

Preparation of a Polyimide Foam*

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Synopsis

The reaction of phenyl isocyanate with phthalic anhydride to form N-phenylphthalimide is strongly solvent dependent and catalyzed by tertiary amines. Water and alcohol promote imide formation, but Lewis acids and organometallic compounds are ineffective. In DMSO solvent, benzophenone tetracarboxylic dianhydride (BTDA) and polymethylene polyphenol isocyanate (PAPI) polymerize with the evolution of carbon dioxide to yield a foamed polyimide. The solvent-freed open-celled foams exhibit exceptional fire resistance and thermal stability.

INTRODUCTION

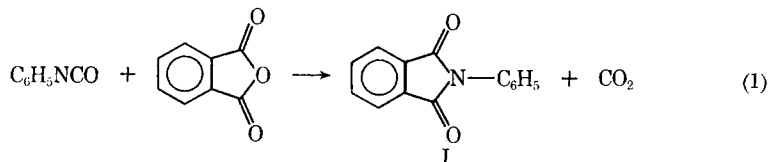
Aromatic polyimide polymers of various types are being developed and used in increasing amounts because of the better thermal stability and resistance to fire inherent in the imide structure.¹⁻⁴ The most generally used method of polyimide synthesis requires the dehydration of an amide acid formed from a diamine and dianhydride.^{5,6} An alternative approach to polyimide synthesis exists in the literature; isocyanates and anhydrides react to form imides and carbon dioxide.⁷⁻⁹ Despite the implied utility of this reaction for making polyimides, relatively little is known about it. The first report of an aromatic imide, N-phenylphthalimide, was recorded by Dains¹⁰ as the reaction product of phthalic anhydride and phenyl isothiocyanate; Hurd and Prapas¹¹ prepared the same product from the reaction of phenyl isocyanate and phthalic anhydride for 19 hr at 180°C (85% yield). Hurd and Prapas found that the reaction could be carried out in refluxing pyridine (63% yield) and that perchloric acid was ineffective as a catalyst. From this evidence they deduced a mechanism involving reaction of partially polarized anhydride and isocyanate functions.

We have examined this reaction more fully with the objectives of preparing polyimide polymers and of conducting the reaction such that the carbon dioxide evolved would serve as the blowing agent for polyimide foams. This report describes the results of our study.

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RESULTS

We chose as a model system the reaction of phenyl isocyanate with phthalic anhydride, eq. (1):



The reaction could be followed readily by measuring the carbon dioxide evolved. Product N-phenylphthalimide was determined by isolation from the reaction mixture and was identified by infrared spectral comparison with authentic material. The experiments were conducted by heating the solution, noting the temperature at which gas was first evolved, and then raising the temperature slowly to maintain a moderate evolution of gas. The reaction was considered complete when no further gas was evolved at the reflux temperature of the solvent. The results for a number of solvents are shown in Table I.

TABLE I
Effect of Solvent on Imide Yield

Solvent	Gas evol. temp., °C	Final temp., °C	Yield, %	Time, hr	CO ₂ yield, %
DMSO	55	189	79	0.8	100
DMAc	66	168	74	1.8	84
HMPA	50	220	30	3.5	89
DMF	84	158	36	1.3	100
xylene	—	126	0	2.5	0
DOP	200	252	65	3.5	90
pyridine	—	120	13	143.0	—
diglyme	65	162	48	5.5	39

Clearly, polar solvents favor the reaction in terms of reaction time and initial gas evolution temperature. In nonpolar solvents such as dioctyl phthalate, or without solvent, high temperatures are required for any reaction at all. The marked discrepancies between carbon dioxide yields and imide yields observed in some solvents most probably arise from reaction of phenyl isocyanate with the solvent. Certainly with DMF amidine formation is known,^{12,13} and DMAc may react similarly.^{13,14} HMPA reacts extensively with phenyl isocyanate at elevated temperatures.^{15,16} Some reaction with DMSO may have occurred as well.^{13,15-17}

