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**THE SYNTHESIS OF DECYLOXY SUBSTITUTED AROMATIC
POLYAZOMETHINES FOR INCREASED SOLUBILITY**

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Polymer Branch
Nonmetallic Materials Division

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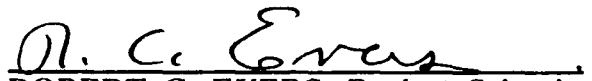
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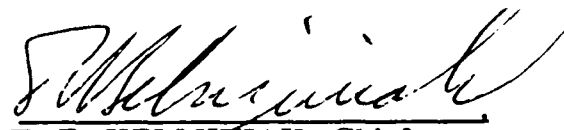
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An aromatic polyazomethine (PAM) was prepared by two routes from 2,5-didecyloxyterephthaldehyde monomer and 1,4-phenylenediamine. The extended chains prepared were comparable in molecular weight to the literature values for previously prepared polyazomethines based on solution viscosity values. However, the PAM polymers prepared exhibited total solubility only in protonating acidic media.						
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Wright Research and Development Center, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. Robert C. Evers as the Materials Laboratory Project Scientist. Coauthors were Marilyn R. Unroe and Bruce A. Reinhardt, Materials Laboratory (WRDC/MLBP). This report covers research conducted from December 1987 to December 1988. The authors wish to thank personnel of the Materials Integrity Branch, WRDC/MLSA, Systems Support Division, Materials Laboratory, for mass spectrum and elemental analysis determinations.

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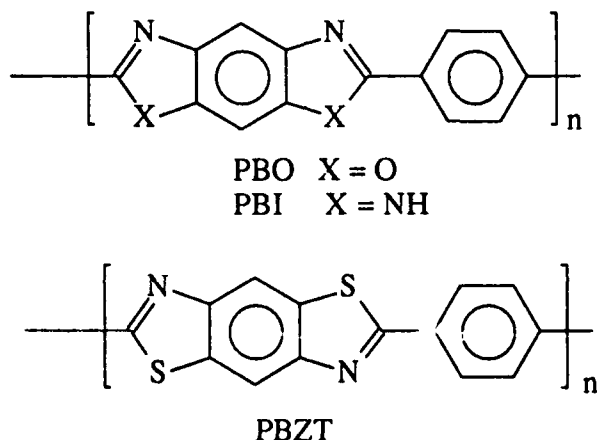
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SECTION I

INTRODUCTION

Recent Air Force approaches to improve the solubility of the polybenzobisazole (PBZ) rigid rod polymers in solvents other than strong protonating acids have employed the use of pendant solubilizing units on the *p*-phenylene spacers of the rigid rods. The unsubstituted rigid rods typically are high in tensile strength and modulus with intrinsic viscosities in dilute solution of 13-30 dL/g (Reference 1).



As molecular weight build-up occurs during the condensation polymerization, the polymer will have a tendency to fall out of solution if certain reaction conditions are not maintained. The driving force for this research has been to avoid or minimize the amount of extraneous work required to keep the polymer in solution while achieving high molecular weight. Attempts to alter the solubility with symmetrically and asymmetrically substituted heterocyclic (References 2 and 3), aromatic (Reference 4) and alkyl (Reference 5) pendants have proven unsuccessful since acidic solvents were still required to totally solubilize the polymers.

Little was known about the effects of pendant long chain *n*-alkoxy groups on the solubility of rigid rod polymers until a report appeared in the literature which described the

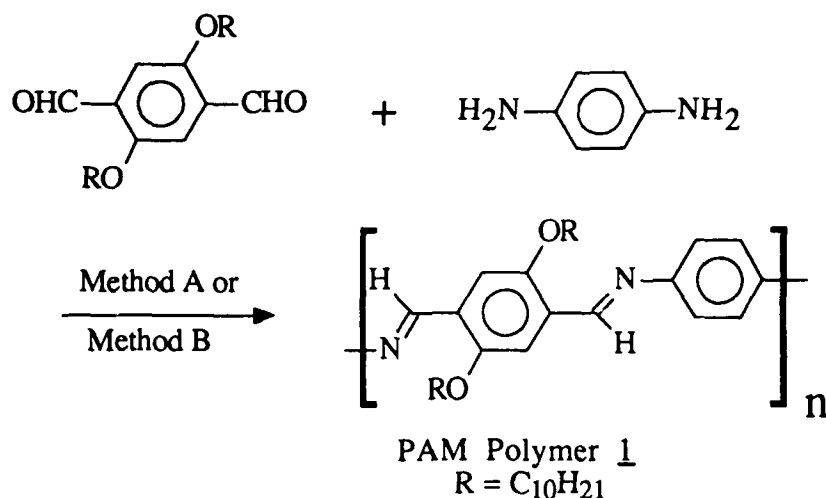
preparation of a polyimide with symmetrically substituted dialkoxy pendants on a *p*-phenylene spacer (Reference 6). The polyimides were totally soluble in 1,3-dimethyl-2-oxo-*p*-hydropyrimidine with inherent viscosities in dilute solution of only 0.4-0.8 dL/g (0.5%, 25°C). Rod like and extended chain polyesters (References 7 and 8) and polyamides (Reference 8) were also synthesized with even numbered long chain alkoxy groups of 2 to 16 carbon units long with the only exclusion being the ten carbon long unit. The use of *n*-alkoxy pendants was even more recently extended to include polyazomethine (PAM) polymers which exhibited room temperature solubility in chloroform; however, these extended chain polymers were of low molecular weight and inherent viscosity (Reference 9) when compared to asymmetrically substituted PAM polymers prepared earlier in amide solvents at room temperature (η_{inh} up to 2.0 dL/g, 0.5%, H₂SO₄) (Reference 10). These high molecular weight PAM's also required strong protonating solvents to totally solubilize the polymers for solution viscosity measurements.

