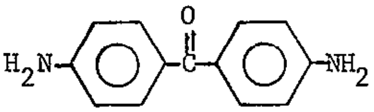
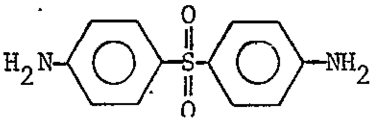
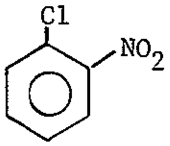
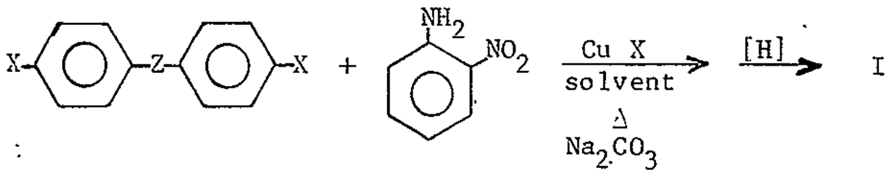
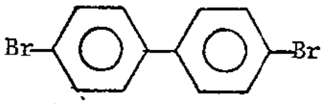
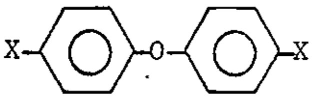
Amine	Low Bid Cost on 10K lb/year Basis $/lb (Supplier)
	$4.50 (duPont)
	- (OSHA restricted-carcinogen)
	$15.00 (Ash-Stevens)
	$5.50 (Roberts Chem)
Co-reactant	
	$0.39 (Chem. Mkt. Rpt., 15 July 1974)

II. PRECURSOR AROMATIC DIHALO COMPOUNDS

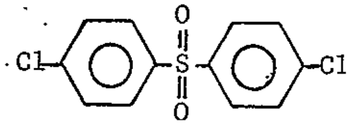




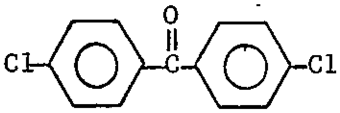
- (Whittaker Corp.)



- No bid



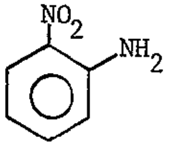
$18 (K & K)



$500 (K & K)

$0.75/lb (Chem. Mkt. Rpt. 15 July 1974).

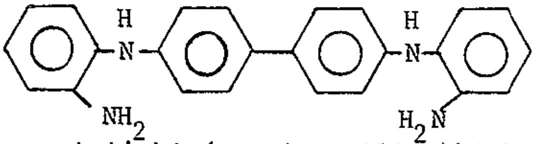
Co-reactant



$0.40 (Chem. Mkt. Rpt. 15 July 1974)

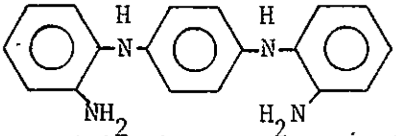
A brief description of the salient factors which contribute to the reactivity of the various species and results to be anticipated by substitution of the -Z- group in both types of reactions above has already been given.

Based on these considerations, without prior information on yield and assuming equivalent processing costs and yield for the various routes, it is apparent that the most economical systems will derive from the WRD developed NABI tetraamines, i.e.,



4,4'-bis(o-aminoanilino)biphenyl
BAB

and

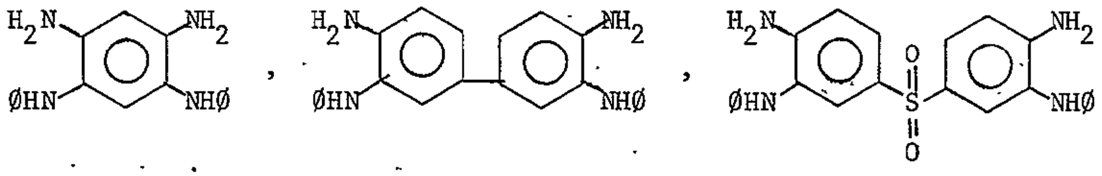


1,4-bis(o-aminoanilino)benzene
BABE

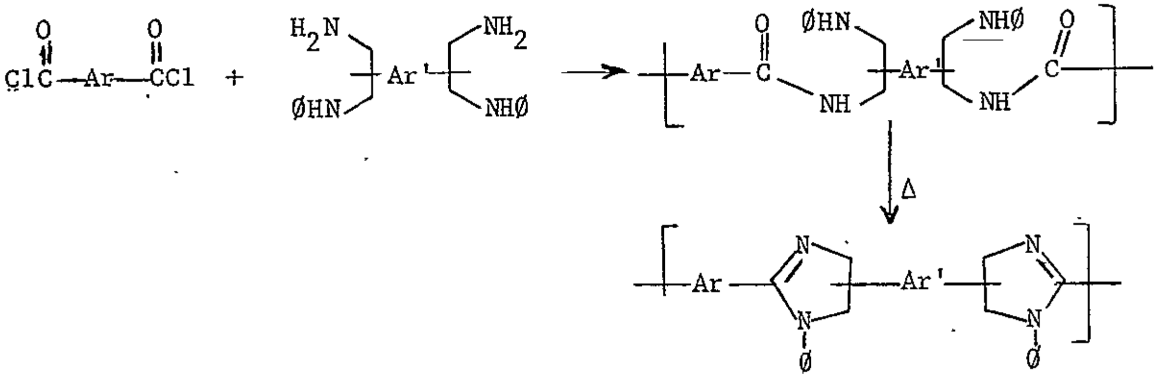
These systems not only are the most attractive from an already nearly optimized synthesis standpoint, but should also provide improved thermomechanical performance. The suppression of T_g by such groups $-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-$, -O-, $-\overset{O}{\overset{\|}{C}}-$, interposed between phenylene groups is well documented.(11-13)

3.3 DIBASIC ACID CONSIDERATIONS

Recent Russian work(11) on N-phenyl substituted benzimidazole polymers (Table I) indicate the differences in polymer softening



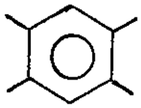
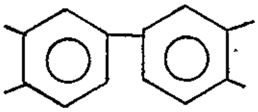
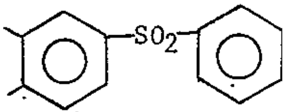
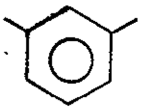
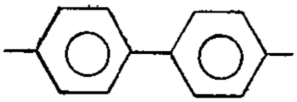
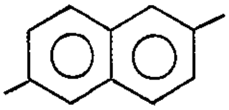
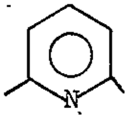
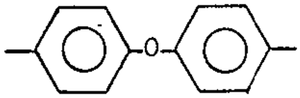
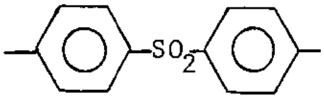
temperature (S.T.) and decomposition temperature (D.T.) when three tetramines were polymerized with diacid chlorides of various aromatic dicarboxylic acids according to the following general equation:



The first row of Table I presents the data obtained for the polymers from terephthaloyl chloride and the three tetramines; subsequent rows describe the net changes from the p-phenylene polymer values.

TABLE I

THERMAL PROPERTIES OF POLY-N-PHENYLBENZIMIDAZOLE(11)

	Tetramine Moiety (-Ar^1-)					
						
Acid Moiety (-Ar-)	S.T. (°C)	D.T. (°C)	S.T. (°C)	D.T. (°C)	S.T. (°C)	D.T. (°C)
	380	450	360	490	345	470
	-10	+40	-50	-20	-45	+30
	-35	-20	+25	-10	+10	-15
	+10	-30	+5	-40	+15	-20
	-50	-30	-70	-40	-65	+10
	-60	+40	-15	-20	-75	-30
	+10	-20	-35	-25	-70	-20

No systematic increase in polymer softening or decomposition temperatures is descernible over the p-phenylene polymer systems by changing the acid component (except perhaps the 2,6-naphthalene moiety). A general trend toward lower values is noted when bridged flexibilizing ether and sulfone groups are introduced. This same trend is probably operative in NABI systems but is not to be assumed, a priori. Other considerations such as thermooxidative stability and relative polymer thermomechanical characteristics were considered before the choice of NABI polymer system was finalized.

4.0 TETRAMINE SYNTHESIS

The biphenylene and p-phenylene based NABI forming tetramines were prepared as shown in Route B using procedures previously established at WRD. The biphenylene tetramine was prepared on a 0.5 mole scale in overall yield of 72%. Details of the procedures are found in the Experimental Section.

The melting behavior of 4,4'-bis(oaminoanilino)biphenyl is unusual. Differential Scanning Calorimetry (DSC) scans of this material are shown in Figures 1 and 2. In the first DSC run in each figure (top line), two endotherms are apparent. Visually this is seen as a sintering or softening often referred to as premelting of the material with crystal re-orientation at the lower endothermic temperature. The second represents a true melt where the material sharply liquifies.

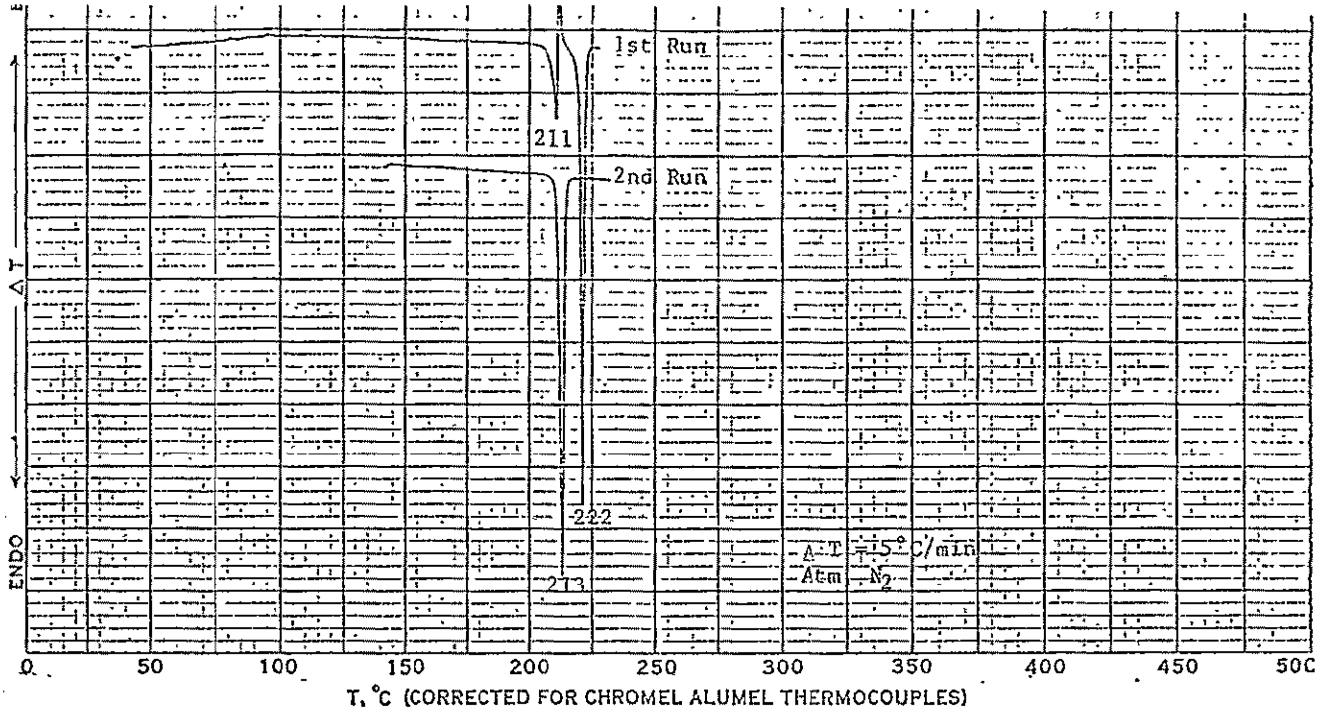
In Figure 1, the molten amine was allowed to cool at a rate of ~5°C/min and the DSC was rerun. During this run, only one endotherm (213°C) was observed approximately correspondent to the lower-temperature endotherm of the initial run (211°C). A fresh sample of NABI amine was used to obtain the first DSC run in Figure 2, and again two endotherms (211° and 222°C) were observed. This time, however, after melting, the DSC sample was removed from the sample chamber and quenched rapidly. The quenched sample was again run in the DSC (run 2, Figure 2) and the endotherm occurred at 222°C corresponding with the higher-endotherm of the first run. A slight endotherm was observed at the lower temperature, possibly due to incomplete crystal reorientation during cooling. A more rapid quenching of the molten sample may have eliminated this endotherm.

The presence of two crystalline forms (allotropy) is a most plausible explanation. As a result, visual melting point determination cannot be used to estimate the purity of this amine whereas DSC can be used.

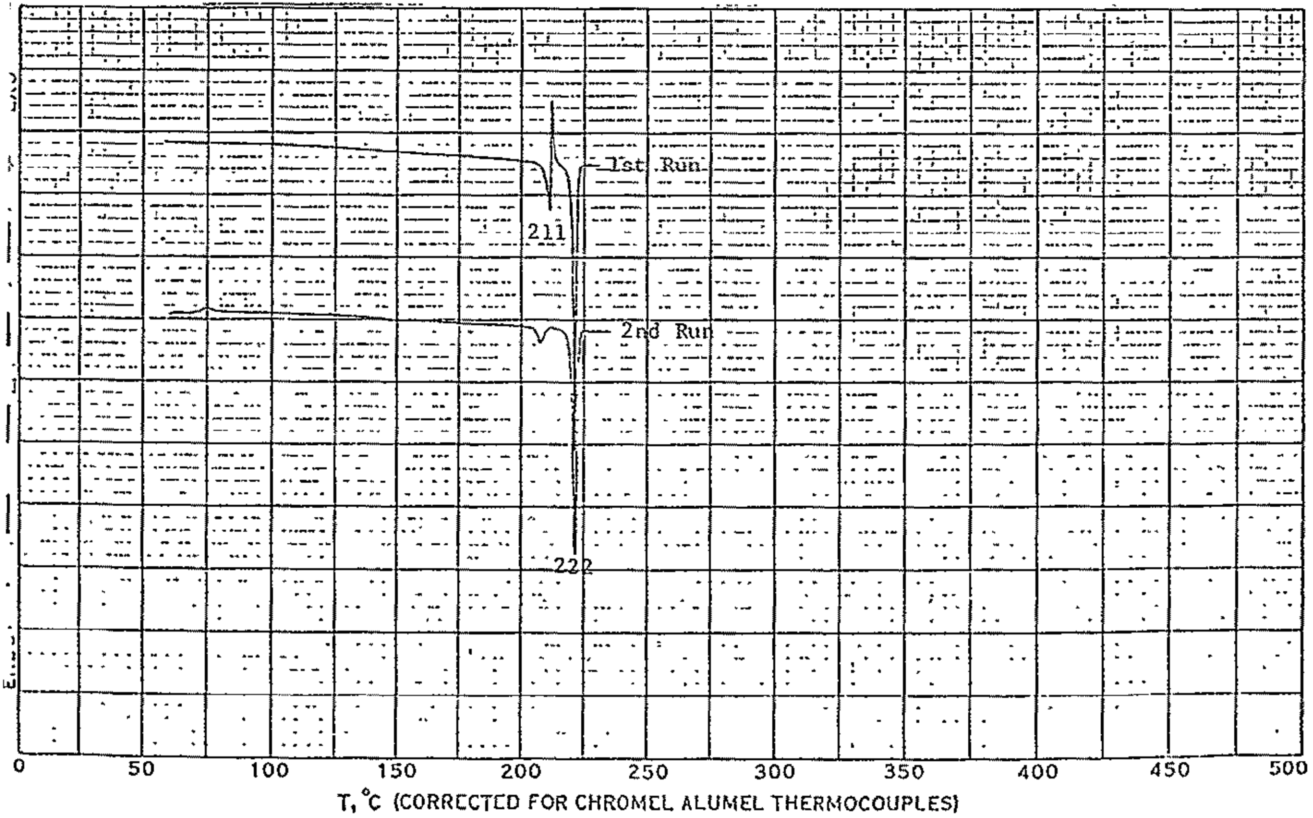
Purification of the tetramine has previously been done utilizing a mixed solvent system: DMF-methanol-benzene. This generally resulted in a poor recovery (30-40%) of off-white crystals which, judging by the results heretofore, could be considered polymer grade.

Other solvent systems were investigated in an attempt to obtain a higher recovery of the amine at higher purity. An alternate solvent system, benzene-tetrahydrofuran (THF), can be utilized providing the tetramine is initially fairly pure. Thus, crude amine yielded 70% recovery of white platelets upon recrystallization from THF/benzene (1/8), including treatment with charcoal. However, two recrystallizations are required for the crude amine.

An even better recrystallization solvent was found to be 1,2-dichloroethane. In a typical procedure, the crude amine was dissolved in boiling solvent (6% solution), treated with charcoal, filtered and allowed to cool to yield 75% of white platelets. Concentration of the mother liquor (by distillation) gave an additional 12% of material of approximately the same purity along with the recovery of 80% of the solvent. Tetramine purity was determined by DSC.



Melting Characteristics of 4,4'-Bis(o-Aminoanilino)Biphenyl FIGURE 1



Melting Characteristics of 4,4'-Bis(o-Aminoanilino) Biphenyl FIGURE 2

5.0 PRELIMINARY POLYMERIZATION STUDIES

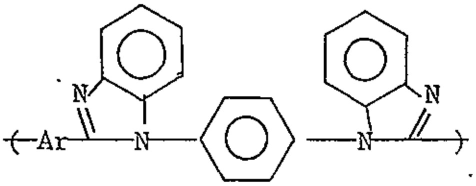
Preliminary polymer preparations were carried out with the following objectives.

