



Project Summary

Synthesis of Aromatic Polyimides for Use as Solid Sorbents

R. A. Markle

High surface area, high sorbent, polyimide powders designed to replace or complement Tenax[®] GC were obtained in high yield from pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenylsulfone (DADS) by precipitation polymerization in tetrahydrofuran (THF) solvent. The intermediate polyamide-acid powders were cyclodehydrated to high BET surface area (25-50 m²/g) polyimide powders by slowly heating to 230-240 C in an evacuated rotary evaporator. About 40 weight percent of the powder was in the 200-500 μm particle diameter range desired for sorption sampling of vapor-phase organics. The polyimide powders are obtained as 0.01-1.0 μm diameter, loosely agglomerated, platelets and rod-like particles. Preliminary evaluation of the powder sorption/desorption characteristics with benzene vapor shows them to have greater capacity than Tenax but to have less desirable breakthrough characteristics due to slower sorption kinetics ascribed to inadequate connecting pore volume. However, desorption occurs smoothly and quantitatively at 100 C.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Hazardous organic vapors may be present in air at concentrations as low as a few nanograms per cubic meter

and still present a potential biological threat. Preconcentration of such vapors is thus necessary in many cases to provide sufficient sample for accurate air analysis. The available methods for preconcentrating vapor-phase organics include the use of sorbent cartridges, cryogenic systems, and solvent impingers. Preconcentration using porous polymeric sorbents has been the most successful and useful procedure. Tenax GC is the most used and most versatile sorbent commercially available at present.

However, Tenax GC (porous powder poly-2,6-diphenyl-para-phenylene oxide) has several performance deficiencies that would be very desirable to correct. These include low retention and breakthrough volumes for high volatility organic compounds. In fact, the more polar volatile organics such as acrylonitrile and acetonitrile, vinyl chloride, methylene chloride, acrolein, and propylene oxide cannot be adequately analyzed using Tenax GC. In addition, Tenax GC is subject to high background, or column bleed, due to slow release of prior adsorbed compounds or slow thermal breakdown of the polymer structure. Also, the elution or artifact peaks is a particular problem.

Consequently, the intent of this work was to prepare new porous polymeric sorbent powders for use in determining air concentrations of potentially hazardous vapor-phase organic compounds. New sorbent materials that are superior to Tenax GC needed to be developed with as many of the following properties as possible:

- Greater adsorption capacity for the

- more volatile vapor-phase organics
- Greater selectivity in adsorption and thermal release of multiple pollutants
- Improved thermal properties (i.e., minimal background or bleed contribution to eluted volatiles for analysis)
- Minimal artifacts formed during collection of reactive organic compounds
- Low water vapor retention
- Resistance to reactive inorganic gases such as ozone, NO_x and SO_x.

Procedures

Straightforward, practical procedures for purifying to 99.9+ percent were developed for all four monomers—PMDA, DADS, DADM, DCPDA. (DADM is 4,4'-diaminodiphenylmethane and DCPDA is 2,6-dichloro-p-phenylenediamine.) These monomers are usable to prepare reproducibly the three desired polyimides as their fine-particle-precipitated polyamide-acid precursors in tetrahydrofuran. Total polymer yields, as desired, met or exceeded 100 grams from three polymerizations of each monomer pair (from polymerizations of DADS/PMDA). The molecular weights (M_v) of the polyamide-acid intermediate polymers were consistent with those reported by prior workers. The DADS polymers had an M_v of 7,000 with the M_v for DCPDA and DADM polymers about 3,000 and 10,700 respectively.

The polyamide-acids were readily cyclodehydrated in dry powder form to the polyimides. Based on TGA results, the polyimides are all stable to ~250 C with only minor weight losses of 1-3 weight percent, which are attributable to physical losses of water and adsorbed solvents. Above ~250 C the weight losses continue at an accelerated rate, indicating that chemical changes are occurring.