The objective of this research was threefold. First, we wished to prepare a novel 2,5-didecyloxyterephthalaldehyde monomer by a shorter and cheaper route than what was reported for similar monomers (Reference 9). Secondly, we wished to prepare a symmetrically substituted PAM using this novel monomer and to achieve high molecular weight based on similar solution viscosity values for the asymmetric alkoxy substituted PAM's (Reference 10). Finally, we wished to study the effects of this overlooked pendant group on the solubility of the extended chain type polymer in nonacidic solvents in order to ascertain any potential for improved solubility of the rigid rod PBZ's in such media.

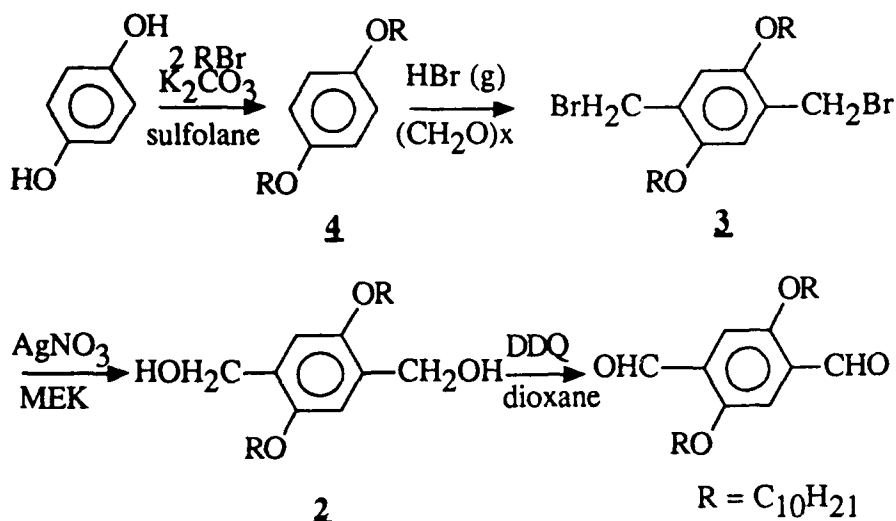
SECTION II

RESULTS AND DISCUSSION

PAM polymer **1** was prepared by the condensation of 2,5-didecyloxyterephthalaldehyde and *p*-phenylenediamine in two different solvent systems. The first method, Method A, employed the use of the reported literature conditions with anhydrous hexamethylphosphoramide:N-methylpyrrolidone (HMPA:NMP) whereas Method B employed the use of *n*-dodecylpyrrolidone (LP-300 or surfadone) as the solvent.



The dialdehyde monomer was prepared by the oxidation of diol **2** with 2,3-dichloro-5,6-dicyanohydroquinone (DDQ) in moderate yield using a modification of a reported procedure (Reference 11). Diol **2** was prepared in low yield from bisbromomethyl compound **3** using silver nitrate and 50% aqueous methyl ethyl ketone in the absence of light (Reference 12). Compound **3** was prepared by the halomethylation of 1,4-didecyloxybenzene (**4**) using a procedure previously reported (Reference 13) in which hydrogen bromide gas is generated *insitu*. Diether **4** was prepared from the alkylation of the *insitu* generated dipotassium salt of hydroquinone with 1-bromodecane using a modification of a reported procedure (Reference 14).



Attempts to prepare the dialdehyde monomer directly from compound **3** by known literature procedures (References 15 and 16) proved just as unsuccessful as the attempts to use other various well known oxidizing reagents which oxidize *o*-alkyl and short chain length *o*-alkoxy alcohols and diols similar in structure to **2** up to their corresponding aldehydes (References 12, 17-19). Other attempts (References 20-21) to prepare the dialdehyde monomer directly from 2,5-didecyloxyterephthalic acid (Reference 22) and 2,5-didecyloxydidecylterephthalate (Reference 22) afforded low yields of impure dialdehyde. An attempt to prepare 2,5-didecyloxyterephthaloyl dichloride by a novel chlorination procedure (Reference 23) to the desired monomer for a PAM polymer prepared *via* the method previously described (Reference 9) was also unsuccessful.

The physical characterization of PAM polymer **1** is summarized in Table 1. The inherent viscosities of **1** prepared by either procedure compare favorably with the inherent viscosities found by Morgan *et al.* for an asymmetric methyl substituted PAM prepared by solution methods ($\eta = 0.70 - 2.0$ dL/g, H_2SO_4 , 0.5%, 30°C) and a methoxy substituted PAM prepared by melt condensation ($\eta = 1.1$ dL/g, H_2SO_4 , 0.5%, 30°C) (Reference 10). Polymer **1** was partially soluble at room temperature in sulfuric acid, *o*-dichlorobenzene, NMP, tetrahydrofuran, 1,1,2,2-tetrachloroethane and a 3:1 wt/wt mixture of

tetrachloroethane:phenol. It was totally insoluble in N,N-dimethylacetamide, methylene chloride, and formic acid. The polymer was soluble at room temperature by protonation in methanesulfonic acid (MSA). Again the high molecular weight PAM was only soluble in a strong protonating medium. From a plot of both the reduced and inherent viscosities versus concentration at 30°C the intrinsic viscosity of polymer 1 prepared by Method A was determined to be in the range of 1.35-1.6.

Table 1. Physical Characterization of PAM Polymer 1.

Method Used	Wt/wt conc (%)	Elem. Anal. Calc'd (found)	η_{inh} at 30°C (conc) ^a	η_{red} at 30°C (conc) ^a
A ^b	17	C 78.71 (78.62)	1.72 (0.5%)	2.74 (0.5%)
		H 9.71 (9.59)	1.65 (0.25%)	2.04 (0.25%)
		N 5.40 (5.37)		
B	18	C (78.28)	1.69 (0.5%)	
		H (9.62)		
		N (5.37)		
B	8		1.27 (0.5%)	

^a Values in dL/g in MSA, 30°C.