1. More closely document polymerization (both amide formation and ring closure) rates with various acid derivatives.
2. Demonstrate that relatively high molecular weight polymer could be obtained (e.g., tough material).
3. Briefly investigate foaming characteristics of the (pre)polymers.
4. Attempt to establish the best initial approach for foam formation.
5. Evaluate changes in glass transition temperature and cursory examination of polymer properties.

5.1 POLYMERIZATION WITH 1,4-BIS(o-AMINOANILINO) BENZENE (BABE)

With these objectives in mind, the p-phenylene-based tetramine was utilized in the separate experiments as outlined below (experimental details are found in the appropriate section).

The acid derivatives were chosen to yield an increasing distance between the benzimidazolene groups of the linear polymer, i.e. the-Ar- "end-to-end distance" to be progressively increased.

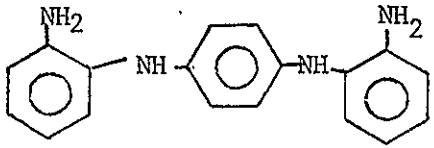


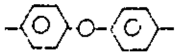
The selected sequence included those-Ar-moieties (shown in Table III) derived from the corresponding diphenyl esters (or anhydride in the case of o-phthalate).

Polymer characterization is presented in Table III. Those polymers which failed to show an apparent Tg transition at <450°C may be described as "brick-dusts". In most cases, the prepolymer formed by heating for 1 hour at 250°C failed to exhibit melting or softening to initial temperatures as high as 450°C. Those polymers whose apparent Tg values are indicated to be ≥450°C failed to show any transitions by DSC at temperatures to 450°C. Some advancement with further heating of the ground prepolymer at temperatures of 400°C and above does occur as indicated by the nominal increases in η_{inh}.

TABLE II

PRELIMINARY POLYMERIZATIONS OF 1,4-BIS(O-AMINOANILINO)BENZENE WITH VARIOUS AROMATIC ACID DERIVATIVES



—Ar—	Acid Component	η_{inh}* (H_2SO_4) after Time (hr)/at Temp (°C)		Apparent Tg	Remarks
	Phthalic anhydride	0.35	(1)/(400)	> 450°C	Brittle solid
		0.32	(4)/(400)	> 450°C	
	Diphenyl isophthalate	0.25	(2.5)/(450)	285°C	
	Diphenyl terephthalate	0.17	(2.5)/(450)	> 450°C	
	Diphenyl-4,4'-bisbenzoate	0.22	(1)/(400)	> 450°C	
		0.24	(2)/(400)	> 450°C	
		0.29	(3)/(400)	> 450°C	
	Diphenyl-4,4'-oxybisbenzoate	0.29	(1)/(400)	--	
		0.47	(2)/(400)	277°C	
		0.93	(3)/(400)	278°C	

---

* 0.5% solution at 25°C

Subsequent DSC scans to higher temperatures led to the discovery of an intense endotherm at extremely high temperatures (~560°C). When the thus "melted" prepolymers were cooled and re-scanned, apparent Tgs more in line with anticipated values were obtained. Table III lists two polymers which exhibited this anomalous behavior along with their apparent "melting points" and Tgs. Figure 3 shows the DSC curves of one of these which is typical of this unexpected behavior.

TABLE III

ENDOTHERMIC TRANSITIONS AND SUBSEQUENT BASELINE DEFLECTIONS OF SOME NABI POLYMERS

Initial Polymer	Apparent mp, °C*	Apparent Tg, °C*
BABE/Diphenyl-4,4'-bisbenzoate	560	340
BABE/Diphenyl terephthalate	555	321

*DSC, ΔT = 20°C/min (Tg obtained from 2nd run)

It should be noted that the temperatures at which these endothermic transitions (melting points) occur are beyond the decomposition points of most organic materials and thus may be in actuality thermal rearrangements(1) to a polymer of yet undefined structure. It should also be noted that at this temperature (560°C) the NABI polymer resulting from the condensation of BAB and phthalic anhydride had lost 11% of its weight by TGA.

In all of the above cases the resulting material is colored but brittle. Attempts to take a NABI polymer which *does* have a discernable Tg (BABE + diphenyl isophthalate) to this temperature led to decomposition of the polymer — no endotherm was observed.

These requisite cure temperatures coupled with the brittle nature of the BABE (phenylene based) derived systems provided impetus to discard the BABE tetramine and shift emphasis to the versatile BAB (biphenyl based) tetramine.

---

(1) A literature survey of thermal decomposition of organic compounds has disclosed that 1-phenylimidazole thermally rearranges to 2-phenyl imidazole at 510°-540°C prior to decomposing at 600°C. Benzimidazole itself begins to decompose between 400° and 430°C. I. B. Johns, E. A. McElhill and J. O. Smith, *J. Chem. and Eng. Data* *7*[2] 277 (1962).

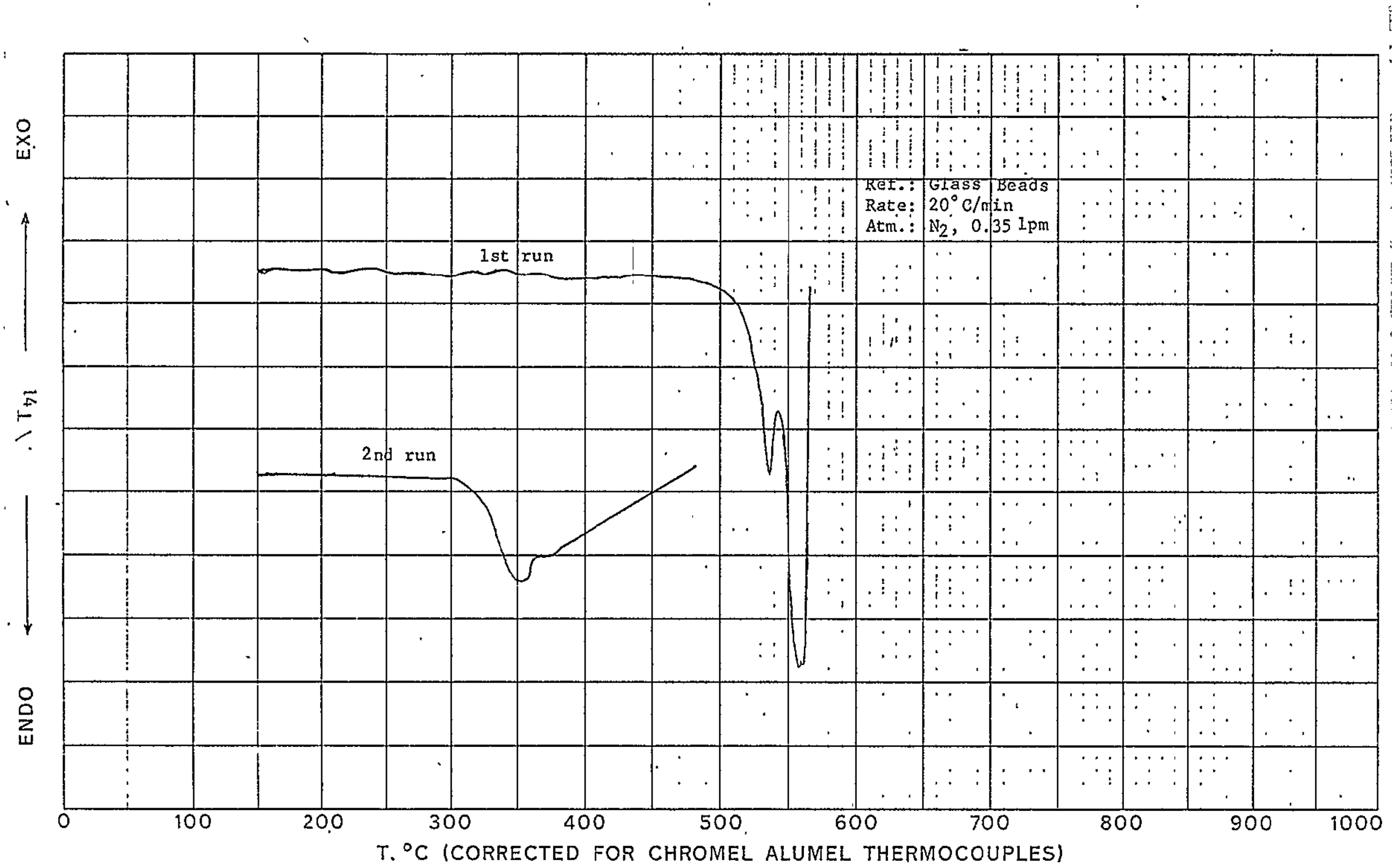
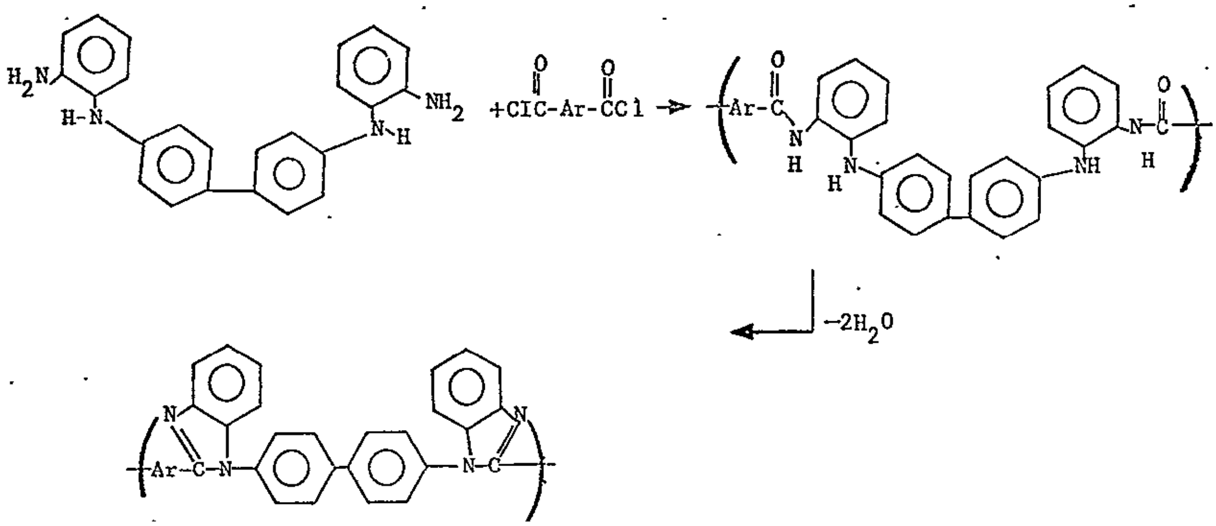


Figure 3 DSC Scan of BABE/Diphenyl-4,4'-bisbenzoate Polymer

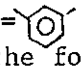
5.2 POLYMERIZATIONS WITH 4,4'-BIS(o-AMINOANILINO) BIPHENYL (BAB)

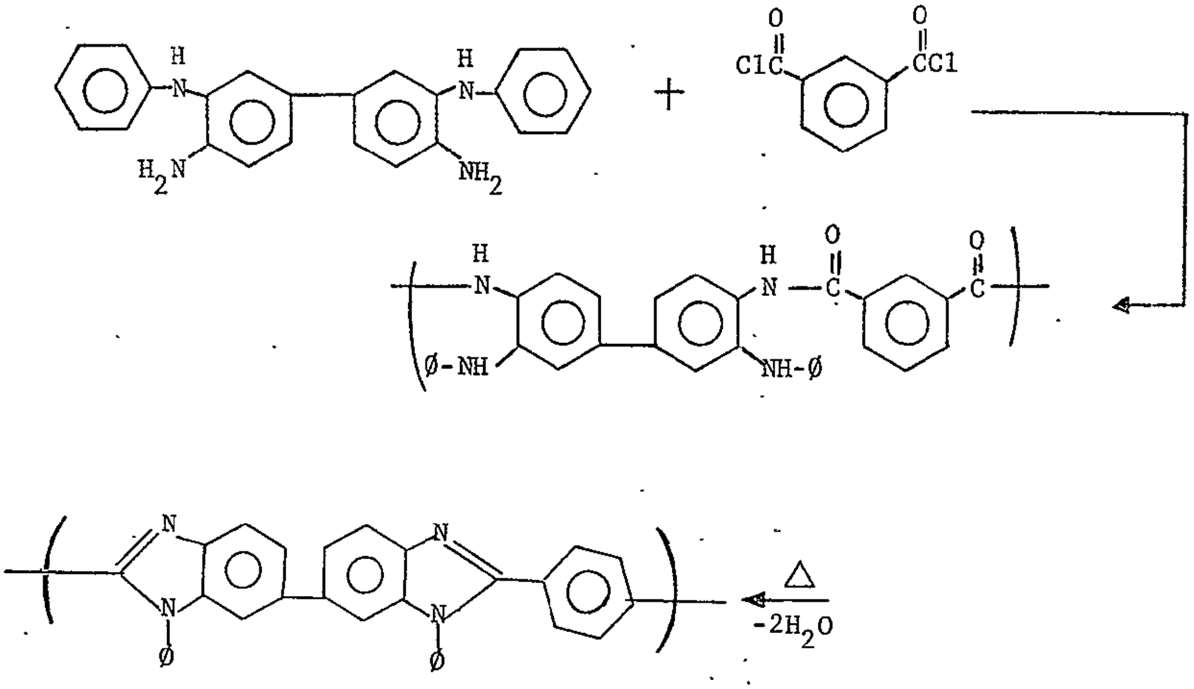
5.2.1 Solution Polymers from Aromatic Acyl Chlorides

Initial investigations were concerned with polymer preparation by solution methods. The purpose of the study was to determine the feasibility of initial high polymer formation as the polyamide precursor (I) and subsequently, by thermal cyclo-dehydration, form the N-arylene polybenzimidazole II. Formation of a foamed item was anticipated, with the by-product water to act as the blowing agent.



5.2.1.1 Isophthaloyl chloride as co-reactant

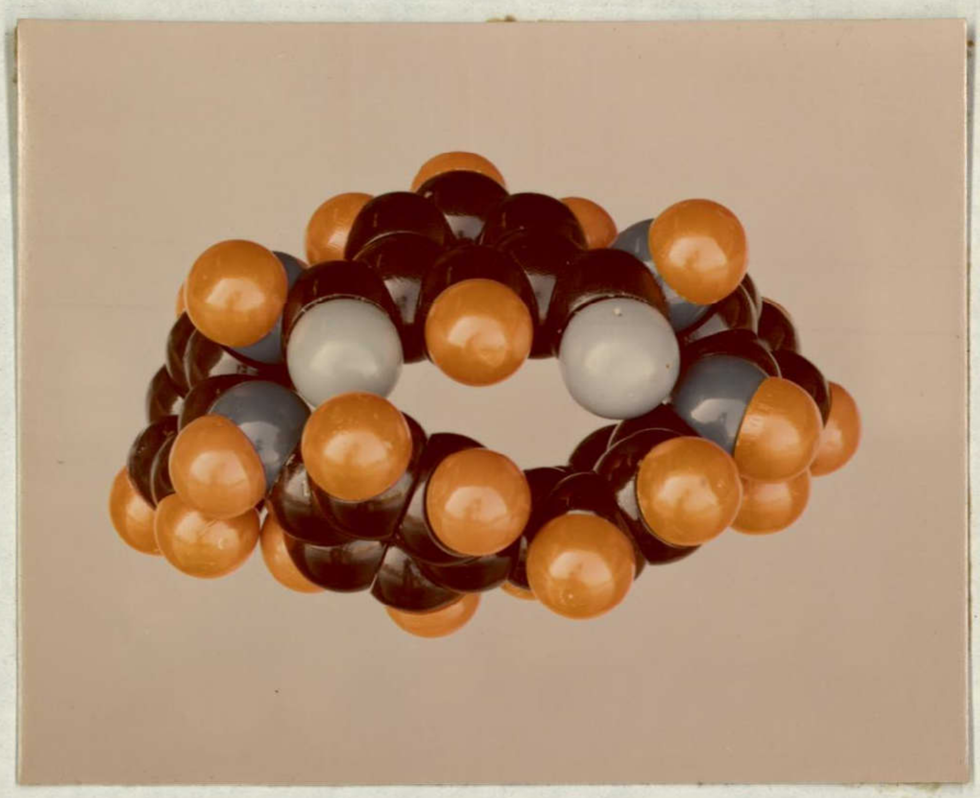
Our initial reaction using iso-phthaloyl chloride (—Ar = ) resulted in an unexpected observation. Korshak(1) reports the formation of reasonably high molecular weight (uncyclized) polyamide from the reaction of isophthaloyl chloride with 3,3'-dianilino-4,4-diaminobiphenyl in DMAC. This amine is anticipated to have essentially the same reactivity as the NABI forming tetramine:



We did not isolate high molecular weight material from overnight room temperature reaction. We did observe a somewhat crystalline precipitate after 20 hours reaction time which redissolved when the mixture was warmed to 70°C. The reaction was held at 70° for 4 hours and worked up by quenching in water. A yellow amorphous solid was obtained in quantitative yield which did not melt below 300°C. The infrared spectrum was inconclusive, although an amide-carbonyl absorption at $1660\ \text{cm}^{-1}$ was present. This unexpected result led us to consider a macrocyclic structure as a contaminant by-product of the polymer foaming reaction.