In DMSO the reaction does respond to the presence of bases. In Table II are presented the effects of selected catalyst-solvent combinations on the reaction. The lower initial gas initiation temperature observed with the base-DMSO systems as compared to the acid-diglyme systems indicates a base-catalyzed process.¹⁸⁻²¹ Except for stannic

TABLE II
Effect of Catalyst on Imide Yield

Solvent	Catalyst	Gas evol. temp., °C	Final temp., °C	Yield, %	Time, hr	CO ₂ yield, %
DMSO	—	55	189	79	0.8	100
DMSO	DABCO	25	189	79	2.3	100
DMSO	Et ₃ N	25	189	78	2.5	92
DMSO	Sn(Oct) ₂	25	189	70	7.5	86
DMSO	Pb(naph) ₂	30	189	87	2.5	86
DMSO	Bu ₃ P	30	189	67	5.5	94
diglyme	—	65	162	48	5.5	39
diglyme	H ₂ O	48	162	54	3.0	54
diglyme	BF ₃	57	162	45	2.3	45
diglyme	SnCl ₄	87	162	89	10.0	75

chloride-diglyme, the yields of imide are also consistent with this hypothesis.

The lack of reaction in pyridine seems inconsistent, however, with the results of Hurd and Prapas¹¹ who had observed a 63% yield in 5 hr in this solvent. We were unable to duplicate their yields in dry pyridine; but with as little as 0.4 equivalents of water (based on isocyanate) in the pyridine, comparable rates and excellent yields were obtained.

Subsequent investigation of this phenomenon revealed that proton-containing bases such as water and alcohols facilitate imide formation. Water could cause the hydrolysis of isocyanate to 1,3-diphenylurea, and ureas are known to react with anhydrides to form imides.²² In the case of alcohols, carbamates could form and provide an alternative pathway to imide.²³ To check this possibility, the effect of ethanol on the isocyanate-anhydride reaction was examined in refluxing pyridine solution. The rate of formation of imide, as measured by infrared spectra, is in fact slightly enhanced by the addition of ethanol. The reactions were followed until no phthalic anhydride was detectable. The relative reaction rates and product distributions are shown in Table III.

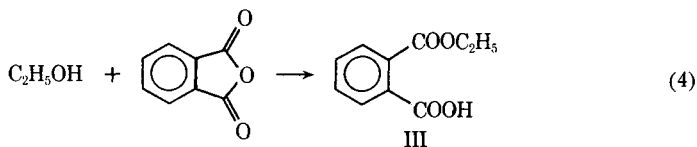
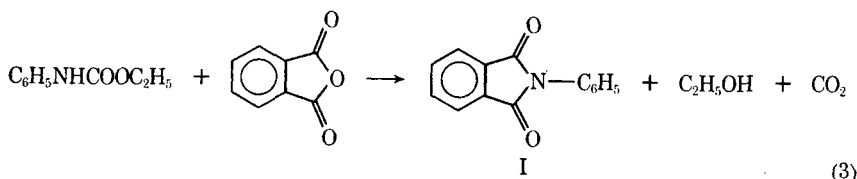
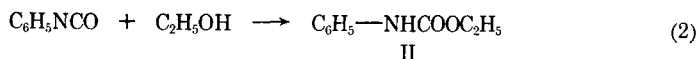
The addition of ethanol causes rapid formation of the carbamate, eq. (2). As long as anhydride is present, the carbamate converts slowly to imide

TABLE III
Effect of Ethanol on Phthalic Anhydride-Phenyl
Isocyanate Reaction in Refluxing Pyridine

Equivalents of ethanol added	Relative rate	Products, mole-% ^a		
		I	III	II
none	1	—	—	—
0.1	5	90 (95)	3 (5)	4.4 (5)
0.5	10	79 (75)	22 (25)	26 (25)
1.0	9	60 (50)	27 (50)	39 (50)

^a Numbers in parentheses refer to calculated yields; see text.

with liberation of carbon dioxide and ethanol, as in eq. (3). The ethanol reacts preferentially with isocyanate to reform carbamate, eq. (2), but ultimately consumes anhydride to form the half ester III, eq. (4). Apparently III cannot function as the anhydride does, or at least not as efficiently, for the reaction slows down considerably once anhydride is consumed. Continued heating will slowly produce more imide at the expense of II and III. The figures in parentheses in Table III are the product distributions calculated according to eqs. (2)–(4).