^b Emission spectrum indicates less than detection limit of 0.015 wt% Li.

The preferred method of preparation of polymer 1 was the reported literature conditions used in Method A (Reference 10). Although LP-300 aided the solubility of the terephthaldehyde monomer, it was not the solvent of choice for dissolving *p*-phenylenediamine. Small needles of diamine monomer were still found in the polymer solution even after 24 h in a more dilute (8% wt/wt) polymerization. It was reasonably certain that the needles were not crystallites of oligomer that were previously observed in polyimides of varying pendant alkoxy length (Reference 5) since the needles were present at the addition of the solvent to the polymerization flask and did not dissolve at any time.

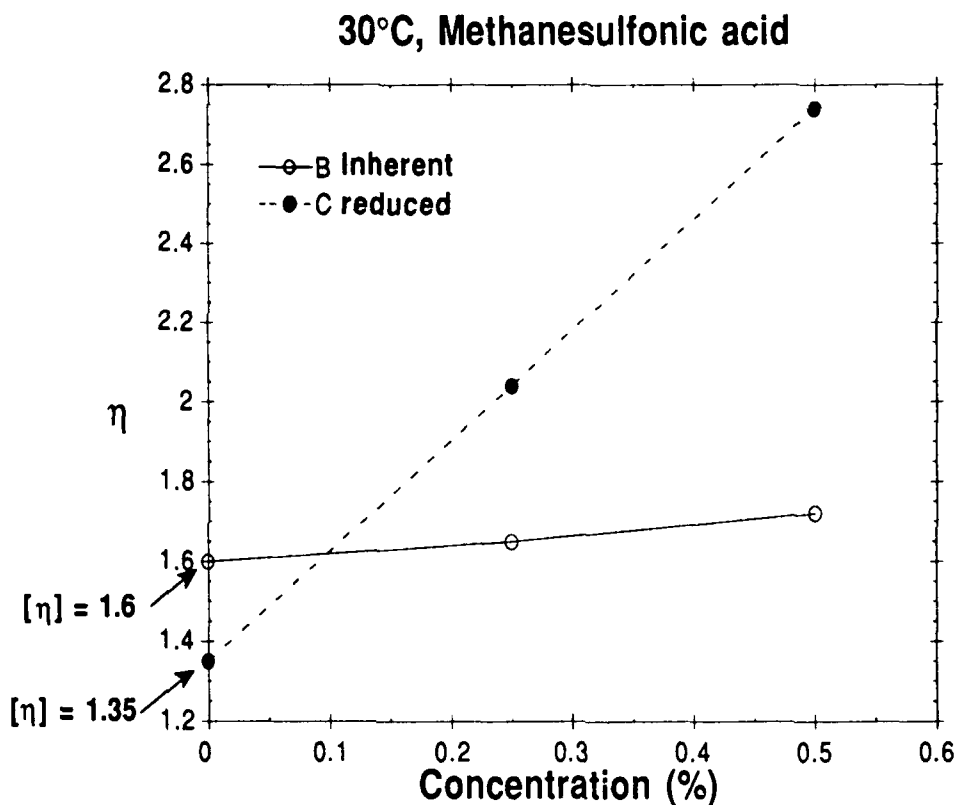


Figure 1. Intrinsic Viscosity Plot of PAM Polymer 1

In conclusion, a symmetrically substituted PAM was prepared from 2,5-didecyloxy-terephthalaldehyde and *p*-phenylenediamine using previously reported condensation conditions. Even though high molecular weight was achieved as evidenced by comparable inherent viscosity values with high molecular weight asymmetric PAM's, the solubility of the extended chain polymer was still limited to protonating acidic media such as MSA. However, a more efficient and cheaper preparation of the dialdehyde monomer was developed which eliminated one step from the synthetic path reported in the literature for similar monomers (Reference 9).

SECTION III

EXPERIMENTAL

All solvents were distilled and stored over molecular sieve where appropriate. LP-300 was used as received. Monomers and reagents were dried and stored in a dessicator before use. All inherent viscosities were determined in solutions of polymer in MSA in a 150 bore Cannon-Ubbelohde viscometer. Melting points were uncorrected. Fourier transform infrared (FTIR) spectra were performed on a Beckmann IR-33 using nitrogen purge under the conditions specified. Proton nuclear magnetic resonance (^1H -NMR) spectra were performed on a Varian Model 360M under the conditions specified using 10% solutions.

Preparation of PAM Polymer 1

Method A: 2,5-Didecyloxyterephthaldehyde (1.0032 g, 2.25 mmol), *p*-phenylenediamine (Aldrich, zone refined, 0.2429 g, 2.25 mmol) and lithium chloride (Aldrich, 0.28 g) were weighed into a 25-mL polymerization flask. The solids were purged with nitrogen for 0.5 h before the transfer under nitrogen of a purged solution of 1:1 HMPA:NMP (7 mL) to make a final wt/wt concentration of 17%. The solution was stirred for a total of 120 h at room temperature under nitrogen. The polymer was isolated by precipitation into methanol (500 mL) and air dried to afford a yellow-orange powder (1.13 g, 97%).

Method B: 2,5-Didecyloxyterephthaldehyde (2.3 mmol) and *p*-phenylenediamine (2.3 mmol) were weighed into a polymerization flask and purged under nitrogen for 0.5 h before the addition of LP-300 (GAF Chemicals). The polymerization was stirred for 20-24 h under nitrogen at room temperature. The polymer was isolated by precipitation into methanol (350 mL) and air dried to afford a bright orange powder (93-99%).