The reaction was repeated with the same result. Workup included simple filtration and water washing of the original precipitate. DSC scan showed a weak exothermic peak between 330°-360°C and no other transitions. On re-running the same sample, the exotherm had disappeared. This exotherm is attributed to further reaction, probably partial ring closure.

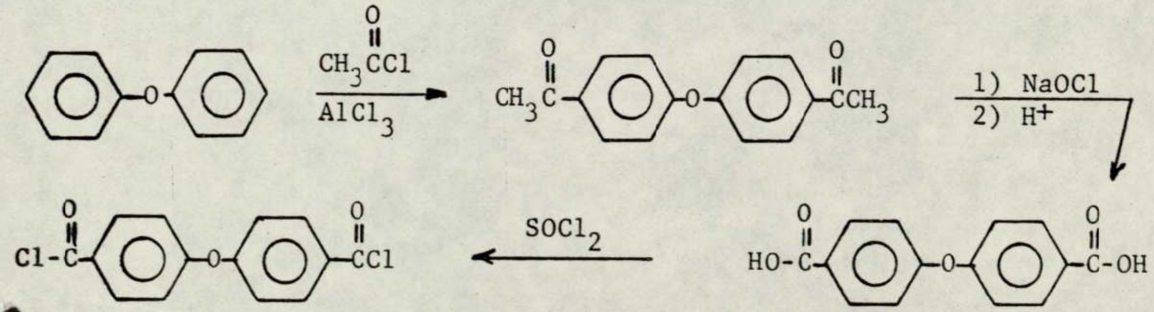
The photograph shown below is a molecular model of the tentatively proposed macrocyclic structure. Light blue represents carbonyl oxygen, dark blue - nitrogen, black - carbon, and orange - hydrogen.



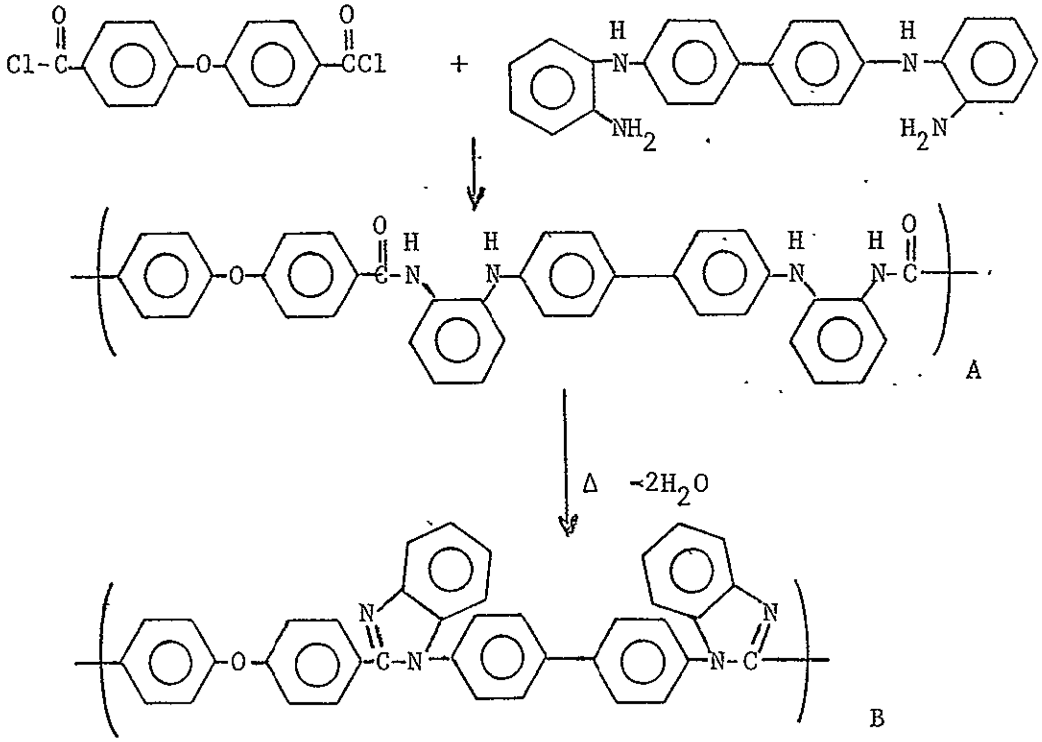
The very good molecular "fit" of the m-phenylene moiety (and incidently p-phenylene) between the primary amine groups which are simply positioned back over the two adjacent rings of the biphenyl system, yields a strain-free configuration with considerable flexibility and even relatively unhindered rotation of the various ring and amide components. Of course, the monomer used by Korshak cannot undergo such a macrocyclic formation.

5.2.1.2 4,4'-Oxy-Bis(Benzoylchloride) as Co-reactant

The difficulties encountered in attempting to prepare a linear precursor polyamide from isophthaloyl chloride and BAB suggested an alternate -Ar-structure. A more extended acid chloride which sterically prohibits formation of the macrocyclic intermediate is available at moderate cost by the following reaction sequence:

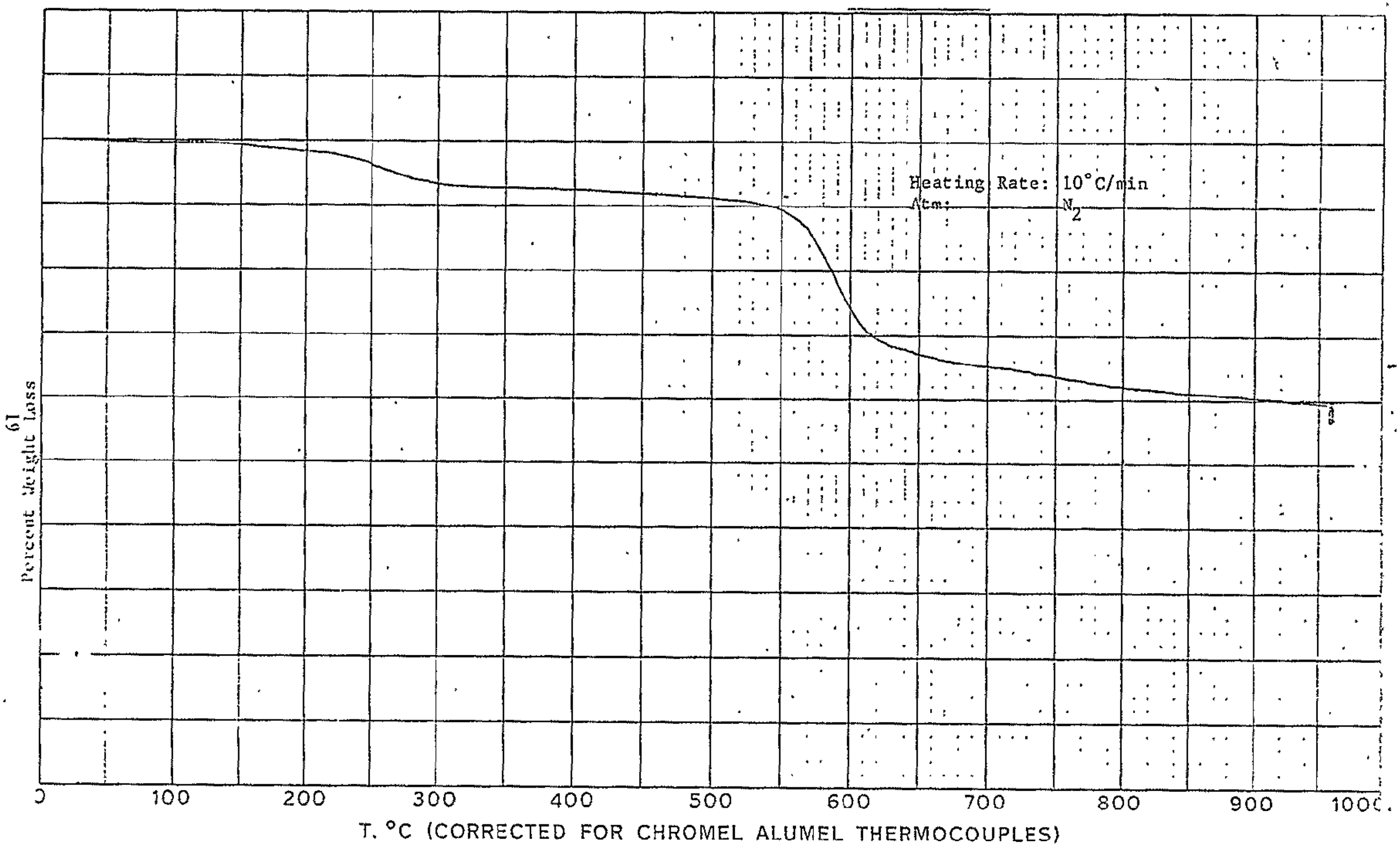


Low temperature polymerization (0°C) in dry DMAC yielded the desired precursor polyamide, albeit in relatively low molecular weight (η_{inh}=0.28 in 75/25 sym-tetrachloroethane/phenol). The infrared spectrum is consistent with the proposed structure with no residual acid or primary amine functionality apparent (see A below).



The TGA scan of the isolated product is shown in Figure 4. The onset of water loss (by cyclodehydration) to form the benzimidazolene structure begins at approximately 145°C [PMT 140°-160° (dec)]. The 7% weight loss to 400°C agrees well with the theoretical weight loss of 6.1%. Figure 5 is a TGA scan of ring closed material (B above) obtained after heating the polyamide at 375°C for one hour under a dry nitrogen atmosphere (η_{inh} 0.36, 75/25 sym-tetrachloroethane/phenol). Char yield at 800°C is 68%.

It had been hoped that the precursor polyamide would be sufficiently thermoplastic at the cyclodehydration temperatures to allow facile foam formation. A foam formed during the excursion to the 375°C postcure temperature. However, the density (~20 lb/ft^3) and cell configuration was not of good quality. The foam was more of a knitted microballoon configuration than the fully fused continuous three-dimensional substructure desired.



Heating Rate: 10°C/min
Atm: N_2

Figure 4. TGA of Polyamide from 4,4'-oxybis(benzoylchloride) and 4,4'-Bis(*o*-aminoanilino)biphenyl (A)

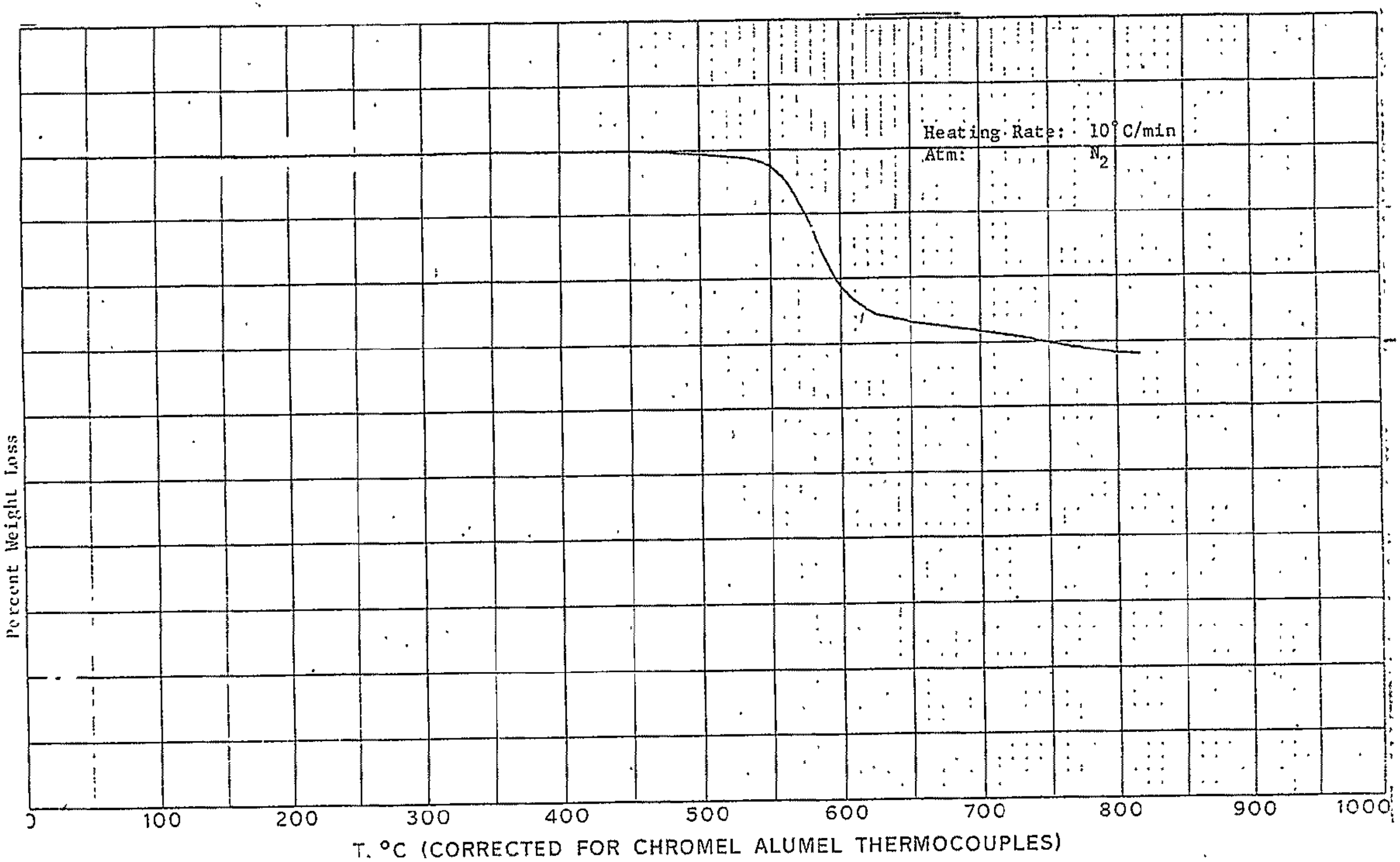


Figure 5. TGA of NABI from 4,4'-oxybis(benzoylchloride) and 4,4'-Bis(o-aminoanilino)biphenyl (B)

A second preparation of the precursor polyamide using scrupulously dried solvent (DMAC) and twice recrystallized monomers yielded high molecular weight polymer, as evidenced by relatively tough fiber formation when the reaction mixture was drowned in methanol (ηinh = 0.83). TGA scans of both the uncyclized and ring-closed materials are virtually identical to those shown in Figures 2 and 3. The foaming characteristics were (rapid heating to 375°C under N_2) appreciably different, however. The density was ~40 lb/ft^3 with larger bubbles and a more irregular substructure than previously obtained. Two obvious reasons for the differences are:

1. considerably larger particle size

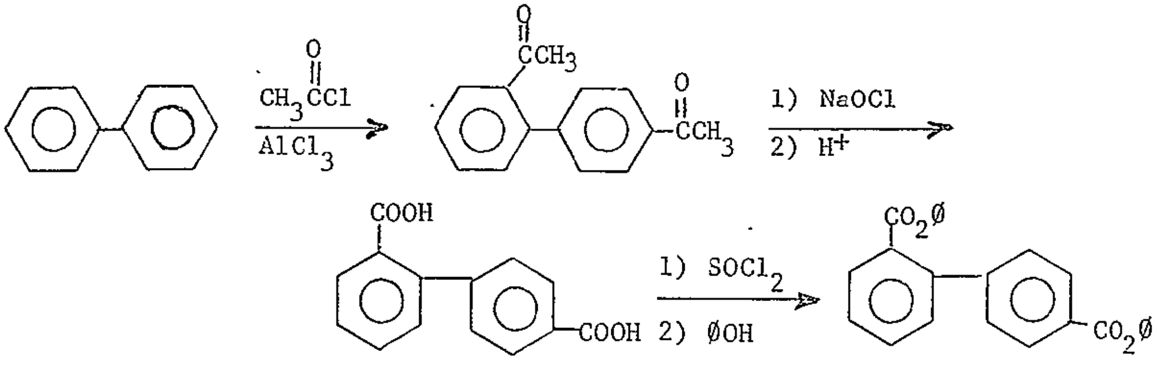
2. a significantly higher melt viscosity at the foaming temperature

Although the incorporation of additional volatile fluxing agents would certainly aid in foam formation, more promising results were obtained in other polymerization methods which are outlined in the subsequent section(s).

5.2.2 Diphenylester Derived Polymers

Reaction of the versatile BAB tetramine monomer with various diphenyl esters in phenol-fluxed melt condensations yielded the results described in Table V below.

These esters were the same as those utilized in the BABE-derived polymers above (Section 5.1) with one exception - in place of diphenylterephthalate, a relatively inexpensive isomer of the more rigid diphenyl-4,4'-bisbenzoate was substituted; viz. diphenyl-2,4'-bisbenzoate. This was prepared by the following route:



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In each case, low molecular weight prepolymers, as evidenced by the low η_{inh}, were obtained after a one hour advancement at 250°C. During this time $\sim$90% of the phenol (both added flux and reaction by-product) had been lost. The prepolymers remained an essentially solid melt during the 250°C exposure and showed no tendency to foam.

The prepolymers were pulverized (-60 mesh) and given a final cure at 400°C for one hour under nitrogen. The advanced polymers fused (with the exception of the 4,4'-bisbenzoate) but did not foam during the thermal schedule. They failed to foam even under vacuum at 400°C. After cooling, the polymers were brittle and were readily pulverized in a mortar.