The polyimides are recovered after the cyclodehydration as powders which in two cases (DADS and DCPDA polyimides) are recovered with appreciable fractions in the desired particle size range of 200-500 μm . It is likely that the percentage of this particle size fraction can be increased by manipulating certain polymerization variables, such as the PMDA addition rate and the reaction temperature/time cycles and by standardizing and controlling the powder handling and size classification procedures.

Results and Discussion

Approximately 100 grams or more of three experimental polyimide powder sorbents based on pyromellitic dianhydride (PMDA) reaction with one of three carefully selected aromatic diamines including 4,4'-diaminodiphenylsulfone (DADS), 2,6-dichloro-p-phenylenediamine (DCPDA), and 4,4'-diaminodiphenylmethane (DADM) were prepared in tetrahydrofuran (THF) solvent and characterized. These polyimides were selected for scale-up studies on the present program as the most promising sorbents of 61 polyimides synthesized and studied in a prior EPA program.

The DADS/PMDA polyimide powders were found to be reproducibly obtainable products with excellent potential sorbent characteristics. These polyimides appear to have promise either as replacements for Tenax GC or as complementary sorbents used in tandem with Tenax. The DCPDA and DADM polyimides, on the other hand, are not promising candidates based on a preliminary assessment of their properties.

The polyimides were prepared in three approximately equalized batches to obtain a measure of the reproducibility of the processes and their products. The procedures used in the prior work were followed as closely as possible. In this convenient precipitation polymerization procedure, the monomers, purified to 99.9+ percent purity, are reacted in tetrahydrofuran, which is a solvent for the monomers but a nonsolvent for the intermediate polymer products (polyamide-acids). The polymers are thus obtained directly as finely divided solids of approximately the desired mesh size when dried. These powders are then converted chemically to the desired polyimides by a thermal cyclodehydration process which involves heating under vacuum to 230 C in a rotating reaction chamber.

How reproducible these processes are and whether the products obtained have sorption properties that make them suitable for field or commercial use as reusable adsorption resins for collection and analysis of vapor-phase organics in ambient air needed to be determined. The important polymer properties that might affect their ultimate sorbent performance were:

- Polymer yield
- Molecular weight
- Powder particle size
- Powder surface area (BET)

- Thermal stability
- Sorption characteristics

All the polyimides were obtained in >90 percent yields. The promising DADS polyimides could in fact be obtained in nearly quantitative overall yield. The important question not yet answered is how much of the product can be prepared in the desired macroscopic (200-500 μm) particle size range that is most practical for actual use in packing columns for air pollution monitoring. In the present work about 30-40 percent of the DADS products were in this range, while the DCPDA product were with one exception 50-67 percent in this range. The DADM products were only 3-5 percent in the desired range with the bulk of the products (85-91 percent) in the range of <105 μm .

The surface areas were determined by the BET nitrogen adsorption technique (Table 1). This method is the most accurate technique available for measuring absolute surface areas, especially in the range $\geq 10 \text{ m}^2/\text{g}$. The value found for Tenax (25 m^2/g) is in agreement with the manufacturer's and reported values. The surface areas of the DADS polyimides (with two exceptions) were quite reproducible in the range 26-38 m^2/g . One value of 50 m^2/g was determined (Polyimide No. 3, <212 μm particle size). Interestingly another sample (>212 μm particle size) of the product measured 34 m^2/g . This is very close to both the mean and the median value for all the DADS Polyimide surface areas (32 m^2/g). These values may be greater than those found for the standard commercial product Tenax GC (24 m^2/g). However, the experimental error in measurement may be as great as ± 50 percent so that $34 \pm 17 \text{ m}^2/\text{g}$ and $25 \pm 12 \text{ m}^2/\text{g}$ is perhaps a more correct way to express the results, showing that they do not differ from Tenax to a statistically significant degree. It is concluded that the DADS polyimide surface areas are at least as high as Tenax and that values significantly greater than 32 m^2/g , can probably be obtained by optimizing the DADS polymerization and product recovery procedures.