2,5-Didecyloxyterephthaldehyde

A solution of DDQ (Aldrich, 3.61 g, 16 mmol) in 1,4-dioxane (72 mL) was added dropwise over a period of 45 min to a cooled solution (10°C) of diol **2** (3.58 g, 8 mmol) in 1,4-dioxane (143 mL). After addition of the DDQ the flask was allowed to warm to room temperature and

was then heated to 110°C for 48 h. The crystalline DDQH that formed upon cooling was collected and washed with diethyl ether (2 X 100 mL). The filtrate was distilled to dryness by rotary evaporation to afford a brown residue. The residue was suspended in 4:1 cyclohexane: methylene chloride and chromatographed on a silica gel column (2.5 cm dia X 45 cm H) to remove the dialdehyde as the first yellow band down the column (2.36 g). The product was recrystallized from hot isopropanol (200-mL) to afford light yellow needles (1.99 g, 56%); mp 84-85°C. Elem. Anal. calcd for C₂₈H₄₆O₄: C, 75.29; H, 10.38. Found: C, 75.11; H, 10.44. Mass spectrum (EIMS): m/z = 446 (10, M⁺), 166 (100, M-2 C₁₀H₂₁). ¹H-NMR (10%, CDCl₃): δ = 10.6 (s, 2H-CHO), 7.5 (s, 2H_{arom}), 4.1 (t, 4H-₂OCH₂-), 2.1-0.5 (m, 38H_{alkyl}) ppm (Figure 2). FTIR (KBr): ν = 3050, 2920, 2850, 1681, 1470, 1430, 1220, 1030 cm⁻¹ (Figure 3).

Preparation of 2,5-Didecyloxyterephthaldehyde Using Lithium 9-BBNH (Reference 20)

To a 25-mL three-necked roundbottom flask fitted with nitrogen inlet and rubber septa were added 2,5-didecyloxyterephthalic acid (Reference 22) (0.50 g, 1.04 mmol), 9-BBN (Aldrich, 0.23 g, 1.04 mmol) and THF (1.5 mL). The nitrogen purge was begun immediately and the opaque yellow solution was stirred at room temperature until hydrogen gas evolution ceased (about 1 h). A solution of freshly prepared 0.87M lithium 9-BBNH (References 24, 25) was transferred into the flask. Within 2 min after injection the solution changed to a clear yellow. By 3 min the solution had changed to a cloudy white. TLC at 15 min on a silica gel strip (1:1 cyclo-hexane:ethyl acetate) showed only starting material remained with some other impurities. The solution was poured into water (150 mL) and extracted twice with two portions of diethyl ether (50 mL each). The ethereal layers were distilled by rotary evaporation to give a white solid (0.86 g). Subsequent solvation in hot toluene (30 mL) and

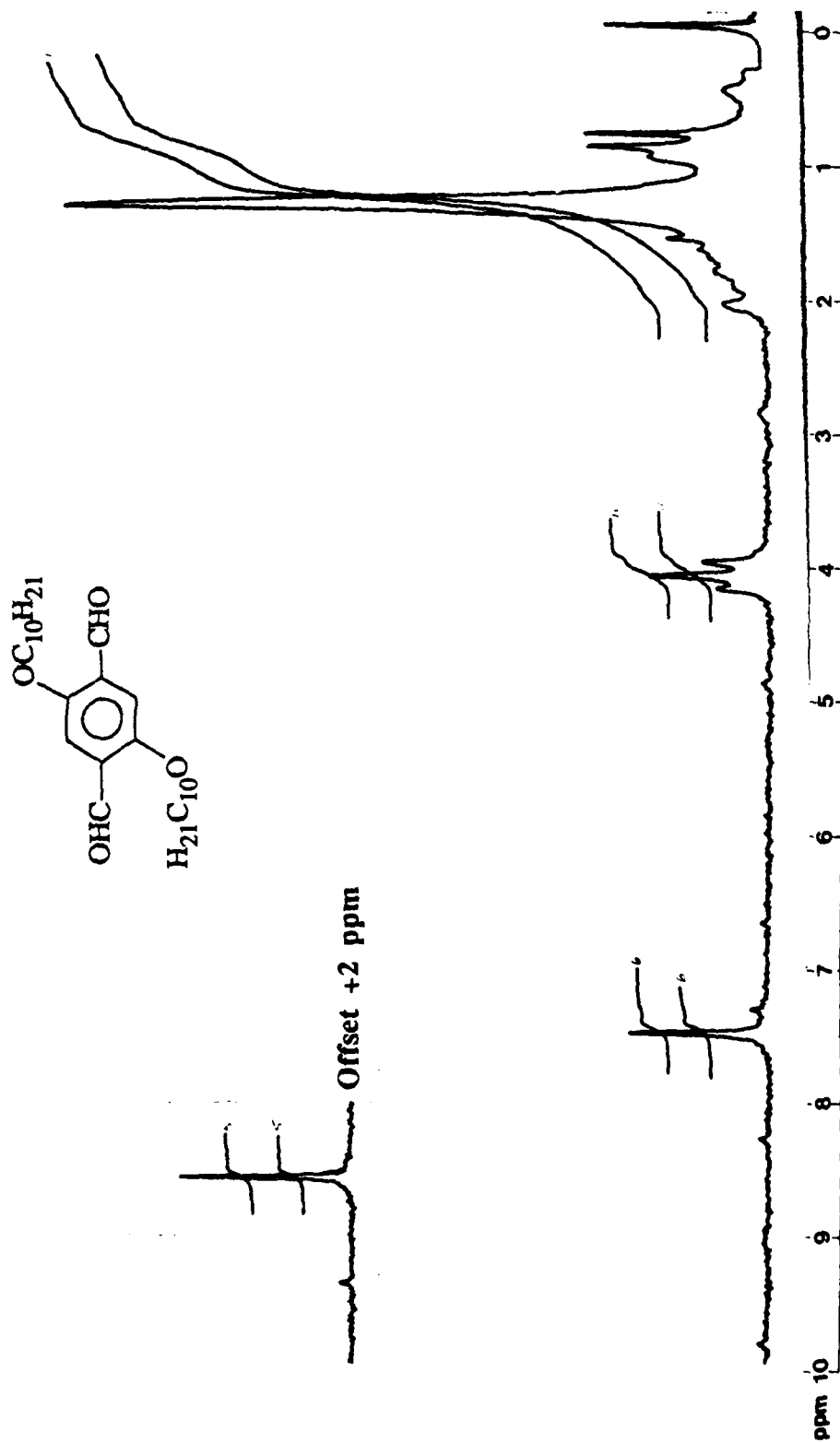


Figure 2. $^1\text{H-NMR}$ Spectrum of 2,5-Didecyloxyterephthalaldehyde.