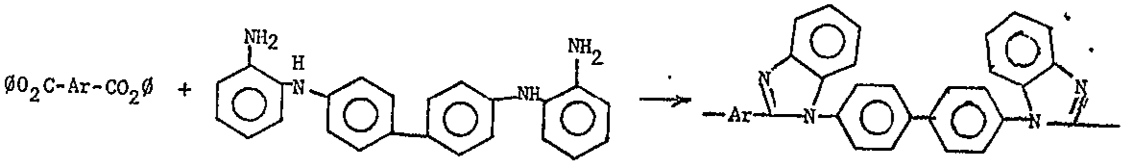
The 4,4'-bisbenzoate polymer exhibited much the same behavior as those derived from BABE (Section 5.1). Intense endotherms were apparent at 525°C and 575°C (major) when a DSC scant was run. After holding at 580°C for ten minutes, the sample was cooled and re-run to display an apparent Tg at 400°C (where none was visible prior to the initial scan) with no subsequent endotherms up to 580°C.

Table IV lists these results with the apparent Tg as determined by DSC. These Tg values are only preliminary and in fact the observed transition may not even represent the glass transition temperature. Other measurements such as specific heat or specific volume would have to be performed to verify that the DSC transitions are indicative of the true Tg. In the apparent Tg values, anomalous results are evident. For example, polymer containing the flexible diphenyl ether moiety generally displays a Tg lower than the same polymer system containing a m-phenylene moiety.

The apparent glass transition temperature is profoundly affected by the structure of the acid component and may generally be correlated to both rigidity and symmetry of the -Ar- segment of the polymer backbone. Char yield (Y_C^{800}) in nitrogen in all cases was between 63 and 68% with the initial decomposition point between 520° and 540°C.

TABLE IV

PRELIMINARY POLYMERIZATIONS OF 4,4'-BIS(o-AMINOANILINO)BIPHENYL WITH VARIOUS DIPHENYL ESTERS OF AROMATIC DICARBOXYLIC ACIDS



Acid Component	ηinh after* 1 hr at 250°C (m-cresol	ηinh* after additional 1 hr at 400°C (H_2SO_4)	(m-cresol)	Apparent Tg**	Remarks
Diphenyl isophthalate	0.07	0.23	0.27	287°	Brittle solid
Diphenyl-4,4'-bisbenzoate	0.12	0.12	0.15	400°***	Brittle solid
Diphenyl-4-4'-oxybisbenzoate	0.09	0.39	0.41	308°	Tough solid
Diphenyl-2,4'-bisbenzoate	0.15	0.25	0.21	248°	Brittle foam

---

* 0.5% solution at 25°C

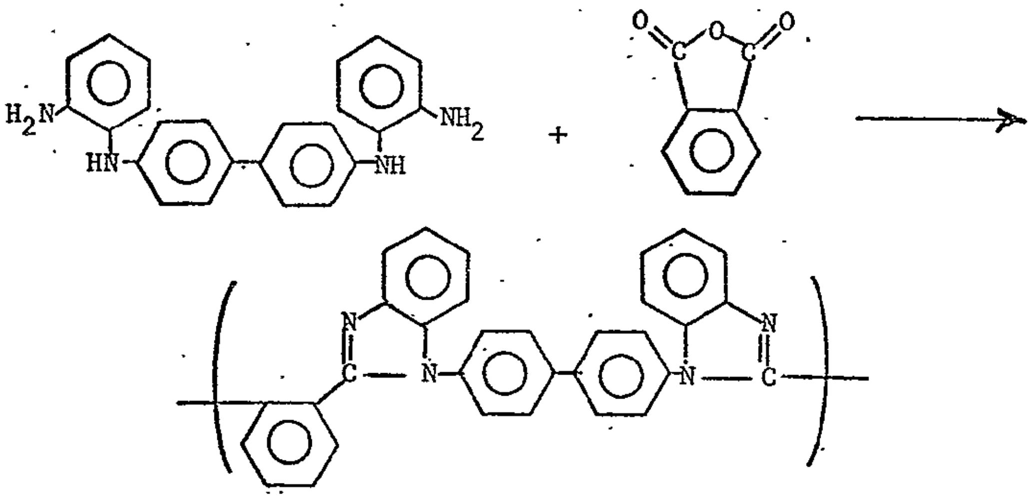
** Measured by DSC at $\Delta T = 20°C/min$ in N_2, T_g taken as the inflection point of the ΔT vs temperature curve

*** Heated in N_2 to 580°C, held 10 min then rerun; T_g transition appeared at 400°C

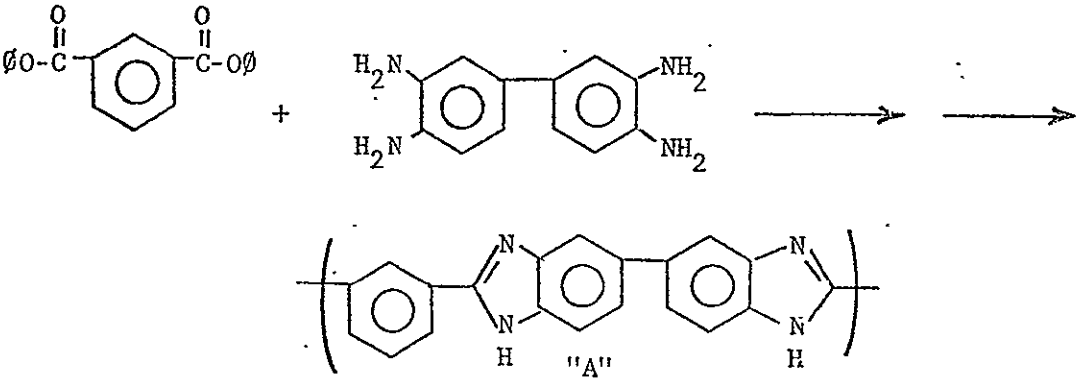
5.2.3 Phthalic Anhydride Derived Polymers

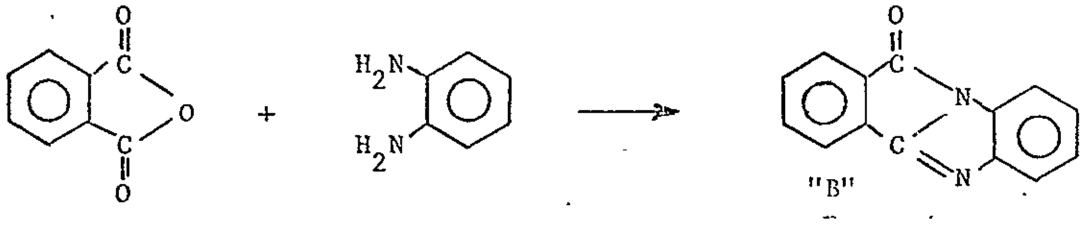
The sluggish nature of the polymerization reaction using esters of dicarboxylicacids prompted us to initiate studies of more reactive species to use as alternate co-monomers with BAB

The unique structure of the NABI forming tetramines allows reaction to the desired high polymer to be carried out using appropriate aromatic dicarboxylic acid anhydrides as chain extension agents.



The use of anhydrides in normal PBI technology (A below) is, of course, generally disallowed due to facile formation of the corresponding pyrrone structure (B below).





The reaction volatiles (phenol and water), produced as a result of the polymer forming reaction between esters of aromatic dicarboxylic acids and appropriate tetramines, are utilized, at least in part, as blowing agents for foam production. This requires adjustment of the foaming schedule to compensate for the continuous relatively slow production of these volatiles. Thus, the use of anhydrides is attractive from three standpoints:

1. More rapid polymerization reaction.
2. The amount of flux/blowing agent may be independently varied, allowing much closer control of prepolymer formation and reproducibility.
3. Cost effectiveness.

5.2.3.1 Initial Studies

Preliminary test tube scale studies were carried out in a manner similar to the previous evaluations.

Phenol fluxed (50% volatile) melt condensation of BAB and PA (phthalic anhydride) for one hour at 250°C (Wood metal bath temperature) yielded a foamed prepolymer which retained its integrity despite the low level of polymer advancement.

After cooling, the material was ground (-60 mesh) and given a final cure at 400°C for one hour. The prepolymer fused, refoamed and solidified within a few minutes to give a very tough foamed structure which was difficult to pulverize.

A second series of experiments evaluated the effect of prolonged cure at 250°C. It was felt that perhaps prolonged cure at 250°C would result in a corresponding increase in the inherent viscosity which would also be reflected in an increase in the inherent viscosity of the post-cured material. Table V provides a comparison of these results with the original results obtained from a one hour cure at 250°C plus one hour at 400°C postcure.

TABLE V

EFFECT OF PROLONGED CURE AT 250°C ON
INHERENT VISCOSITIES OF NABI POLYMERS

Acid Component	Tetramine	η_{inh}*(dl/g) after 250°C (Time, hr)	η_{inh}*(dl/g) after 400°C (Time, hr)	Comments
Phthalic Anhydride (PA)	BAB	0.26** (1.0)	0.79**, 1.14 (1.0)	Tough foam
		1.14 (16.25)	3.25 (1.0)	Tough foam

---

* As 0.5% solution in H_2SO4

** m-Cresol substituted as solvent

For the PA/BAB polymer additional time at 250°C does increase the inherent viscosity considerable with an additional increase occurring during the postcure at 400°C.

The final PA/BAB polymer has a Tg of 344°C and was obtained as a foam of ~14 lb/ft^3 density. TGA of this material under N_2 indicates a sharp weight loss starting at 520°C and continuing for ~100°C (Figure 6). Weight loss at 800°C was 37% (Y_C^{800}=63%), indicating equivalent thermal stability to that of the ester-derived polymers in the section above.

The most striking conclusion is the marked difference in polymerization rate. The phthalic anhydride system with its equivalent thermal stability and high Tg coupled with its low cost and ready aviliability is unquestionably the most attractive system developed to date.

5.2.3.2 Crosslinked Polymer Investigations

The high molecular weight polymer attainable (as evidenced by ηinh >3.0) when stoichiometric quantities of PA and BAB are reacted under appropriate thermal conditions indicates a particularly clean polymer forming reaction. The combination of these relatively low cost nonomers also results in a much faster reaction rate than that obtained with the more commonly used diphenyl esters of appropriate aromatic acids.

A fairly uniform, tough foam of ~14 lb/ft^3 density for the linear PA/BAB polymer has previously been mentioned. The resulting material was thermoplastic, however, and under high thermal load softens and flows in the manner common with other systems of this general type. Foam collapse and subsequent flow prior to char formation would probably reduce the insulation characteristics to an unacceptable leve.

An obvious method of minimizing (even preventing gross) flow is crosslinking. The production of such a polymer is readily obtained in a melt processing fashion under pressure. However, to prepare a low density foam from a crosslinked material requires control of a number of variables which are all interrelated.

Crosslinking is readily attainable by using inexpensive bis-anhydrides such as commercially available benzophenone tetracarboxylic acid dianhydride (BTDA) and pyromellitic dianhydride (PMDA).

The idealized structure of the crosslinked polymer (BTDA) is shown below.

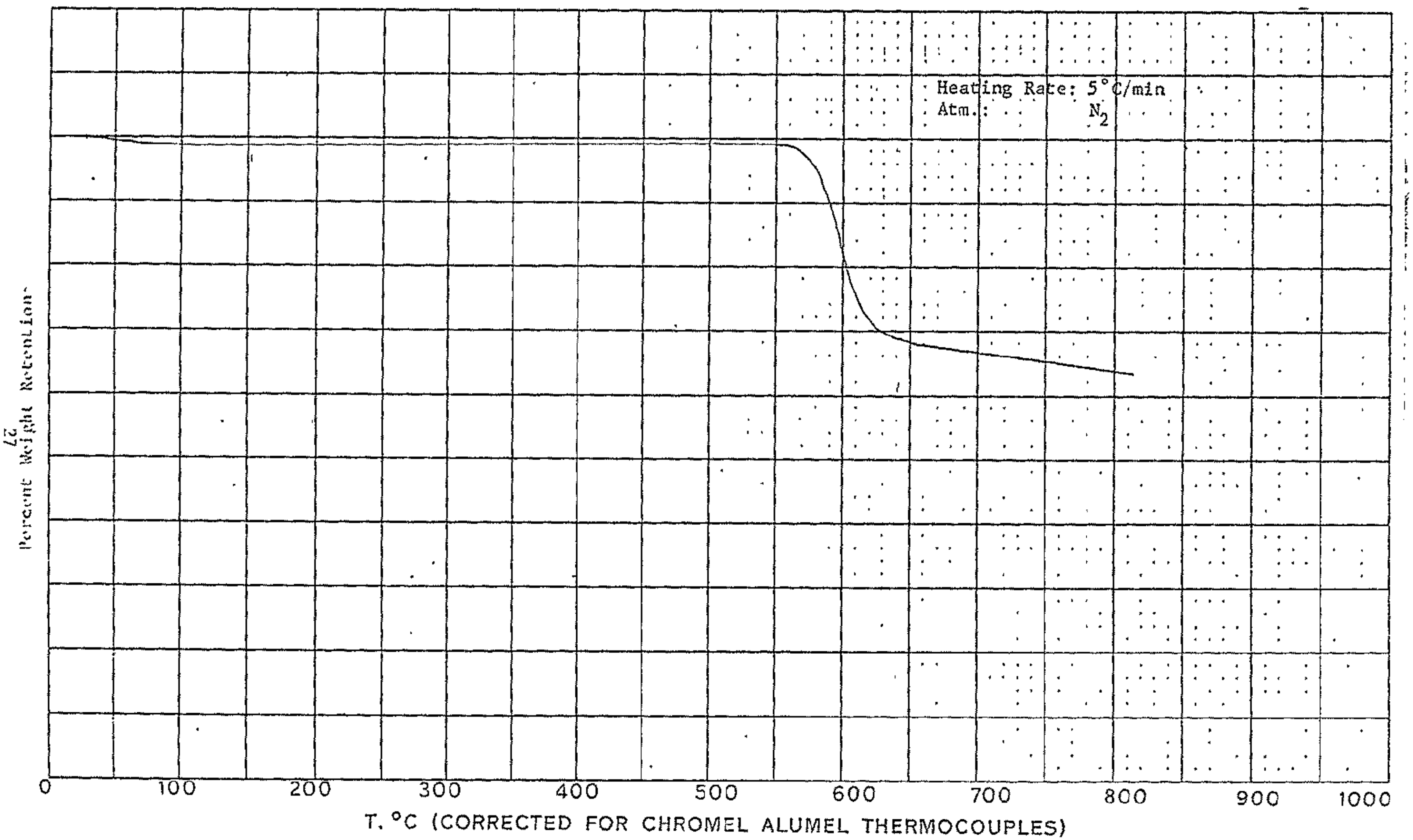
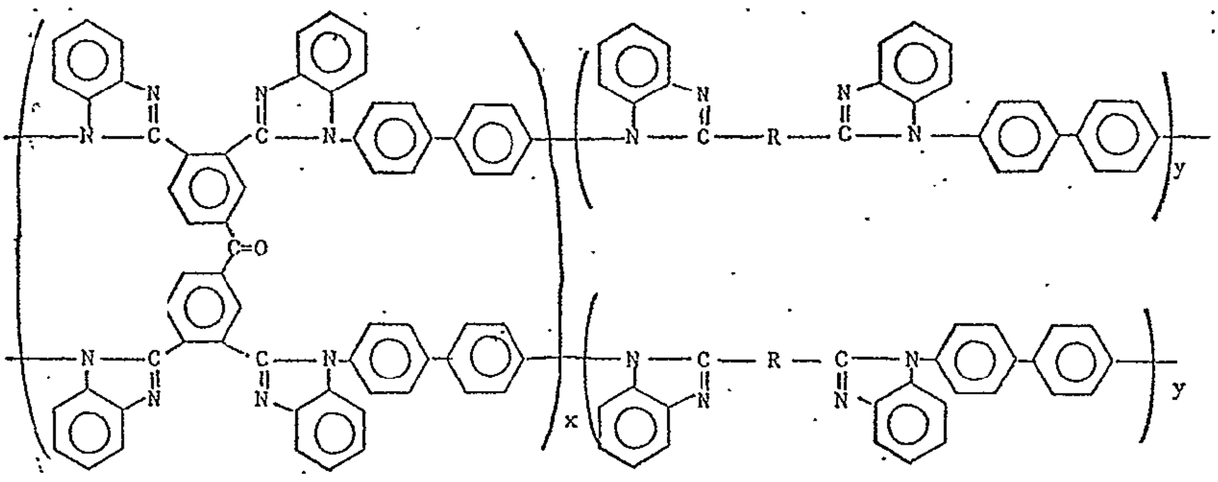


Figure 6. TGA Curve of BAB/PA Polymer



where R = o-phenylene, etc.

$\frac{x}{y}$ = 0.05 to >1

5.2.3.2.1 Benzophenone Tetracarboxylic Dianhydride Crosslinked NABI Polymers

Evaluation of foam/polymer characteristics using varying molar ratios of PA/BTDA in conjunction with BAB were begun on a small scale. These preliminary experiments utilized phenol (50%) as a flux which serves a two-fold purpose:

1. Accelerates the anhydride/amine reaction, and
2. Acts as both a solvent and blowing agent for subsequent foam formation.

As mentioned earlier, a number of factors partake in the formation of a foamed material. Premature gellation, in the case of a crosslinked system, is a significant factor. Careful control of temperature (and rate of increase) in the case of thermally activated foams, as is the case here, plays an important part. Viscosity at a given temperature similarly determines cell size and distribution. The preliminary experiments involved various equivalent ratios of PA to BTDA between 95/5 to 70/30. These systems were evaluated by monomer mixing, plunging into a 250° oil bath and noting foam rise and quality. All produced foamed material which retained integrity at the 400°C postcure temperature. The less crosslinked systems demonstrated more shrinkage upon exposure to the higher temperature while the more highly crosslinked systems were slightly more brittle at room temperature. Cell size and distribution are virtually the same in all cases, rather porous with fairly large cells.