Recently, Meyers²⁴ has published his results on the reaction of pyromellitic dianhydride with 4,4'-diisocyanatodiphenylmethane under similar reaction conditions. He has proposed a seven-membered cyclo-adduct of the anhydride and isocyanate functions. In our opinion, his spectral evidence is more suggestive of a hydrolysis reaction product resulting from water in the solvent or starting materials. As we have indicated above, water and other nucleophiles can accelerate the isocyanate–anhydride reaction in some solvents.

POLYMERIZATION

The results on the model compounds were used to design a low-temperature polymerization system to produce a rigid foam. (A high-temperature process to produce a rigid polyimide foam is described by Frey.²⁵) In order to obtain the fastest reaction rate at ambient conditions, we wanted a polar solvent system, a basic catalyst, and an alcohol. The system selected employed DMSO as solvent and a tertiary amine-containing polyol. The polyol performed the dual functions of increasing the reaction rate and providing a polymer matrix to trap the generated carbon dioxide. Without it, too much of the carbon dioxide escaped, resulting in a high-density, extremely hard microcellular material. The surfactant was chosen to afford uniform cell structure and to provide cell opening at the proper time to vent the excess carbon dioxide.

The foam ingredients were compounded as described in the experimental section under "Foam Systems." The isocyanate and benzophenone tetra-

TEMPERATURE PROFILE OF CURING BUN

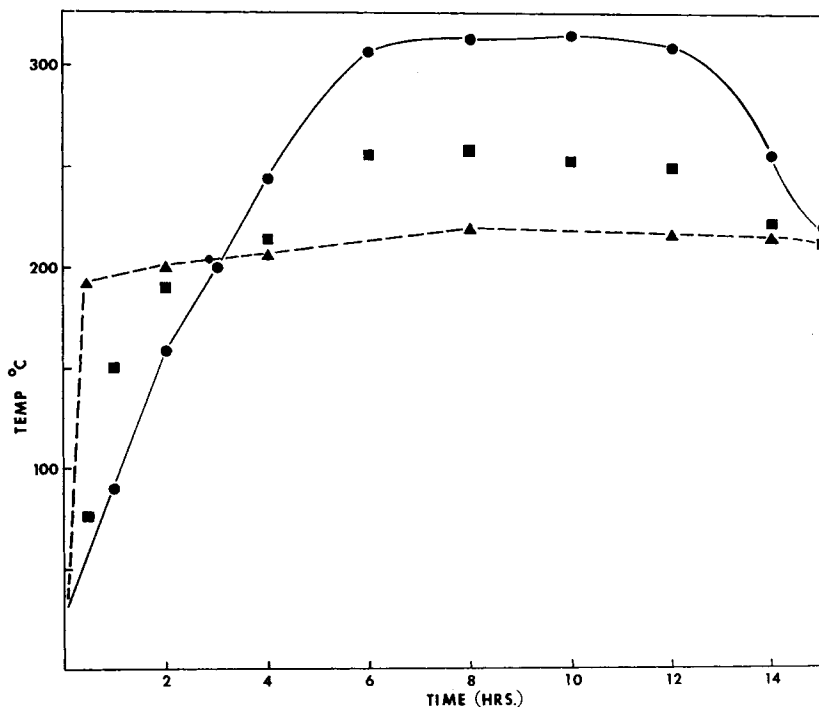


Fig. 1. Temperature profile of curing bun: (●) center of 4.5-in. thick bun; (■) 1 in. from surface; (▲) surface of bun.

carboxylic dianhydride (BTDA) in equivalent amounts were thoroughly mixed to a viscous, but tractable slurry. To this was added with vigorous mixing a solution of the other components in DMSO. The foaming process commenced within a few seconds and proceeded with considerable heat evolution. Large buns could be poured using the usual urethane metering and mixing equipment.