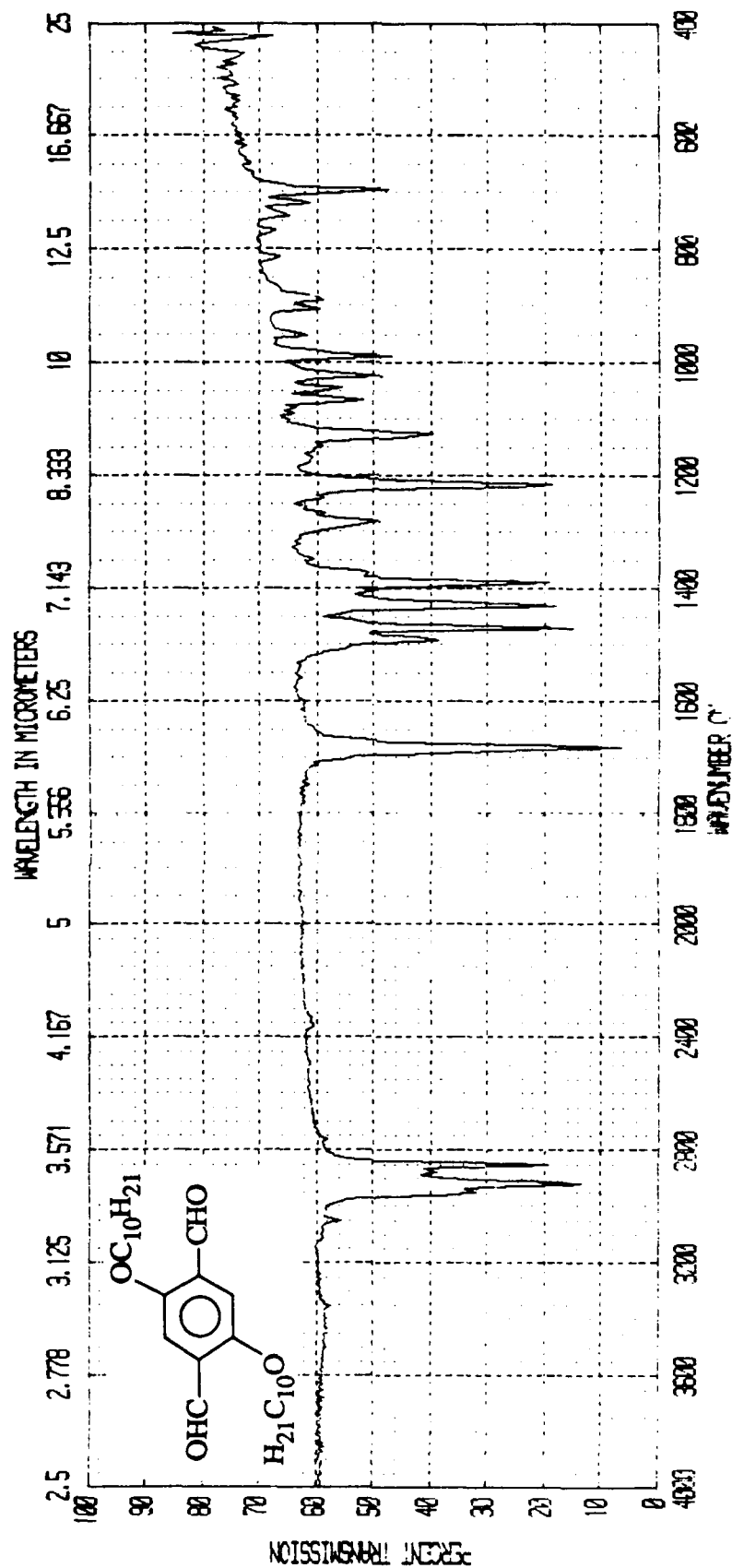


Figure 3. FTIR Spectrum of 2,5-Didecyloxyterephthalaldehyde.

filtration afforded a white solid from the filtrate (0.23 g) which was determined by mass spectral analysis to contain a mixture of diacid starting material, some dialdehyde and 2,5-didecyloxy-4-(hydroxymethyl)benzoic acid: mp 108-110°C. Mass spectrum (EIMS): m/z = 478 (1, M^+), 464 (4, M^+), 447 (1, M^+), 43 (100, $(C_3H_7)^+$).

Preparation of 2,5-Didecyloxyterephthaldehyde From 2,5-Didecyloxy-didecylterephthalate

In a modification of a reported procedure (Reference 21) fresh lithium aluminum hydride (Aldrich, 1.88 g, 52.3 mmol) was flushed with nitrogen in a dry 250-mL three-necked roundbottom flask fitted with nitrogen inlet and rubber septa for 1 h. A solution of diethylamine (7.72 g, 106 mmol) in isooctane (48 mL) was slowly transferred into the flask and resulted in the generation of hydrogen gas in the slurry. To the flask was transferred a suspension of 2,5-didecyloxydidecylterephthalate (Reference 22) (10.0 g, 13.1 mmol) in isooctane (150 mL). The grey-green suspension was stirred for 16 h at room temperature under a nitrogen atmosphere. At 16 h an aliquot was taken from the flask, neutralized in dilute hydrochloric acid and extracted with diethyl ether. The organic layer was compared with known standards by TLC on a silica gel strip (hexane; 4:1 petroleum ether:methylene chloride) to indicate the presence of dialdehyde monomer, partial reduction to monosubstituted alcohol and diol **2**. The solution was poured into dilute hydrochloric acid (500 mL) and extracted twice with diethyl ether until no color remained in the acidic layer. The ethereal layers were combined, washed with 10% aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. The solvent was distilled by rotary evaporation to give a yellow residue which in turn was chromatographed on a silica gel column (Woelm DCC, 5 cm dia X 30 cm H) using 4:1 petroleum ether:toluene to remove the mixed product.