A second approach yielded encouraging results. This approach involved the addition of chain extending/crosslinking agent to the preformed amine terminated prepolymer. The first two reactions were carried out using PA/BTDA in 80/20 molar ratio. A prepolymer was prepared by reacting BAB and PA in a 10/8 ratio in the presence of 20% (by weight) of phenol (flux). The material was advanced at 250°C for 45 minutes with a concomittant loss of 60% of the fluxing agent.

In the first experiment the BTDA crosslinking agent was added to the hot prepolymer mixture and stirred in by hand. The mixture gelled much too rapidly to allow adequate mixing.

In a second experiment, the prepolymer (amine terminated) was cooled and ground together with the BTDA crosslinking agent. The mixture (~40 mesh) was placed in a 250° oil bath which was heated to 400°C in ~45 minutes. The resultant foam had a much finer cell size and texture than any previous attempts.

Following this lead we then refined the methodology as follows:

1. A prepolymer was prepared in the following molar ratios (BAB/PA): 100/95, 100/90, ---, 100/50 in 5 mole precent increments by heating a phenol fluxed mixture (~50% solids) from 250°C to 360°C over a two hour period under nitrogen. Phenol boiled out during the interim (0-5% remaining). The resulting cooled material varied from bright red brittle solids to dense foams as the stoichiometry approached unity.

2. The prepolymer was then redissolved in hot phenol (~50% solids), cooled to ~75°C and the appropriate (stoichiometry for residual amine) amount of BTDA added. After solution had occurred the tubes were placed in a Wood's metal bath at 250°C and heated to 460°C over a one hour period. These test tube experiments showed a general decrease in ultimate foam density to ~2.5 lb/ft^3 in the region of 100/80/20 to 100/70/25 stoichiometry. Foam quality also appears to be superior in this region. Figure 8 describes the trend in densities as the stoichiometry was varied. It should be recognized that the foaming conditions were not optimized.

As the advancing polymer is foamed by gaseous phenol, the gell point (i.e., the time at which significant crosslinking occurs to essentially immobilize the foaming mass) may determine the overall density. In the lightly crosslinked systems, apparently the gell point is reached much later in the thermal schedule <u>after</u> the majority of the blowing agent has escaped. Secondly, the viscosity buildup rate may not be sufficient to prevent premature flow and foam collapse at a particular time/temperature point.

Those samples which had less than 60 mole percent chain extending phthalic anhydride (i.e., 100/60/20, 100/55/22.5, 100/50/25), that is, those with the highest crosslink density, showed considerable shrinkage and coalescence of the foam in the bottom of the tube. The skins are very dense with a shiny dark surface. The material had shrunk away from the wall of the tube and in the highest crosslinked case, actually had folded within itself (Figure 7).

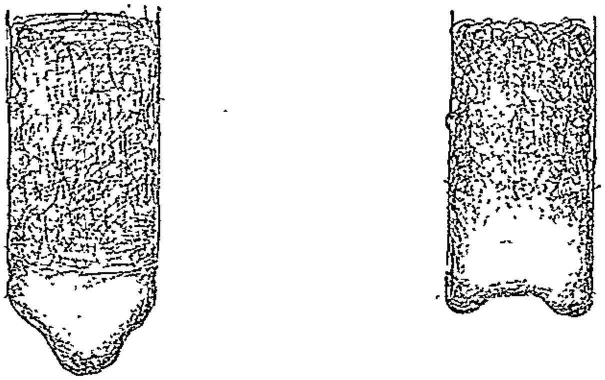


Figure 7. Foam Shape from Test Tube Experiments

The thermal and thermo-oxidative stability of the crosslinked systems seem to be at least equivalent to the linear thermo-plastic polymers. Figures 9 and 10 are TGA scans of the foam (2.7 lb/ft^3) developed from BAB/PA/BTDA in the ratio of 100/70/15 . The appearance of the sample after the N_2 run is noteworthy. A black char remained which showed no evidence of melting or flow from the original cubic shape. Linear systems evaluated previously invariably showed gross flow and deformation during the thermal schedule.

The marked improvement in both density and foam quality by crosslinking opened a very large area for investigation. Obviously the variables which control the foam characteristics are not easily evaluated or controlled separately.

5.2.3.2.1.1 Cell Control Additive Study

A small batch of prepolymer at the 100/70/15 (BAB/PA/BTDA) ratio was prepared to study the effect (if any) on both the overall density and cell size and configuration using surfactants suggested by Dow Corning Corporation, Midland, Michigan. The four surfactants included Dow Corning Products No. 190, 193, 197 and 470A. These are all polyglycol polysiloxanes without hydrolyzable Si-O-C bonds contrary to most other surfactants, particularly those used in polyurethane foam manufacture.

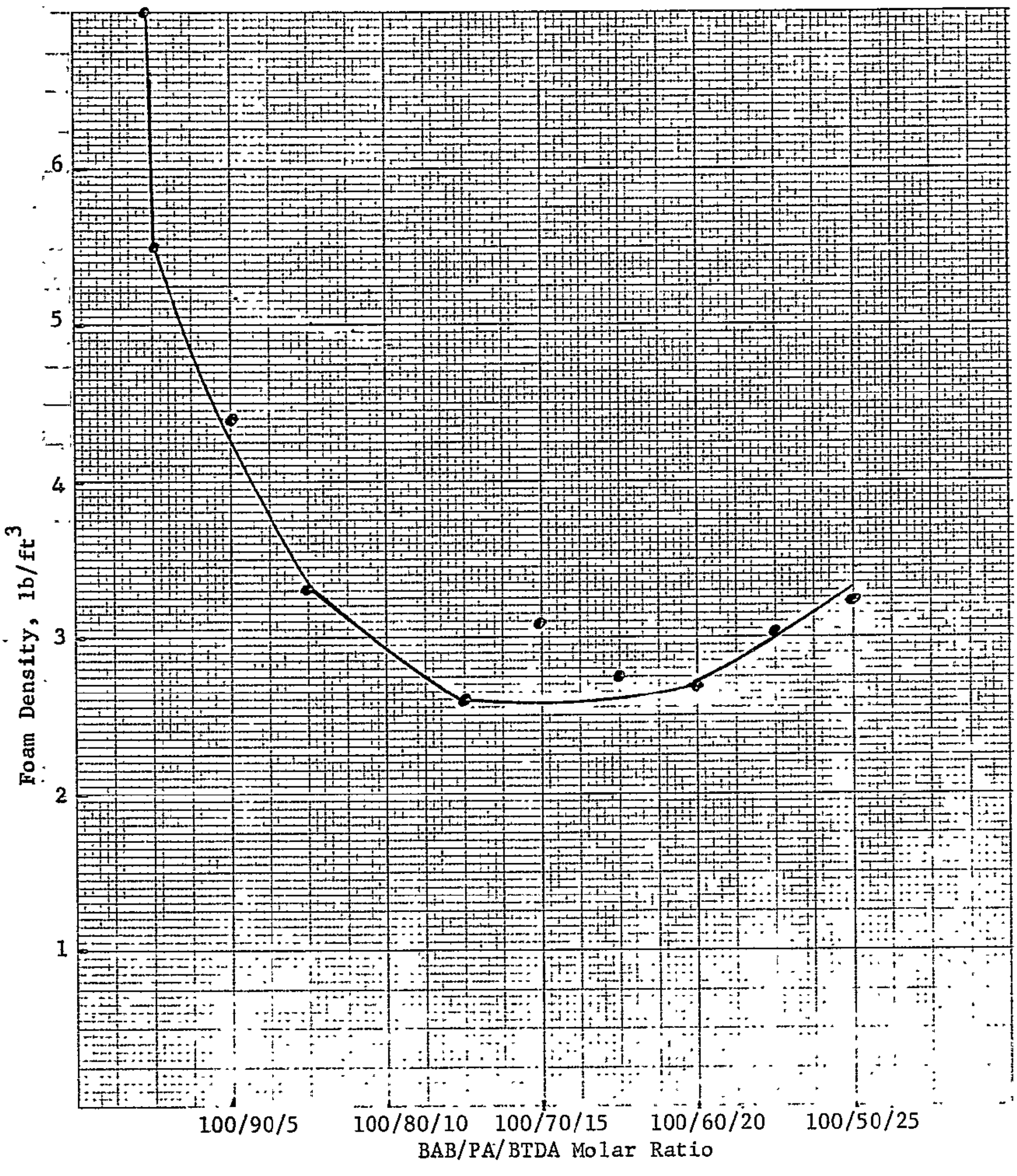


Figure 8 Variation in Foam Density with Different Stoichiometries

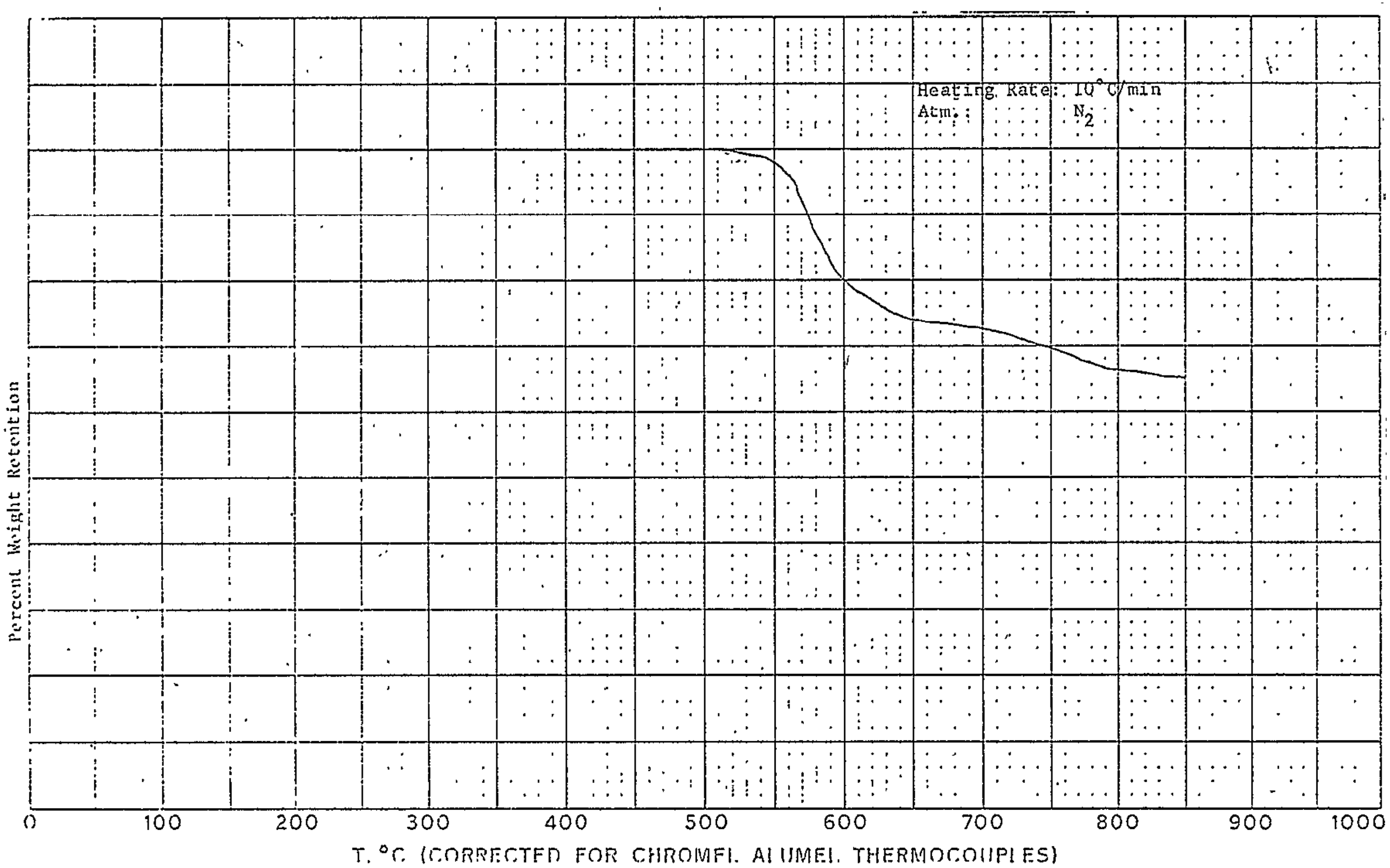


Figure 9. TGA of BAB/PA/BTDA (1/0.7/0.15) (N_2)

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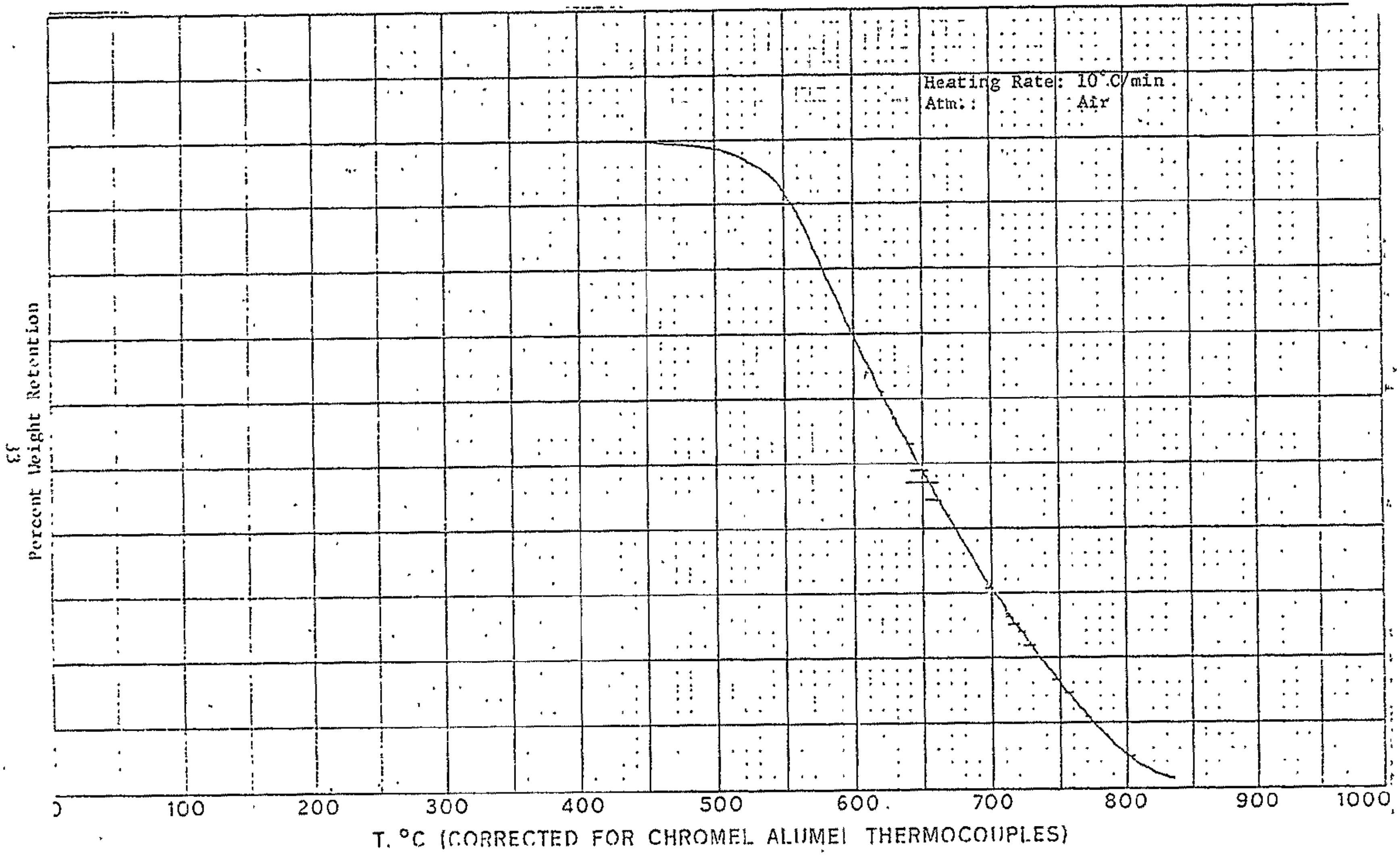


Figure 10 TGA of BAB/PA/BTDA (1/0.7/0.15) (Air)

The surfactants were first evaluated by determining their gross solubility behavior in hot phenol. All four showed very poor (negligible) solubility in phenol at 40°C but dissolved quite readily at ~100°C. Since the foaming action proceeds at temperatures between 230° and 450°C the low temperature insolubility was not expected to present any particular problems.

Since these recommended materials have no easily hydrolyzable Si-O-C bonds, they would not be expected to suffer degradation and loss of effectiveness in the hot phenolic solution of NABI forming materials. Only one of the four tested (at 1% of the total solids concentration) showed no detrimental effects. DC 193 yielded a foam which was essentially equivalent to a control with no surfactant. The other three (DC 190, 197 and 470A) yielded foams of higher density albeit with finer cell size and more uniform distribution. DC 197 provided the best cell configuration.