Although the foams so produced possessed good physical properties, removal of the DMSO was desirable. Since the foams were predominantly open-celled, most of the solvent, up to 80%, could be stripped readily at 100°C and 1–10 mm pressure. Some malodorous decomposition products of DMSO (dimethyl sulfide, dimethyl disulfide, dithiomethoxymethane)²⁶ were removed also. Removal of the remaining DMSO required heating the foams to 200–230°C for short periods (1–2 hr).

During this second stage of heating, a characteristic exothermic reaction was observed in all the foam samples. In thick (5 × 12 × 12 in.) sections, this exotherm was sufficient to raise the internal temperature of the sample 80–120°C above ambient and caused some charring on the earlier samples

TABLE IV
Foam Elemental Analyses

	C	H	N	S	Ash
Theory (imide + urethane)	74.3	4.0	6.3	0	0
A (mild cure)	70.6	3.8	6.6	0.5	0.9
B (severe cure)	73.9	2.7	6.7	0.03	1.4

(see Fig. 1). The exotherm occurred in the absence of oxygen and in samples devoid of excess isocyanate or anhydride as nearly as could be determined by infrared techniques. At the end of the curing cycle, the foams were essentially sulfur free and analyzed reasonably well for mixed poly(urethane-imide) (Table IV).

The excellent thermal stability and fire resistance of the foam are detailed in Table V. Samples held at 450°F (232°C) in air for 14 days suffered weight losses of less than 2% with no loss of compression strength

TGA PROFILE OF POLYIMIDE FOAM

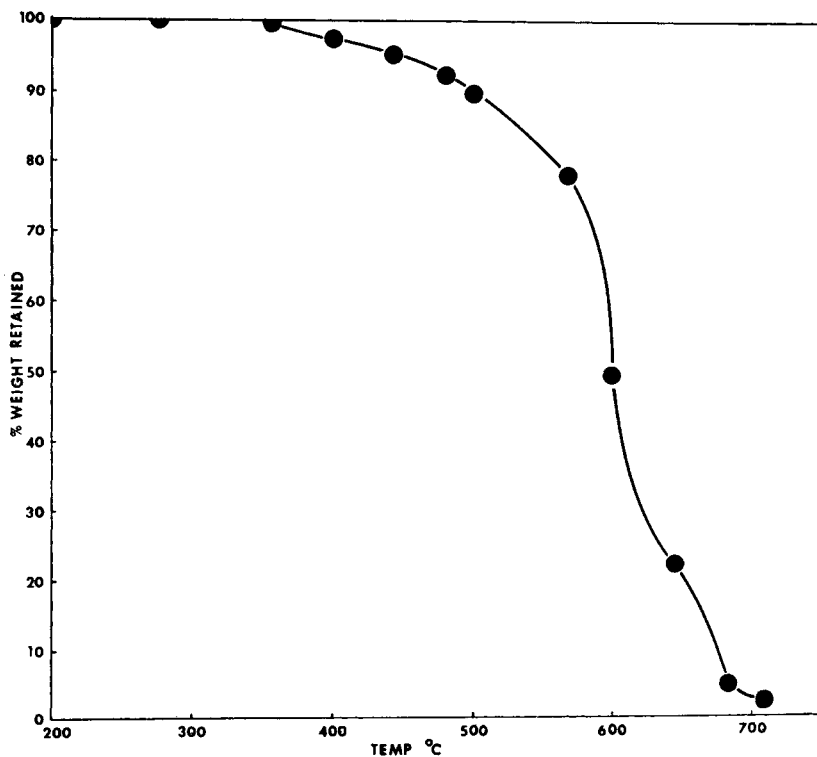


Fig. 2. TGA profile of polyimide foam.