Recrystallization from 2-propanol (50 mL) afforded yellow needles of impure dialdehyde with an elevated melting point (0.92 g, 16%): mp 92-95°C.

Diol 2

Compound **3** (11.11 g, 19.3 mmol), silver nitrate (Kodak, 17.48 g, 103 mmol) and 50% aqueous methyl ethyl ketone (300 mL) was stirred as a suspension at room temperature in the absence of light for 27 h until thin layer chromatography (TLC) on a silica gel strip (2:1 hexane:methylene chloride) indicated the absence of starting material. The silver bromide salts were filtered from the solution, washed with diethyl ether (2 X 100 mL) and air dried in the absence of light. The salts were extracted with boiling 1:1 hexane:toluene (400 mL) to remove residual product and filtered. The filtrate was cooled in the refrigerator and the white powder was collected by filtration and dried in a 90°C oven at reduced pressure. The ethereal solution from the reaction was separated from the aqueous layer, washed with water (100 mL), and dried over anhydrous magnesium sulfate. After distillation of the solvent by rotary evaporation the greasy white residue (3.84 g) was recrystallized from 1:1 hexane:toluene (50 mL) to also afford additional product as a white powder (2.76 g total, 32%): mp 102-104°C. Elem. Anal. calcd for C₂₈H₅₀O₄: C, 74.61; H, 11.18. Found: C, 74.65; H, 11.21. Mass spectrum (EIMS): m/z = 450 (17, M⁺), 43 (100, (C₃H₇)⁺). ¹H-NMR (min sol CDCl₃): δ = 7.0 (s, 2H_{arom}), 4.7 (s, 4H-CH₂O-), 4.0 (t, 4H-OCH₂-), 2.4-0.8 (m, 38H_{alkyl}) ppm (Figure 4). FTIR (KBr): ν = 3376, 2934, 2916, 2850, 1617, 1206, 1036 cm⁻¹ (Figure 5).

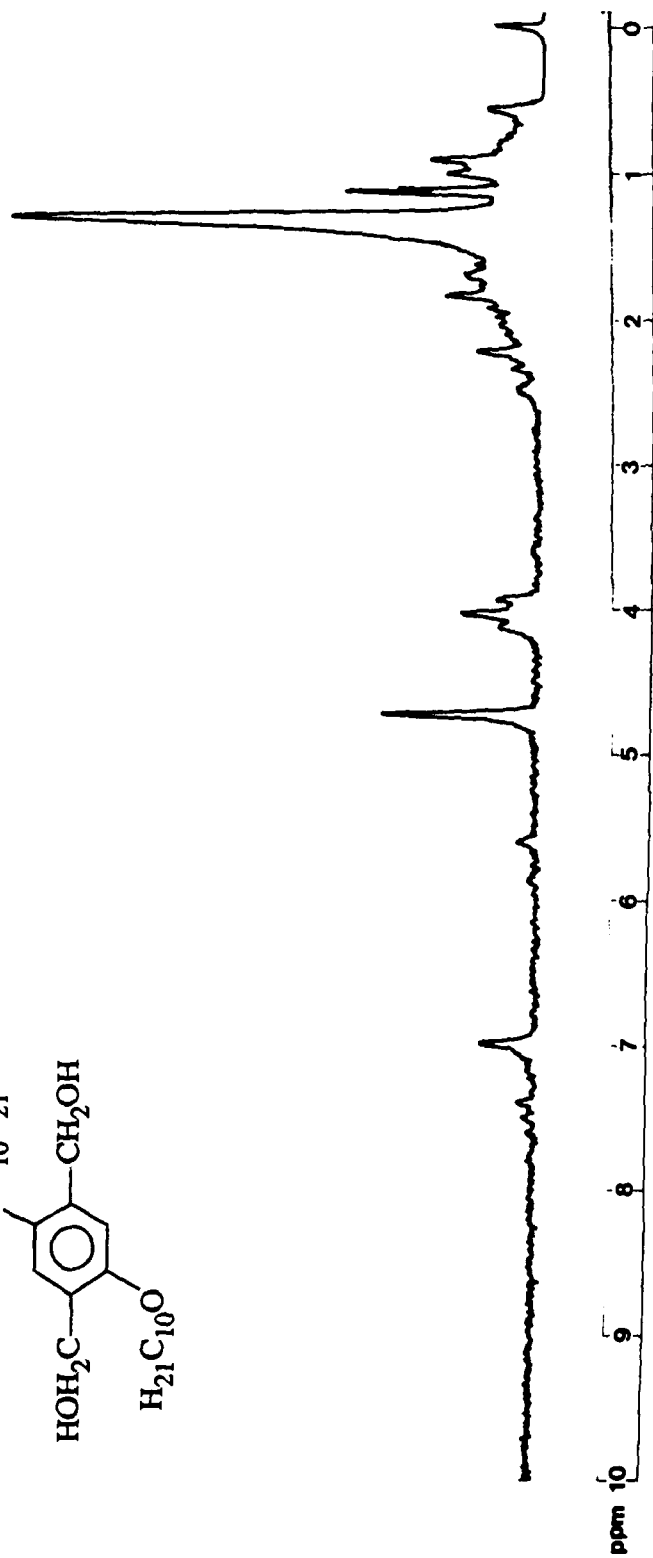
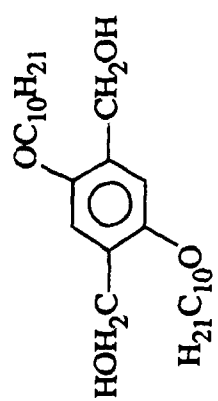


Figure 4. $^1\text{H-NMR}$ Spectrum of Diol 2.