The densities of equal batch sizes, foamed simultaneously, were as follows:

DC 190	6.3 lb/ft^3
DC 193	2.9 "
DC 197	4.6 "
DC 470A	7.3 "

5.2.3.2.2 Pyromellitic Dianhydride (PMDA) Cured NABI Polymers

With the completion of the screening study of the BTDA crosslinked BAB/PA system at various crosslink densities, an equivalent study was initiated using PMDA. The results indicate a more brittle nature of the cured polymer, at least in the stoichiometries evaluated (BAB/PA/PMDA - 100/80/10, 100/75/12.5, 100/70/15, 100/65/17.5). The prepolymer (BAB/PA) approach was utilized in the 100/70/15 instance, while mixed monomers were employed in the other three. In all four, the co-reactants were dissolved in phenol at ~100°C and heated in a Wood's metal bath from 160°C to 260°C over a one hour period and then postcured one hour at 420°C. Ultimate densities were approximately equal (~4 lb/ft^3) with a relatively large open cell structure.

A thermogravimetric analysis trace (Figure 11) shows an improvement in Y_C^{800} in nitrogen in comparison to the BTDA crosslinked system (72% vs 66%). The specimen was not pre-dried and consequently shows a 2% weight loss between 150°-200°C.

The brittle nature of the PMDA crosslinked polymer was a significant factor in suspending further investigation using this monomer. The remainder of the program was completed using BTDA as the sole crosslinking co-monomer.

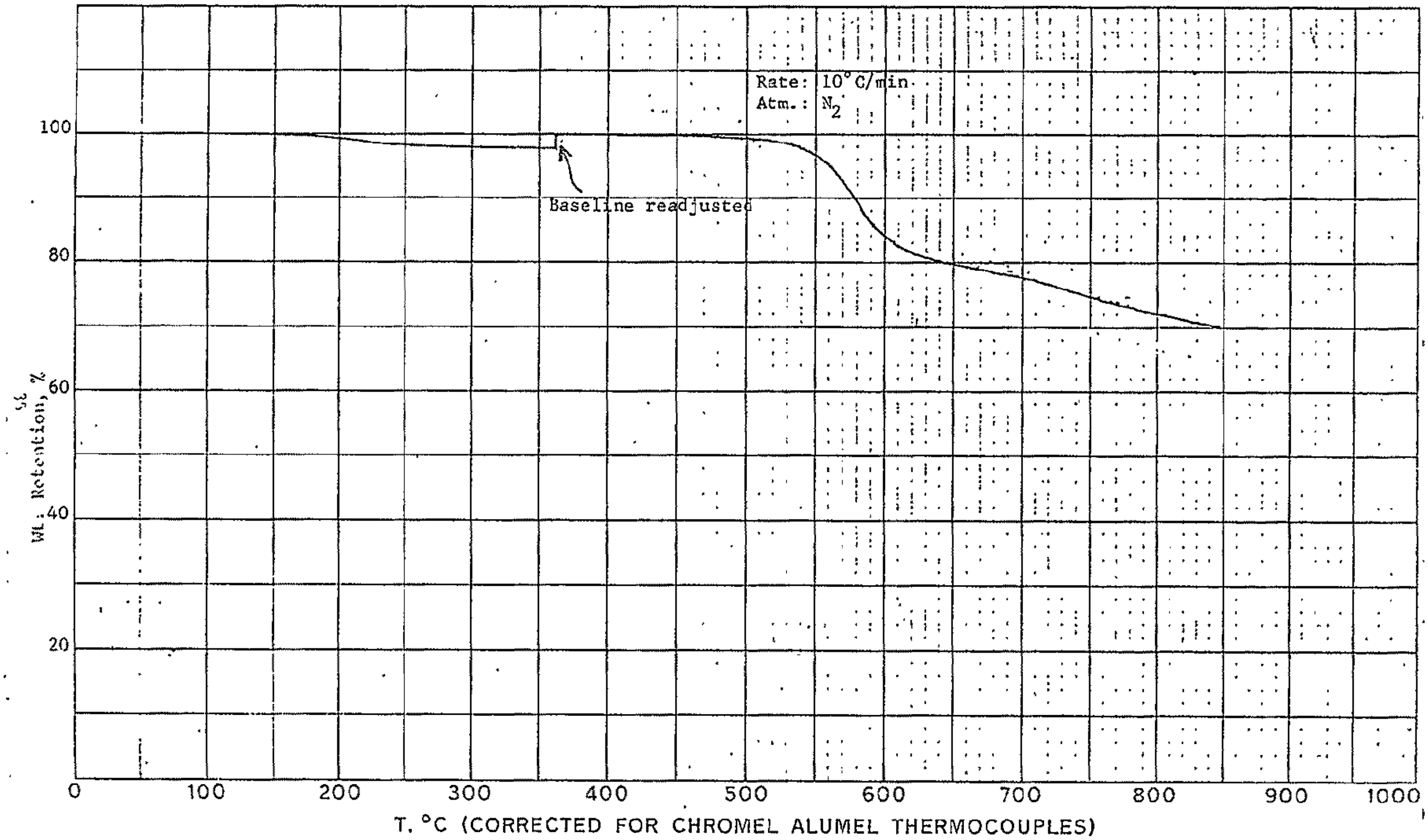


Figure 11. TGA of BAB/PA/PMDA (100/70/15) (N_2)

5.3 FREE FOAM PARAMETER STUDIES

The previous experiments were all carried out in test tubes (15 or 20 mm diameter) using a Wood's metal heating bath which allows very rapid and essentially uniform heat transfer to occur. This technique, while useful in screening studies,does not simulate a "real world" production technique for large batch foaming operations.

To more closely approximate these conditions a general optimization of the BAB/PA/BTDA system was initiated in forced air ovens using larger sample sizes. Preliminary results show the anticipated differences in foamed material. Generally, higher densities are obtained with severe nonuniformity of cell structure occasionally observed.

The time between gellation (induced by crosslinking) and volatile (blowing agent) release is a most critical area. As the rising foam is progressively heated, the natural insulation from the outer skin to the center of the foaming mass induces a significant thermal gradient which, of course, sets up differences in the critical foam forming parameters.

The initial studies involved free-foaming experiments in nitrogen purged beakers which have proven to be a realistic approximation of metal tooling in our work on PBI foams. A distinct difference in the PBI methodology and the incumbent NABI systems is due to the crosslinking requirement of the latter. This difference, coupled with the differences in reaction rate and volatile evolution, not surprisingly, disallows direct adaption of PBI technology to NABI foams.

Experiments briefly evaluated four general areas: 1) solvent type; 2) solvent content; 3) temperature profile; 4) prepolymer content. These are all interdependent variables which cannot be optimized separately and must be adjusted with accumulation of pertinent data.

A simple change in solvent from phenol to the more volatile dimethyl acetamide surprisingly yielded very poor results. Low molecular weight, brittle material was obtained which did not show any promise as a useful material.

Table I lists the free-foaming experiments performed. In the all monomer systems, phenol is the exclusive solvent/blowing agent. Addition of prepolymer was facilitated by dissolving the requisite anhydrides in m-cresol prior to mixing.

TABLE VI

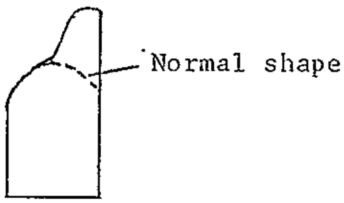
FOAMING EXPERIMENTS USING BAB/PA/BTDA IN 100/70/15 MOLAR RATIOS

Reactants	Blowing Agents (% by Weight)	Temperature Profile	Cured Foam Density	Quality
Monomers	50	To 400°C in 25 min	4.9	Good
↓	50	To 230°C in 11 min step-cured to 400°C	8.0	Fair
↓	67	To 400°C in 25 min	4.0	Good
50/50*	50	To 220°C in 15 min step-cured to 400°C	7.1	Fair
↓	↓	To 260°C in 15 min step-cured to 400°C	4.1	Good
↓	↓	To 210°C in 15 min step-cured to 400°C	>20	Poor

* 50/50 molar mixture of monomers and prepolymer

These preliminary experiments indicated the desirability of a rapid heatup to the foaming temperature (>230°C). After the initial rise and gel, subsequent step-cures to a final 400°-425°C do not seem to have any effect on either foam quality or density. The temperature gradient set up by the insulative nature of the rising foam was previously mentioned. This is readily seen in some of the foamed samples, where a secondary "blow" is observed.

The general shape is a domed cylinder which is naturally established by the beaker dimensions. Occasionally the secondary foam is apparent by its out-growth from the original foam structure as sketched below.



Cross-section of secondarily blown foam

Alternate foaming techniques to prevent this effect using a free-floating upper surface were then initiated.

5.4 RESTRICTED FOAM RISE TECHNIQUES

The necessity of restraint during the foaming process is required for the "secondary blow" described above. A second advantage obtained by the restraining technique is in establishing more uniform heat distribution in the foaming polymer. A configuration such as sketched below (Figure 12) has proven quite useful in subsequent operations.

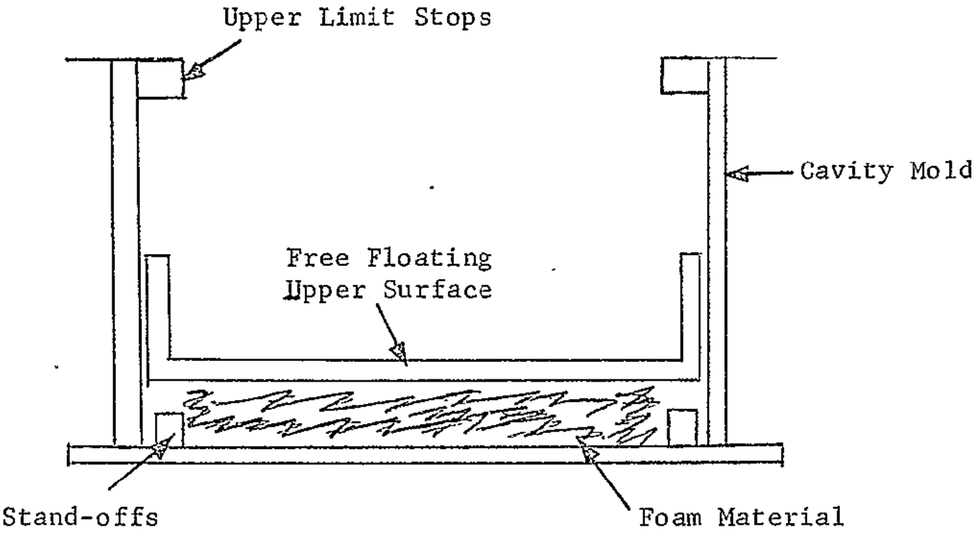


Figure 12. Foaming Fixture for Externally Heated Blown Foam

The apparatus consists of a cavity mold with a proper close fitting (~0.05 in. clearance) free-floating, upper surface. During the preliminary heat-up (prior to the onset of foaming) the upper surface is held above the foam material by the stand-offs located at the periphery. As polymerization proceeds (with application of heat) and the solvent is evolved, the viscosity of the polymer-forming mixture increases to a point where the entire mass begins to rise to contact the underside of the float. The weight of this surface provides sufficient restraint to create a more uniform cell distribution. A more uniform heat distribution results from the hot upper surface being much closer to the, as yet, unfoamed material during the preliminary heat-up and being in direct contact as the foam rises. The rising foam effectively seals the exposed area between the cavity sidewalls and the float, thus preventing serious oxidation problems during the latter phase of foam consolidation. This still allows an adequate path for excess volatile release during the foaming interval.

5.4.1 Restricted Foam Rise Parameter Studies

5.4.1.1 Anhydride Co-Monomers

The restricted foam rise technique has been utilized exclusively during subsequent foaming parameter studies. The extensive preliminary mapping studies needed for foam process optimization were only partially completed during this program. The adjusted variables include the following:

1. Monomer ratio (BAB/PA/BTDA) to accommodate various crosslink densities
2. Flux/blowing agent concentration
3. Flux/blowing agent materials
4. Prepolymer formation (cook time at temperature)
5. Heatup rate

Our first series of experiments, on 7.5 cm diameter billets, was to simply combine the various monomers in the appropriate amount of solvent and heat, with stirring, to effect solution. The mixture was transferred to the restricted rise fixture and the temperature increased at the appropriate rate.

The second procedure was to combine the various monomers in the appropriate amount of solvent and allow partial reaction to occur by heating, with stirring, for a specified time at a particular temperature. Prepolymer cook times were systematically varied between 45 and 120 minutes while only two temperatures have been investigated; viz. 175°C and 190°C. The solvent loss at both temperatures is negligible. After the prescribed reaction period the molten prepolymer mass is allowed to cool, pulverized and ground to -60 mesh size.

An alternate method of prepolymer formation included prepolymer cook at ~30% volatile content followed by reducing the volatiles under vacuum to various levels. This latter technique is necessary to reduce the total volatile content to less than ~25% where the prepolymer viscosity becomes too high for adequate stirring during the initial cook.

After charging into the foaming fixture, previously described, the part temperature is raised in a forced air oven to either 350°F or 375°F (depending on prepolymer cook temperature) in ~30 minutes. The rate of temperature increase is then held to a particular value. Three discrete foaming temperature heatup rates were utilized; viz. 100°F/hour, 150°F/hour and 200°F/hour. The particular rate is followed to approximately 550°F when all the foaming activity has ceased. The foam is then heated to 650°F over a twenty minute period, held ten minutes, cooled and removed.

Visual examination of skin texture along with cell size distribution and configuration is made at this point. A segment of the foam is cut out to examine the interior cell structure.

Postcure is carried out under dry nitrogen by slow (~200°F/hour) heatup to 775°F and held at that temperature for one hour. The materials are generally red-orange in color with acceptable toughness. The weight loss during postcure is generally ~4 to 6% and is attributed to the effective free volatiles remaining in the foamed specimens after the initial foam forming sequence.

Phenol has proven to be a most effective solvent/blowing agent. Perhaps surprisingly, m-cresol has not proven as efficient, generally yielding foams of poor quality with larger, gross void structures. The overall densities obtained generally range between 4 and 8.5 lb/ft^3.

The foaming volume was increased in two steps from 5.0 cm diameter discs, 2-3 cm high to 15 cm diameter discs up to 4-5 cm in height. Lower density is generally attainable with the larger volume but more irregularity in foam texture (more large voids) results. The insulative character of the foam, coupled with the larger volume and consequently longer heat flow paths is the prime causative factor.

Section I of Table VII describes the results obtained from anhydride co-reactants with BAB. Mold charges were calculated to yield 4.0 lbs/ft^3 (pcf). Circular billet diameter was 7.5 cm with ultimate foam rise to be 5.5 cm for 4 pcf foam. In no case was the 4 pcf target density obtained. Foam rise heights are, of course, an inverse function of density. Section II shows similar results obtained on larger billet specimens. In this section the billet diameters were 15 cm, with an equal (5.5 cm) ultimate foam rise (at 4 pcf).

TABLE VII

CROSSLINKED NABI POLYMER FOAM PARAMETER STUDY
SECTION I
(7.5 cm Billet Diameter)

Identification No.	BAB/PA/BTDA Ratio Additive (wt. %) Solvent (wt. %)	Prepolymer Formation Conditions	Process After Prepolymer Formation	Heat-Up Rate (°F/min)	Ultimate Foam Density (lb/ft^3)	Foam Appearance
PR 00317-90	100/70/15 m-cresol (15) phenol (50)	None	--	30	5.1	Fair
-90A	100/70/15 DC 197 (1) m-cresol (15) phenol (50)	"	--	30	6.4	Fair
-94	100/70/15 ethanol (100) phenol (20)	"	--	10	10.7	Good
-95	100/70/15 ethanol (25) phenol (10)	"	--	10	8.5	Good
-96	100/80/10 ethanol (25) phenol (20)	"	--	10	9.1	Poor
-97	100/85/7.5 ethanol (25) phenol (10)	"	--	10	8.5	Fair
-98	100/90/5 ethanol (25) phenol (10)	"	--	12	10.2	Poor
-99	100/90/5 ethanol (25) phenol (10)	"	--	10	9.6	Very poor
-100	100/90/5 DC 193 (2) ethanol (25) phenol (10)	"	--	10	24.1	Very poor, gross voids
-102	100/90/5 DC 193 (0.5) ethanol (25) phenol (10)	"	--	10	18.2	Very poor
-18	100/90/5 phenol 33	Advanced 45 min at 175°C	Cooled to -60 mesh ground	6.5	7.2	Fair
-19	100/90/5 phenol 33	Advanced 60 min at 175°C	Cooled, ground to -60 mesh	6.5	6.4	Good
-20	100/90/5 phenol 20	Advanced 45 min at 175°C	Cooled ground to -60 mesh	6.5	6.3	Fair
-21	100/90/5 except m-cresol (30)	Advanced 45 min at 175°C	Cooled ground to -60 mesh	6.5	6.1	Good
-22	100/90/5 m-cresol (15)	Advanced 45 min at 175°C	Cooled ground to -60 mesh	6.5	11.3	Very poor
-23	100/90/5 m-cresol (20)	Advanced 45 min at 175°C	Cooled ground to -60 mesh	6.5	5.7	Very poor
-24	100/90/5 m-cresol (15%)	Advanced 90 min at 175°C	Cooled ground to -60 mesh	6.5	7.5	Fair

TABLE VII (Continued)

CROSSLINKED NABI POLYMER FOAM PARAMETER STUDY
SECTION II
(15 cm Billet Diameter)

Identification No.	BAB/PA/BTDA Ratio Additive (wt. %) Solvent (wt. %)	Prepolymer Formation Conditions	Process After Prepolymer Formation	Heat-Up Rate (°F/min)	Ultimate Foam Density (lb/ft^3)	Foam Appearance
PR 00317-26	100/90/5 phenol (33)	Advanced 45 min at 175°C	Cooled, ground to -60 mesh	3.2	4.3	Fair
-27	100/90/5 phenol (33)	Advanced 45 min at 175°C	Cooled, ground to -60 mesh	1.6	4.8	Good
-28	100/90/5 phenol (33)	Advanced 45 min at 175°C	Cooled, ground to -60 mesh	2.2	4.4	Fair
-29	100/90/5 phenol (33)	Advanced 45 min at 175°C	Cooled, ground to -60 mesh	2.2	4.4	Fair
-30	100/90/5 phenol (33)	Advanced 60 min at 190°C	Cooled, ground to -60 mesh	3.2	5.3	Good
-31	100/90/5 phenol (30)	Advanced 45 min at 190°C	Cooled, ground to -60 mesh	3.2	5.2	Good
-32	100/90/5 phenol (25)	Advanced 45 min at 190°C	Cooled, ground to -60 mesh	3.2	4.9	Good
-33	100/90/5 phenol (20)	Advanced 45 min at 190°C	Cooled, ground to -60 mesh	3.2	4.2	Poor
-34	100/90/5 phenol (17.5)	Advanced 45 min at 190°C	Cooled, ground to -60 mesh	3.2	6.3	Poor
-35	100/90/5 phenol (30)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	2.2	5.0	Fair
-36	100/90/5 phenol (25)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	2.5	5.8	Fair
-37	100/90/5 *Nucleation Sites (10) phenol (30)	Advanced 45 min at 190°C	Cooled, ground to -60 mesh	5	8.4	Good
-38	100/90/5 *Nucleation Sites (10) phenol 27.5	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	2.2	8.4	Good
-39	100/90/5 phenol (30)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	3.2	6.2	Good
-40	100/90/5 *Nucleation Sites (10) phenol (30)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	3.2	10.6	Good
-41	100/90/5 *Nucleation Sites phenol (30)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	3.2	7.0	Good

*Finely (-20 mesh) ground cured polymer (foam) added to the ground prepolymer prior to final foaming operation.