TABLE V
Properties of Polyimide Foam

Density	3.97 lb/ft ³
K-Factor (open cell)	.26 (Btu)(in.)/(°F)(hr)(ft ²)
Compression, // ^a	34.9 psi
⊥ ^b	45.6 psi
Aging, ΔV	
humid, 158°F, 28 days	+1.2 %
dry, 200°F, 28 days	-0.6 %
dry, 450°F, 14 days	-6.1, 2% wt loss
Compression	
post dry age, 450°F, // ^a	41.4 psi
ASTM E-84 Tunnel	
flame spread rating	10

^a Parallel to direction.

^b Perpendicular to rise direction.

A 6% weight loss was measured in 10 min at 842°F (450°C). TGA data, shown in Figure 2, were determined by holding the sample at constant temperature for 5 min in 40° increments from 240° to 720°C.²⁷

EXPERIMENTAL

Solvent Systems

Pyridine and DMSO were reagent-grade materials dried over Linde 4A molecular sieves. DMF, DMAc, and DOP were reagent-grade solvents used as is. Diglyme was redistilled. *p*-Xylene was distilled and stored over molecular sieves. Phenyl isocyanate was Eastman White Label-grade distilled prior to use, bp 87–88°C at 65 mm.

Model Systems

The apparatus consisted of a 250-ml flask fitted with a stirrer, thermometer, and reflux condenser connected to a manifold which was joined to a wet-test meter and carbon dioxide cylinder.

The flask was charged with 14.5 g (0.1 mole) of phthalic anhydride in 50 ml of solvent, and 11.9 g (0.1 mole) of phenyl isocyanate in 50 ml of solvent was added rapidly. The system was quickly flushed with carbon dioxide and the wet-test meter reading recorded. If no gas was evolved at room temperature, heating was begun and the gas evolution was followed with time and temperature. One-half hour after gas evolution ceased, the flask was cooled to room temperature and the final gas volume was obtained. The product N-phenylphthalimide precipitated from the cooled reaction solvent and was collected and weighed. Where necessary, the solvent was concentrated and second crops of product were obtained. The product, mp 205.5–208°C (lit. mp 204–204°)¹¹ was identified by comparison of its infrared spectrum with that of authentic material.

Foam Systems

A premix of the A component was prepared by vigorous mixing of benzophenone tetracarboxylic acid dianhydride (BTDA) (Gulf Oil Corporation, New York) and PAPI (The Upjohn Co., Kalamazoo, Michigan); the amount of isocyanate was equivalent to the anhydride plus polyol. The B component was composed of a solution in DMSO (or other solvent) of the basic polyol and surfactant. The two components were rapidly mixed and allowed to foam. Toward the end of the strongly exothermic foaming process, sulfurous fumes from the DMSO decomposition were detectable. At the end of the rise, the foam was fairly soft, but was cured to a rigid foam in 1–2 hr.

The solvent was removed from the foams by heating in a vacuum oven for 6–12 hr at 100–110°C and 1–10 mm, and finally at 200–230°C in a nitrogen-purged oven for 1–2 hr. It was noted that thermocouples inserted into the interior of the foam were consistently hotter than the foam surface, due to an exothermic process occurring in the foam. A 5 × 12 × 12-in. block of foam registered 300°C at its center in a 210°C oven. No exotherm was observed at oven temperatures below 150°C. The infrared spectra (KBr disk) of the cured foams showed imide bands at 5.6 and 5.8 μ , and the benzophenone carbonyl at 6.0 μ . The absence of DMSO solvent bands at 9.5–9.75 μ , present in the uncured foams, indicated essentially complete removal of solvent.

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