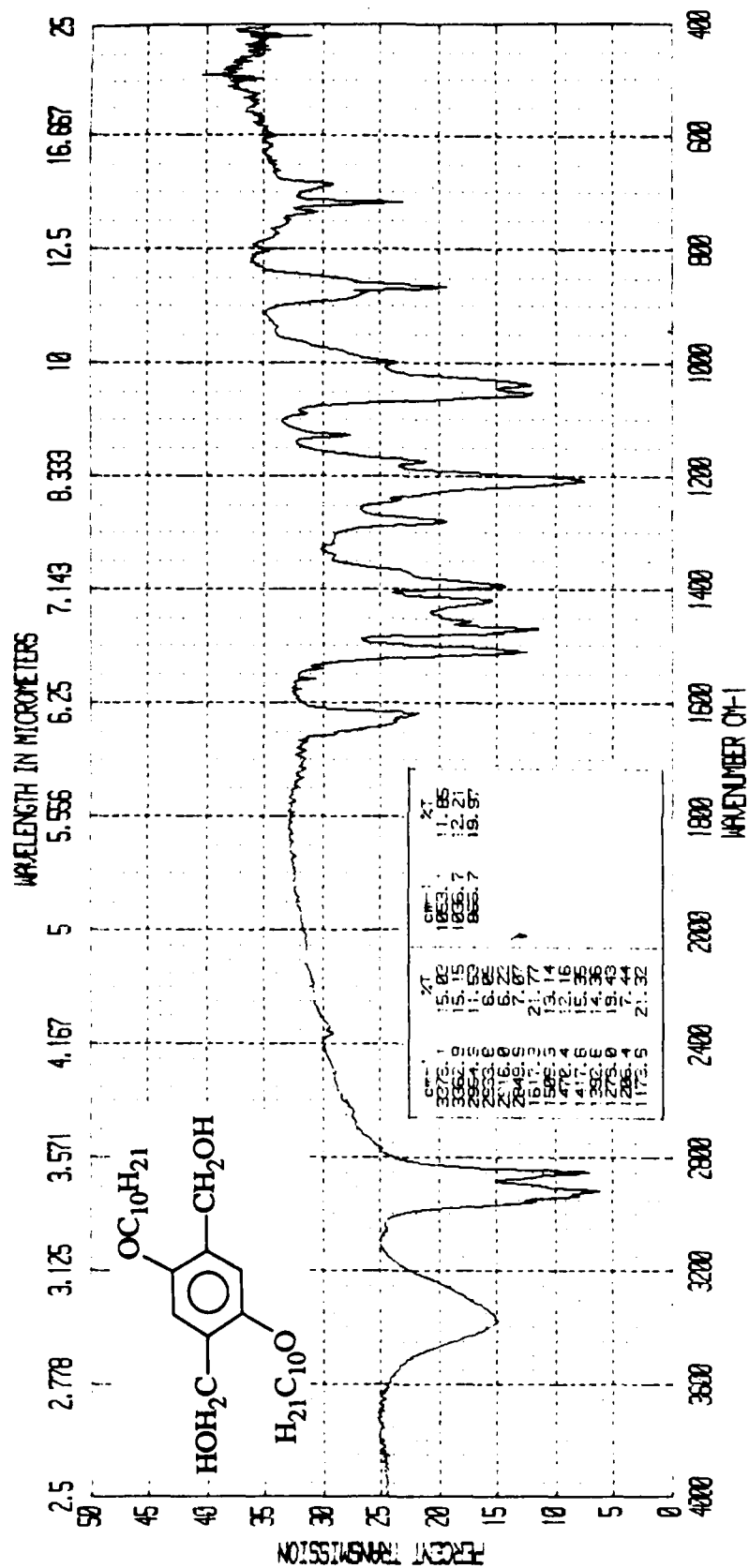


Figure 5. FTIR Spectrum of Diol 2.

Preparation of 2,5-Didecyloxyterephthaldehyde From Diol 2 Using Manganese Dioxide (Reference 12)

A solution of diol **2** (1.00 g, 2.21 mmol), activated manganese dioxide (Aldrich, 8.79 g, 101 mmol), and dry benzene (100 mL) was heated in a flask at 85°C for 8 h under a nitrogen atmosphere at which time TLC on a silica gel strip (3:1 cyclohexane:ethyl acetate) indicated no reaction and the presence of only diol **2**.

Preparation of 2,5-Didecyloxyterephthaldehyde From Diol 2 Using Potassium Permanganate and a Novel Amine Solvent (Reference 17)

A suspension of powdered potassium permanganate (Baker, 0.63 g, 3.99 mmol) in methylene chloride (10 mL) was stirred in a flask at room temperature before the addition of tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1) (Aldrich, 0.002 g) in a quantity to equal 1 mol% per mol substrate. Diol **2** (0.30 g, 0.666 mmol) was added to the flask and the solution was stirred at room temperature for 1 h. TLC on a silica gel strip (4:1 cyclohexane:ethyl acetate) at 0.5 h showed starting material remained. The manganese salts were filtered from the solution over diatomaceous earth packed in a coarse porosity fritted funnel and rinsed with diethyl ether (4 X 20 mL). The filtrate was evaporated to a volume of 50 mL, washed with 2N hydrochloric acid (100 mL), water (50 mL), and the organic layer was evaporated to dryness. The residue was recrystallized from toluene (30 mL) to give a yellow powder (0.17 g, 56%): mp 69-73°C. Mass spectrum indicated the presence of diol **2**, half product, and dialdehyde. Mass spectrum (EIMS): $m/z = 450$ (52, M^+), 448 (24, M^+), 446 (1, M^+), 43 (100, $(C_3H_7)^+$).