TABLE VII (Continued)

CROSSLINKED NABI POLYMER FOAM PARAMETER STUDY
SECTION II
(15 cm Billet Diameter)

Identification No.	BAB/PA/BTDA Ratio Additive (wt. %) Solvent (wt. %)	Prepolymer Formation Conditions	Process After Prepolymer Formation	Heat-Up Rate (°F/min)	Ultimate Foam Density (lb/ft)	Foam Appearance
PR 00317-42	100/90/5 phenol (30)	Advanced 100 min at 190°C	Cooled, ground to -60 mesh	3.2	4.8	Poor
-43	100/90/5 phenol (30)	Advanced 90 min at 190°C	Cooled, ground to -60 mesh	1.6	7.6	Fair
-44	100/90/5 phenol (30)	Advanced 100 min at 190°C	Cooled, ground to -60 mesh	1.6	8.1	Good
-45	100/90/5 phenol (30)	Advanced 90 min at 190°C	Cooled, ground to -60 mesh	3.2	5.0	Excellent skin, poor internally
-46	100/90/5 Ethyleneglycol (30)	Advanced 75 min at 190°C	Cooled, ground to -60 mesh	3.2	--	No foaming action even to 400°C for 30 min.
-47	100/90/5 phenol (30)	Advanced 100 min at 190°C	Cooled, ground to -60 mesh	1.6	6.8	Fair
-48	100/90/5 phenol (30)	Advanced 90 min at 190°C	Cooled, ground to -60 mesh	3.2	6.2	Fair
-43	100/90/5 phenol (30)	Advanced 90 min at 190°C	Cooled, ground to -60 mesh	1.6	6.2	Poor
-44	100/90/5 phenol (30)	Advanced 110 min at 190°C	Cooled, ground to -60 mesh	3.2	11.5	Dense skin
-45	100/94/3 phenol (30)	Advanced 100 min at 190°C	Cooled, ground to -60 mesh	3.2	8.0	Good
-52	100/94/3 phenol (30)	Advanced 100 min at 190°C	Cooled, ground to -60 mesh	1.6	8.9	Fair
-53	100/94/3 phenol (30)	Advanced 120 min at 190°C	Cooled, ground to -60 mesh	3.2	5.9	Good
-53	100/94/3 phenol (30)	Advanced 100 min at 190°C	Stripped to 22% vols, cooled & reground to -60 mesh	3.2	5.6	Good
-54	100/94/3 phenol (30)	Advanced 100 min at 190°C	Stripped to 20% vols, cooled & reground to -60 mesh	3.2	6.6	Fair
-56	100/94/3 phenol (30)	Advanced 100 min at 190°C	Stripped to 25% vols, cooled & reground to -60 mesh	3.2	5.2	Good

5.4.1.2 Partially Esterified Co-Monomers

The reaction between BAB and an anhydride is accelerated by phenol. This may be either due to the reaction proceeding through the phenyl ester or to a simple catalytic effect. The latter is more likely in view of the relative reaction (polymerization) rates of diphenyl esters and anhydrides with BAB. The rate of the analogous reaction between an ethyl ester and BAB lies between these two.

Work was initiated by evaluating the foaming characteristics of a series of polymer forming (crosslinked) mixtures of half-ester/half-acid, anhydride and BAB systems using the restraining apparatus described in an earlier section. The foams were generally prepared by simply refluxing the particular anhydride (BTDA and/or PA) in a small amount of ethanol for two hours (to form the half ester/half acid, not isolated) and adding the appropriate amount of BAB, phenol and anhydride. The reaction mixtures were then heated, at various rates, to produce foam with widely divergent results (variations in density and cell configurations).

Table VIII describes the foaming experiments performed where various heating rates, monomer ratios, solvents and additives, were evaluated.

TABLE VIII

CROSSLINKED NABI POLYMER FOAM PARAMETER STUDY
(Using Half-Esterified Anhydrides)

Identification No.	BAB/PA/BTDA Additive (wt. %) Solvent (wt. %)	Heat-Up Rate (°F/min)	Foam Density (lb/ft^3)	Foam Appearance
PR 00317-90C	100/70/15 phenol (38)	10	8.6	Fair-Good
-92	100/70/15 phenol (38)	10	7.5	Fair
-103	100/90/5 ethanol (48) phenol (19)	6.5 to 350°F 10.0 to 650°F	5.8	Very good skin but large internal voids
-1	100/90/5 ethanol (48) phenol (19)	6.5 to 350°F 5.0 to 450°F 10.0 to 650°F	5.9	Fair
-2	100/90/5 ethanol (48) phenol (19)	6.5 to 450°F 10.0 to 650°F	7.8	Poor
-3	100/90/5 DC 197 (1) ethanol (48) phenol (19)	6.5 to 350°F 2.5 to 450°F 10.0 to 650°F	6.4	Poor
-4	100/90/5 DC 197 (1) ethanol (48) phenol (19)	6.5 to 350°F hold 45 min 2.5 to 450°F 10.0 to 650°F	12.6	Very poor
-5	100/90/5 ethanol (48) phenol (20)	6.5 to 350°F hold 45 min, remove & grind to -40 mesh; re-foam at 6.5 to 350°F 3.0 to 550°F	4.0	Fair
-6	100/90/5 ethanol (48) phenol (20)	6.5 to 350°F hold 45 min, remove & grind to -60 mesh; refoam at 6.5 to 550°F	7.2	Fair
-8	100/90/5 ethanol (50) phenol (40)	5.0 to 350°F hold 45 min, cool & grind to -60 mesh; refoam at 3.5 to 550°F	6.0	Good
-9	100/90/5 ethanol (50) phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min	6.4	Good
-10	100/80/10 ethanol (50) phenol (20)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min	10.6	Poor

TABLE VIII (Continued)

CROSSLINKED NABI POLYMER FOAM PARAMETER STUDY (Using Half-Esterified Anhydrides)

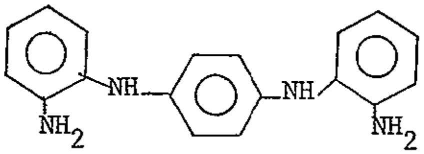
Identification No.	BAB/PA/BTDA Additive (wt. %) Solvent (wt. %)	Heat-Up Rate (°F/min)	Foam Density (lb/ft^3)	Foam Appearance
-11	100/80/10 ethanol (50) phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min	5.5	Poor
-12	100/80/10 ethanol (50) phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min except heat rate 3.5°F/min after required	7.2	Fair
-13	100/80/10 ethanol (50) phenol (20)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350 °F to 550°F at 6.5°F/min except heat rate 3.5°F/min after required	6.0	Poor
-14	100/80/10 ethanol (50) phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min except heat rate 5°F/min after required	5.4	Fair
-15	100/80/10 ethanol (50) phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min except heat rate 5°F/min after required	7.8	Fair
-16	100/70/15 phenol (20)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min except heat up rate 2°F/min after required	7.2	Fair
-17	100/70/15 phenol (30)	5.0 to 350°F hold 60 min, cool & grind to -60 mesh; refoam in hot oven from 350°F to 550°F at 6.5°F/min except heat up rate 2°F/min after required	5.1	Fair

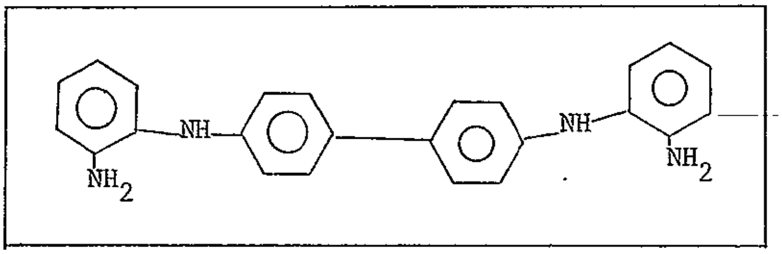
Half esters showed no advantage in either foam quality or density in contrast to polyimide foam technology. It is suggested that further work on these co-monomers with BAB not be considered in depth in any future studies.

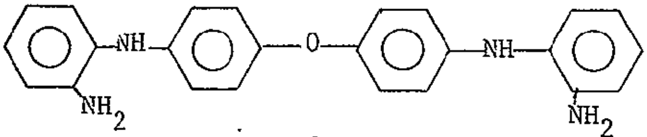
6.0 CONCLUSIONS

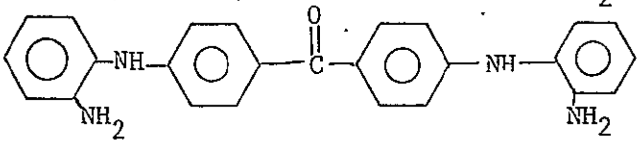
During the current contract period WRD considered a number of alternate NABI forming tetramines in conjunction with requisite aromatic dibasic acid derivatives. The final monomer(s) choice was systematically narrowed and reduced to basically three components from an initial listing of the following:

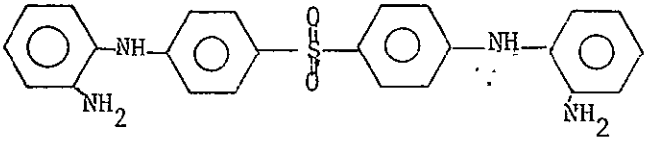
Considered Tetramines



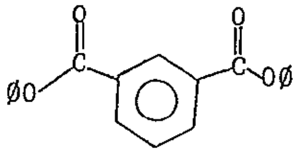


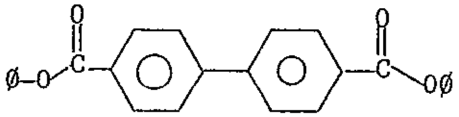


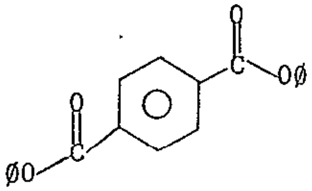


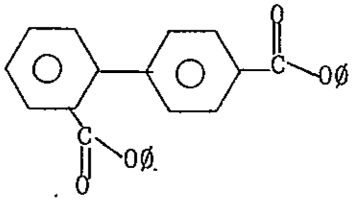


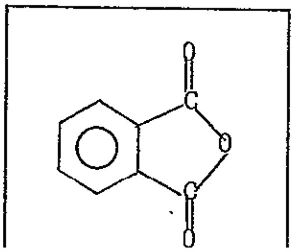
Considered Chain-extending Dibasic Acid Derivatives

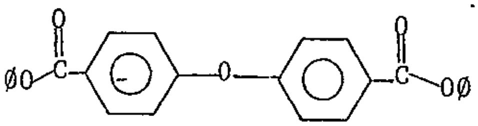












The final three component choice (boxed compounds above) represent the most effective from the criteria established:

1. projected cost
2. anticipated or measured effect on bulk polymer properties
3. anticipated or measured effect on foam formation and properties

Following the monomer selections, a survey was directed toward developing guidelines and limits on foam processing parameters.

Experiments evaluated seven general areas:

1. solvent type
2. solvent content
3. temperature profile
4. prepolymer content
5. crosslink density
6. foaming tool design
7. thickness variation

These interdependent variables cannot be optimized separately and must be adjusted with accumulation of pertinent data.

Rigid foams of acceptable cell structure with densities as low as 2.7 lb/ft^3 were prepared. In general the more highly crosslinked systems were more brittle and more liable to thermal degradation. Optimization of this low cost, high temperature polymeric foam must occur to fulfill needs in both aerospace and commercial applications.

7.0 RECOMMENDATIONS FOR FUTURE WORK

The extensive studies already accomplished should be broadened to include the following, as yet briefly investigated, areas:

1. Nucleation Devices

The admixture of very small (high specific surface area) particles to the prepolymer solutions should allow a smoother release of the volatile blowing agent (flux) at the foaming temperatures. The use of finely divided inorganic fillers would not be expected to seriously detract from the overall thermomechanical properties provided the loading level be kept reasonably low. Slight increases in thermal conductivity should be more than offset by the better regulation and improvements in cell size and geometry. High closed cell content and small cell size are necessary for good insulation characteristics in a foam material.

2. Secondary Blowing Agents

Improvement in both cell quality, flame resistance and polymer toughness may be forthcoming from inclusion of very high boiling partial plasticizers which would only incompletely volatilize through the foam preparation/postcure cycle. Polychlorinated bi- and terphenyls are currently under investigation as potential plasticizers to improve the processability of phenolphthalein polycarbonate under NASA/Ames sponsorship (Contract NAS2-8012). These materials, available in a wide spectrum of boiling point ranges, may nicely serve the proposed multi-purpose ends.

Alternately recommended is the investigation of simple addition/partial replacement of the incumbent phenol flux-blowing agent with higher boiling phenolic materials (e.g., hydroxybiphenly, alkylated phenols, etc.) to provide volatile release throughtout the entire foaming procedure (prior to crosslink induced gelation).

A second alternative would be investigation of blowing agents, per se. Numerous materials are commercially available which decompose within narrow temperature ranges to generate relatively large gas volumes. The inclusion of these materials should yield a volatile "boost" to the rising foam at particular temperatures, best established by an empirical approach.

3. Cell Control Additives

Further investigation of commercially available cell control additives should be carried out. The results acquired to date are inconclusive.

4. Catalysts

The catalysis of the polymerization under study by phenolic materials should be extended to include alternate systems. Investigation of phenolate salts, other heavy metal salts and complexes, as well as representative Lewis acids and bases should prove fruitful. Many commercial, and as yet experimental, systems are the result of almost unique combinations of basic raw materials and "the" catalyst.

5. Prepolymer formation, solvent content, crosslink density, temperature profile, etc. of course should be adjusted according to results and based on previous foam parameter studies.

8.0 EXPERIMENTAL

8.1 MONOMERS

Preparation of 4,4'-Bis[*o*-aminoanilino]biphenyl (BAB)

4,4'-Dibromobiphenyl (156 g, 0.5 mole) was condensed with *o*-nitroaniline (138 g, 1.0 mole) using cuprous iodide catalyst and anhydrous sodium carbonate as an acid acceptor in refluxing nitrobenzene (500 ml) during 16 hours. The resultant 4,4'-bis(*o*-nitroanilino)biphenyl, obtained in 85% yield,was reduced with sodium sulfide in ethylene glycol at 150°C. The yield of 4,4'-bis[*o*-aminoanilino]biphenyl was 132 g (72% yield, mp 211°-222°C) (DSC curve presented in Discussion Section).

Preparation of 1,4-Bis(*o*-nitroanilino)benzene

2-Nitroaniline (55.4 g, 0.4 mole) was reacted with 1,4-dibromobenzene (47.2 g, 0.2 mole) in nitrobenzene (500 ml) in the presence of ∼0.4 g cuprous iodide with sodium carbonate as an acid acceptor (48.0 g, 0.45 mole).at reflux temperature for 30 hours. The yellow suspension gradually became a deep red. The solvent was removed by steam distillation, yielding a dark granular product which was filtered, washed with hot chloroform (250 ml) and dried. Yield, 40.0 g (57%), mp 244.5°-246°C.

Reduction to 1,4-Bis(*o*-aminoanilino)benzene (BABE)

The dinitro precursor [1,4-bis(*o*-nitroanilino)benzene, 10.5 g] was suspended in 500 ml of MeOH with ∼2 g of Raney nickel and heated to reflux. Hydrazine (60 ml) was carefully added over a 2 hour period. After complete hydrazine addition, the mixture was refluxed an additional hour, treated with charcoal, filtered and the solvent removed under reduced pressure to a residual volume of ∼50 ml. After storing overnight in the refrigerator, white crystals (slight purplish tinge) of the desired tetramine were isolated and dried. Yield, 6.5 g (75%), mp 161.5°-162.0 g.