The polyimide made from PMDA, DADA in the THF had the best properties, including the following:

- Polymer yield - 97 to 99 percent of theory
- Thermal stability - stable to 250 C
- Particle size distribution - 40 percent of product 200-500 μm
- Surface area - 26 to 50 m^2/g

Table 1. Polyimides made in THF—Particle Sizes and Surface Areas

No.	Composition	Particle Size Distribution, Weight Percent			Surface Area, m ² /g		
		μm			μm		
		>212	<212->105	<105	>212	<212->105	<105
1	Tenax [®]	--	--	--	--	25	--
	DADS/PMDA	34	27	39	--	--	15 ^(a)
2	DADS/PMDA	31	39	30	26 ^(b)	--	26 ^(b)
	DADS/PMDA	23	39	38	--	50	38
3	DADM/PMDA	5	10	85	--	--	2.4
4	DADM/PMDA	4	8	88	--	--	4.6
5	DADM/PMDA	3	6	91	--	--	2.1
6	DADPM/PMDA	59	38	3	--	0.5	--
7	DADPM/PMDA	33	40	27	--	0.1	--
8	DADPM/PMDA	49	34	18	--	21	--
9a	DADPM/PMDA	67	20	13	--	4.1 ^(c)	--
9b	DADPM/PMDA	42	26	32	32	--	--
10	DADS/PMDA	40	30	30	24	--	--
11	DADS/PMDA ^(d)						

^(a)Cyclodehydration to 300 C.

^(b)Cyclodehydration to 230 C.

^(c)Product 9b.

^(d)N-phenyl imide end groups.

- Sorption characteristics - preliminary tests with benzene indicate substantially greater sorption capacity than Tenax but poorer sorption kinetics, resulting in early breakthrough
- Desorption characteristics - efficient (100 ± 3 percent) recovery of sorbed benzene at a moderate temperature (100 C)

The DADS polyimides made in NMP (solution polymerization) show very low surface areas (<1 m²/g). This appears likely to be due to a combination of factors, including the nature of the polyamide-acid precipitation process from true solution in a polar solvent, the effect of relatively low molecular weight polymer chains on this process, and possible retention of small amounts of NMP by the fine particle product after washing and drying. Immediately after precipitation, the products qualitatively appeared to have high surface areas. After the precipitates were carefully washed with acetone and/or water to remove NMP, they were either vacuum dried at room temperature or freeze dried from a frozen water slurry. During this drying process, a considerable amount of agglomeration invariably occurred. Then, during cyclodehydration up to 230 C, the products further agglomerated to very large particles or even flake or sheet material.

Decided improvement was obtained when DADS/PMDA Product 10, made in THF, was dissolved in NMP and recovered by precipitation using the same

procedures. Precipitation with acetone or water yielded polyimide powders with surface areas of 2 and 4 m²/g respectively when the products were not heated above room temperature during washing and were freeze-dried from a frozen water slurry. It is likely that the higher molecular weight of Product 10 is the reason for this improvement. Although the actual surface areas were still disappointingly low, this does indicate that if the desired higher molecular weight polyamide-acids can be achieved by solution polymerization of DADS and PMDA, further increases in surface area can be expected.

*R. A. Markle is with Battelle Columbus Laboratories, Columbus, OH 43201-2693.
James D. Mulik is the EPA Project Officer (see below).*

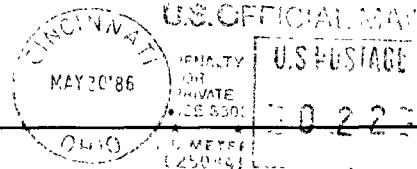
The complete report, entitled "Synthesis of Aromatic Polyimides for Use as Solid Sorbents," (Order No. PB 86-176559/AS; Cost: \$11.95, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
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