Preparation of 4,4'-Diacetyl Diphenyl Ether – Aluminum chloride (133 g, 1.0 mole) was slurried with 250 ml of methylene chloride and cooled to 0°C with an ice bath (salt). A solution of diphenyl ether (85 g, 0.5 mole) in acetyl chloride (78.5 g, 1 mole) was added over 30 minutes at <10°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The orange solution was poured into ∼500 ml of ice/hydrochloric acid and rapidly stirred. A white precipitate formed which was collected, dissolved in benzene (400 ml), extracted with 10% aqueous sodium carbonate and dried over magnesium sulfate. The product was isolated by treating the hot benzene solution with charcoal, filtering, adding hexane to turbidity and cooling. White crystals (98.0 g, 57% yield) were collected (mp 105°-106°). Concentration of the mother liquors yielded an additional 46 g (mp 104°-106°, 26% yield).

Preparation of 4,4'-Oxybis(benzoic acid) — A slurry of commercial bleach (5.25% sodium hypochlorite, 1700 ml), sodium hydroxide (80 g, 2.0 mole) and 4,4'-diacetyldiphenyl ether (51.0 g, 0.3 mole) was heated to ~70°C where chloroform evolution occurred with a concomittant exotherm to 82°C. The reaction was held at ~80° until almost all the solids had dissolved. The insoluble material (1.3 g starting material)was filtered off and the cooled solution was treated with sodium hydrosulfite to destroy excess hyopchlorite. The clear solution was carefully acidified and the collected white product repeatedly washed with water and dried to yield 49.4 g of 4,4'-oxybis(benzoic acid) (mp 332°-334°C).

Preparation of 4,4'-Oxybis(benzoyl chloride) — The crude acid from above was slurried with thionyl chloride(~250 ml) containing a few drops of DMF and heated to reflux under nitrogen for ~0.5 hr. The resultant clear yellow solution was concentrated to dryness to yield an off-white solid. Ligroine (90°-120°, 200 ml) was added and the slurry was heated to reflux (under nitrogen), treated with charcoal and filtered hot. After cooling, large white crystals were isolated and again recrystallized from ligroine to yield 35.0 g (70%) of white crystals (mp 90°-91.5°, DSC scan shown in Figure 13).

8.2 POLYMERS

Polymerization of BAB and Isophthaloyl Chloride

To a stirred solution of 4,4'-bis[o-aminoanilino]biphenyl (3.665 g, 0.01 mole) in DMAC (25 ml), isophthaloyl chloride (2.030 g, 0.01 mole) was added portionwise during 0.5 hr at 10°-15°C. The resulting green solution was stirred overnight at ambient temperature. In the morning, an amorphous solid had precipitated that redissolved upon warming the solution to 70°C. This material was isolated by drowning in water. A yellow amorphous solid was obtained (4.7 g) that did not melt below 300°C. An infrared spectrum showed an absorption at 1660 cm-1 indicative of an amide group.

Preparation of Polyamide from BAB and 4,4'-Oxybis(benzoylchloride) — Dimethyl acetamide was dried over 4A molecular sieves and then doubly distilled over calcium hydride (heart cuts collected) using flame dried glassware and drierite filled U-tube vent.

BAB (3.6645 g, 0.0100 mole) was dissolved in dry DMAC (10 ml) in a 250 ml three-necked flask fitted with a mechanical stirrer, side-arm addition funnel and thermometer. Dry nitrogen was passed over the mixture and a solution of 4,4'-oxybis(benzoylchloride) (2.9511 g, 0.0100 mole) in dry DMAC (10 ml) was added at 0°C over a 65 minute period. The addition rate was slowed toward the end of this period. Stirring was continued overnight at ambient temperature.

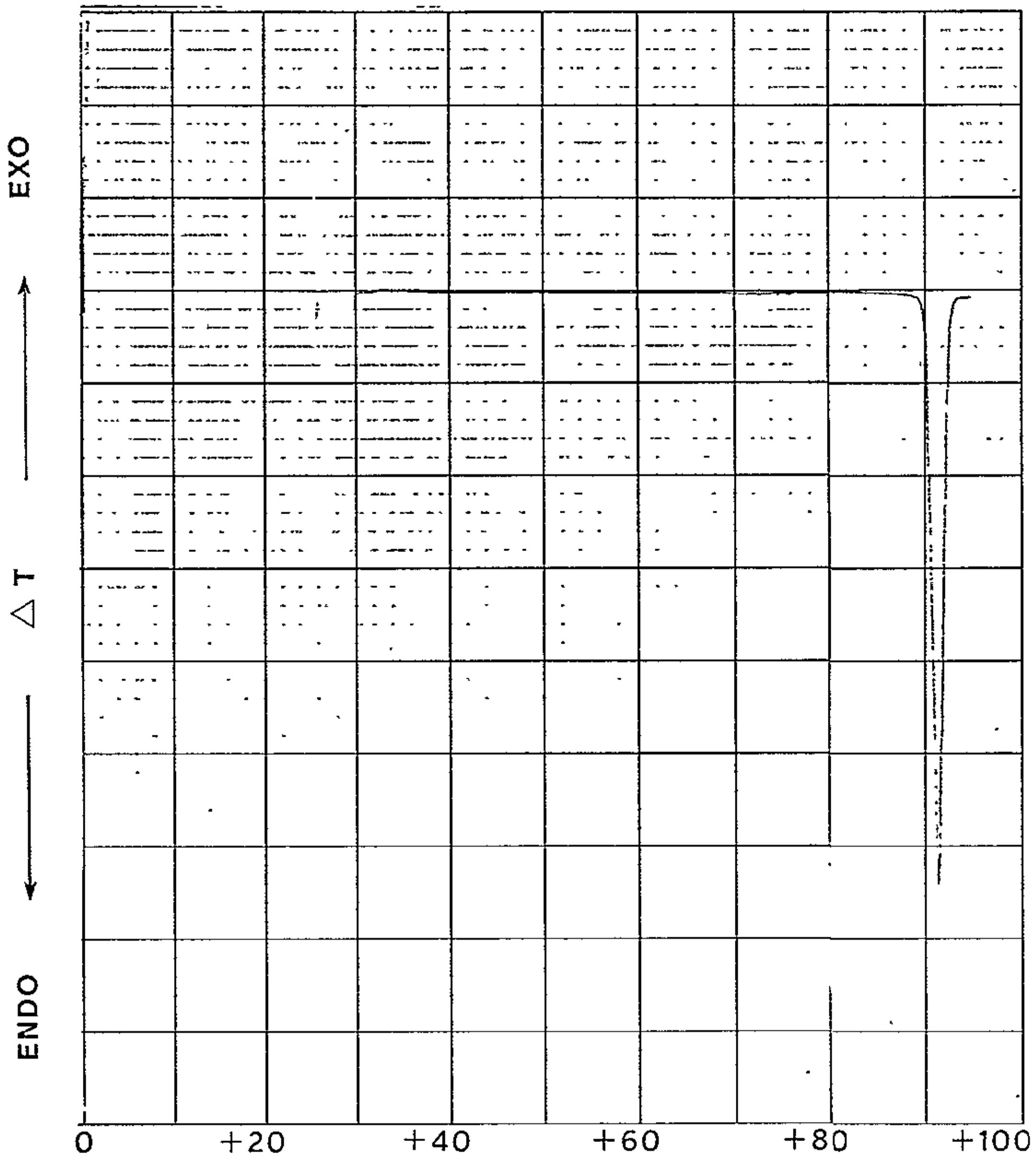


Figure 13. DSC of 4,4'-Oxybis(benzoylchloride),
$\Delta T = 3°C/min$

The viscous solution was poured into churning methanol to yield a tough fibrous polymer which was washed (blender) with 5% aqueous sodium bicarbonate, water and methanol. The off-white powder was dried for 16 hours at 80°C in a vacuum oven. Yield 5.80 g (ηinh = 0.83 in tetrachloroethane/phenol, 75/25).

Polymerization of BAB and Diphenyl Esters

Typical preparation using diphenyl isophthalate - in a polymerization tube under nitrogen 4,4'-bis[o-aminoanilino]biphenyl (0.01 mole, 3.665 g) was dissolved in ca. 10 ml of phenol. This solution was introduced into a preheated oil bath at 190°C. To this light amber solution diphenyl isophthalate (0.01 mole, 3.183 g) was added and the solution heated to 250°C during 3 hours. Pump vacuum was applied to the yellow melt for 25 minutes at 250°C. The molten mass did not foam, however, and was removed from the oil bath and allowed to cool under vacuum. The prepolymer was relatively brittle and exhibited an inherent viscosity (ηinh) of 0.07 (0.5% in m-cresol @ 25.0°C). The prepolymer was pulverized and introduced into an oil bath preheated to 400°C for 1 hour. The polymer failed to foam (even when vacuum was applied) and remained molten after this thermal treatment. Upon cooling, the polymer broke up readily when pulverized in a mortar. Volatile weight loss during the final cure was 10.1%. The ηinh was 0.27 (0.5% in m-cresol @ 25.0°C).

Polymerization of BAB and PA

In a polymerization tube under nitrogen 4,4'-bis(o-aminoanilino)-biphenyl (0.01 mole, 3.665 g) was dissolved in ca. 10 ml of phenol. This solution was introduced into a preheated oil bath at 170°C and phthalic anhydride (0.01 mole, 1.481 g) was added. The homogeneous solution was heated to 250°C during 4 hours with gentle evolution of phenol. At this time, there remained a clear, amber viscous melt. After 1 hour at 250°C, pump vacuum was applied for 10 minutes. The polymer foamed during this period and retained structural integrity as the polymerization tube was removed from the oil bath and allowed to cool under vacuum. The resulting foamed prepolymer was tough with an ηinh of 0.26. The prepolymer was further cured for 1 hr @ 400°C (N_2). During this thermal treatment, the polymer fused, foamed and resolidified within a few minutes. After cooling, the foamed mass was extremely tough and resisted pulverization in a mortar. A volatile weight loss of 8.3% was recorded during this cure and the ηinh was 0.79 (0.5% in m-cresol at 25.0°C).

BABE Polymerizations

Polymerizations using BABE with various diphenyl esters and phthalic anhydride followed the same procedure as outlined above with suitable adjustment for the various stoichiometries.

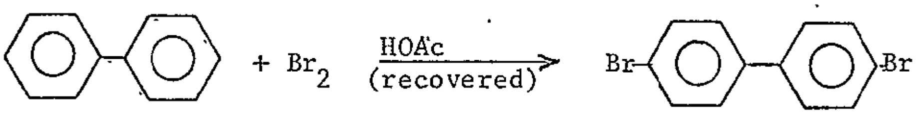
APPENDIX

PRELIMINARY COST EVALUATION

9.0 PRELIMINARY COST EVALUATION

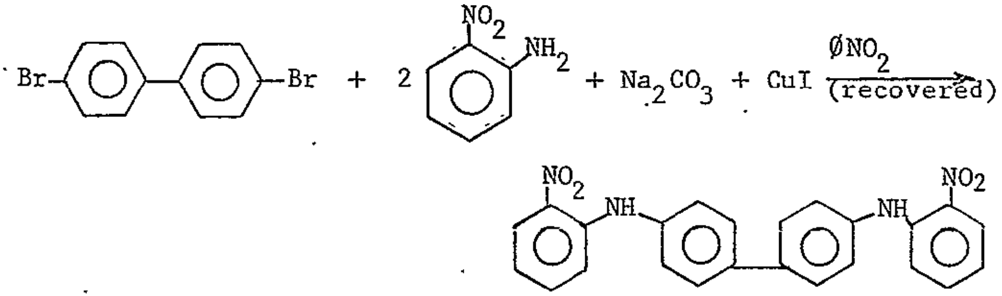
The following data is a point by point breakdown of material costs for production of NABI foam from 4,4'-bis(o-aminoanilino)biphenyl, phthalic anhydride and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (at 5% crosslink level). The raw material costs are based on Chemical Marketing Report dated April 28, 1975 and are representative of high volume quantities. No labor costs are included since these are a direct function of equipment, production volume, etc.

Step I - All reactions at lb-mole scale



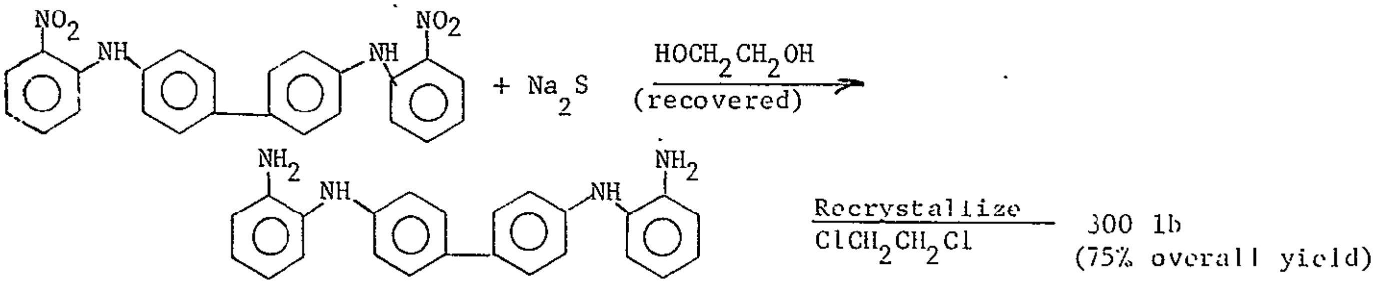
Material	Charge Weight (lb)	Cost/lb ($)	Cost/Run
Diphenyl	154	0.37	56.98
Bromine	170	0.56	95.20
Acetic Acid*	300	0.13	7.65
			156.83

Step II -



o-nitroaniline	280	0.77	215.60
Sodium carbonate	110	0.04	4.40
Cuprous iodide	5	1.50	7.50
Nitrobenzene*	500	0.19	14.25
			241.75

Step III

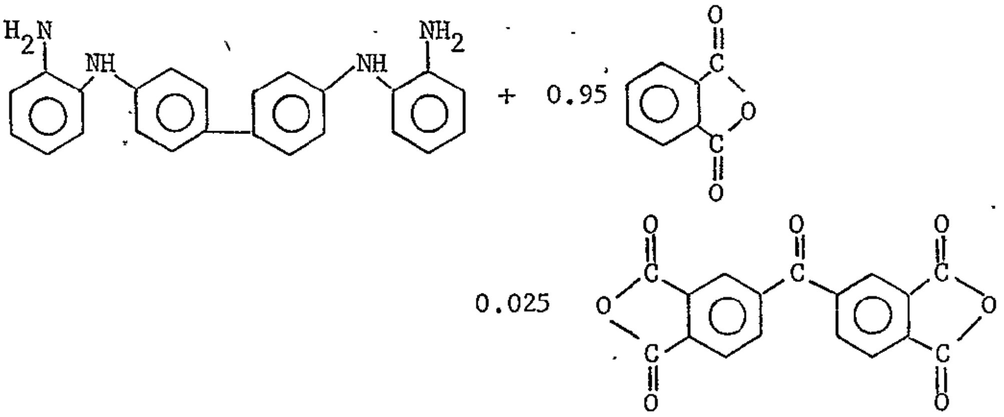


Material	Charge Weight (lb)	Cost/lb ($)	Cost/Run
Sodium sulfide	200	0.08	16.00
Ethylene glycol	500	0.26	14.00
**Ethylenedichloride	5000	0.11	123.00
			153.00

Step I - 156.83
Step II - 241.75
Step III - 153.00
551.58

$\frac{\$551.58}{300\ \mathrm{lb}}$ = $1.83/lb materials cost for NABI tetramine using current recrystallization solvent.

Polymer (foam) costs with current technology (20% phenol)



4,4'-Bis-(o-anilino)biphenyl	366	1.83	669.78
Phthalic anhydride	140.6	0.26	36.56
3,3',4,4'-benzophenonetetracarboxylic dianhydride	7.05	2.50	17.63
*Phenol	100	0.27	3.25
			$727.12
			460 lbs

$\frac{\$727.12}{460\ \mathrm{lbs}}$ = $1.58/lb materials costs for finished foam

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* Recovered - assume 95% recovery (5% loss) + 0.02¢/lb recovery cost

** Not an optimum recrystallization solvent, certainly others more efficient.

10.0 REFERENCES

1. V. V. Korshak, et al., Dokl. Akad. Nauk SSSR 181(4), 885 (1963) CA 69 89788h (1968).

2. E. V. Titov, et al., Ukr. Khim, Zh. 37(8), 790 (1971); CA 75 151228e (1971).

3. Yu. I. Beilis, Zh. Obshch. Khim. 40(4), 745 (1970); CA 73 41221i (1970).

4. R. J. Popova, et al., Zh. Org. Khim, 6(5), 1049 (1970); CA 73 34485j (1970).

5. V. V. Kudryavtsev, et al., Sin. Strukt. Svoistra. Polim, 3 (1970); CA 76 113607r (1972).

6. A. E. Lutskii, et al., Zh. Fiz. Khim, 42(8), 1861 (1968); CA 70 3132a (1969).

7. P. Beltrame, et al., Tetrahedron, 24(7), 3043 (1968).

8. C. Dell'Erba, et al., Tetrahedron, 27(9), 1807 (1971).

9. B. E. Jennings, J. Polymer Sci., Part C, No. 16 (2), 715 (1967).

10. A. A. R. Sayigh, B. W. Tucker, H. Ulrich, The Upjohn Co., US Patent 3,708,439 (1973).

11. V. V. Korshak, et al., Macromolecules, 5(6) 807 (1972).

12. W. Wrasidlo, J. Polymer Sci., A-2, 9, 1603 (1971).

13. P. M. Hergenrother, J. Macromol. Sci.-Revs. Macromol. Sci. C6(1), (1971).