Preparation of 2,5-Didecyloxyterephthaldehyde From Diol 2 Using Cerium Ammonium Nitrate (References 18, 19)

A solution of diol **2** (1.00 g, 2.22 mmol) in glacial acetic acid was heated by oil bath to 60°C to dissolve the diol. Upon cooling the flask to 40°C a solution of cerium ammonium nitrate (Aldrich, 2.55 g, 4.65 mmol) in 50% aqueous acetic acid (20 mL) was added dropwise over a period of 15 min. The flask was heated to an internal temperature of 45°C for a total of 1 h. TLC at 0.5 h on a silica gel strip (4:1 cyclohexane:ethyl acetate) indicated no starting material remained. The yellow solution was poured into water (500 mL) and extracted with methylene chloride (3 X 150 mL). The organic layers were combined, washed with 10% aqueous sodium bicarbonate (260 mL), water (300 mL), and dried over anhydrous magnesium sulfate. The solvent was distilled by rotary evaporation to give a yellow residue (0.87 g). The residue was chromatographed on a silica gel column (Woelm DCC, 1 cm dia X 30 cm H) using 4:1 cyclohexane: methylene chloride to remove the dialdehyde and other higher R_f impurities as the first band and 1:1 cyclohexane methylene chloride to remove the impurities below the dialdehyde on TLC as the second band. Recrystallization of the lower band residue from toluene (10 mL) afforded yellow needles which appeared from mass spectrum to consist of monoalcohol half product and 2,5-didecyloxy-1-hydroxymethyl-4-nitrobenzene (0.17 g, 17%): mp 97-100°C. Mass spectrum (EIMS): m/z = 448 (15, M⁺), 465 (1, M⁺), 43 (100, (C₃H₇)⁺).

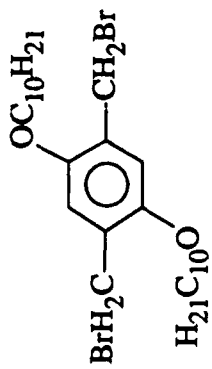
The first band containing the dialdehyde monomer could not be isolated by recrystallization from toluene and consisted by mass spectrum of the dialdehyde contaminated with a compound with assignment as 2,5-didecyloxy-4-(acetoxymethyl)benzaldehyde. Mass spectrum (EIMS): m/z = 490 (3, M⁺), 446 (9, M⁺), 43 (100, (C₃H₇)⁺).

In a modification of another similar procedure (Reference 19) diol **2** (1.00 g, 2.22 mmol), 1 mol% cerium ammonium nitrate (0.01 g, 0.022 mmol), and sodium bromate (Aldrich, 0.33 g, 2.22 mmol) were suspended into a solution of aqueous acetonitrile (70:30, 10 mL) and purged with nitrogen for 10 min before heating the flask to an internal temperature of 80°C.

TLC on a silica gel strip under the conditions previously stated for an aliquot after 2 h heating indicated some starting diol present. An additional quantity of cerium ammonium nitrate was added to make a 10 mol% concentration of catalyst (0.11 g, 0.2 mmol) and the flask was heated for an additional 2 h at 80°C. After work up of the reaction under the procedure previously stated, diol **2** was the only product isolated in any significant quantity (0.40 g, 49% recovery): mp 102-103°C. Mass spectrum (EIMS): $m/z = 450$ (22, M^+), 43 (100, $(C_3H_7)^+$).

Bisbromomethyl Compound 3

To a 1000-mL three-necked round bottom flask fitted with mechanical stirrer, thermometer, and addition funnel was added a suspension of diether **4** (23.30 g, 60 mmol), paraformaldehyde (Aldrich, 11.65 g) and sodium bromide (Strem, 14.86 g, 144 mmol) in glacial acetic acid (440 mL). A solution of sulfuric acid (24.23 g, 247.0 mmol) in glacial acetic acid (18.5 mL) was added dropwise over a period of 15 min and the flask was heated to an internal temperature of 80°C for 5 h. After the solution was allowed to cool to room temperature, the re-sulting white precipitate was collected, washed with water (100 mL) and air dried (38.07 g). Additional product was isolated by pouring the acidic filtrate into ice water (600 mL) and extracting with methylene chloride (2 X 100 mL). The solvent was distilled by rotary evaporation to give a yellow oil (4.42 g). The crude product was recrystallized from boiling hexane (500 mL) to afford a white powder (23.42 g, 68%): mp 94°C. Elem. Anal. calcd for $C_{28}H_{48}Br_2O_2$: C, 58.33; H, 8.39; Br, 27.72. Found: C, 58.35; H, 8.28; Br, 27.53. Mass spectrum (EIMS): $m/z = 578$ (1, M^+ , $^{81}Br^{81}Br$), 576 (4, M^+ , $^{81}Br^{79}Br$), 574 (1, M^+ , $^{79}Br^{79}Br$), 43 (100, $(C_3H_7)^+$). 1H -NMR ($CDCl_3$): $\delta = 6.9$ (s, $2H_{arom}$), 4.5 (s, $4H_{CH_2Br}$), 4.0 (t, $4H_{OCH_2-}$), 2.3-0.6 (m, $38H_{alkyl}$) ppm (Figure 6). FTIR (KBr): $\nu = 3051, 2935, 2918, 2848, 1510, 1468, 1229, 1021\text{ cm}^{-1}$ (Figure 7).



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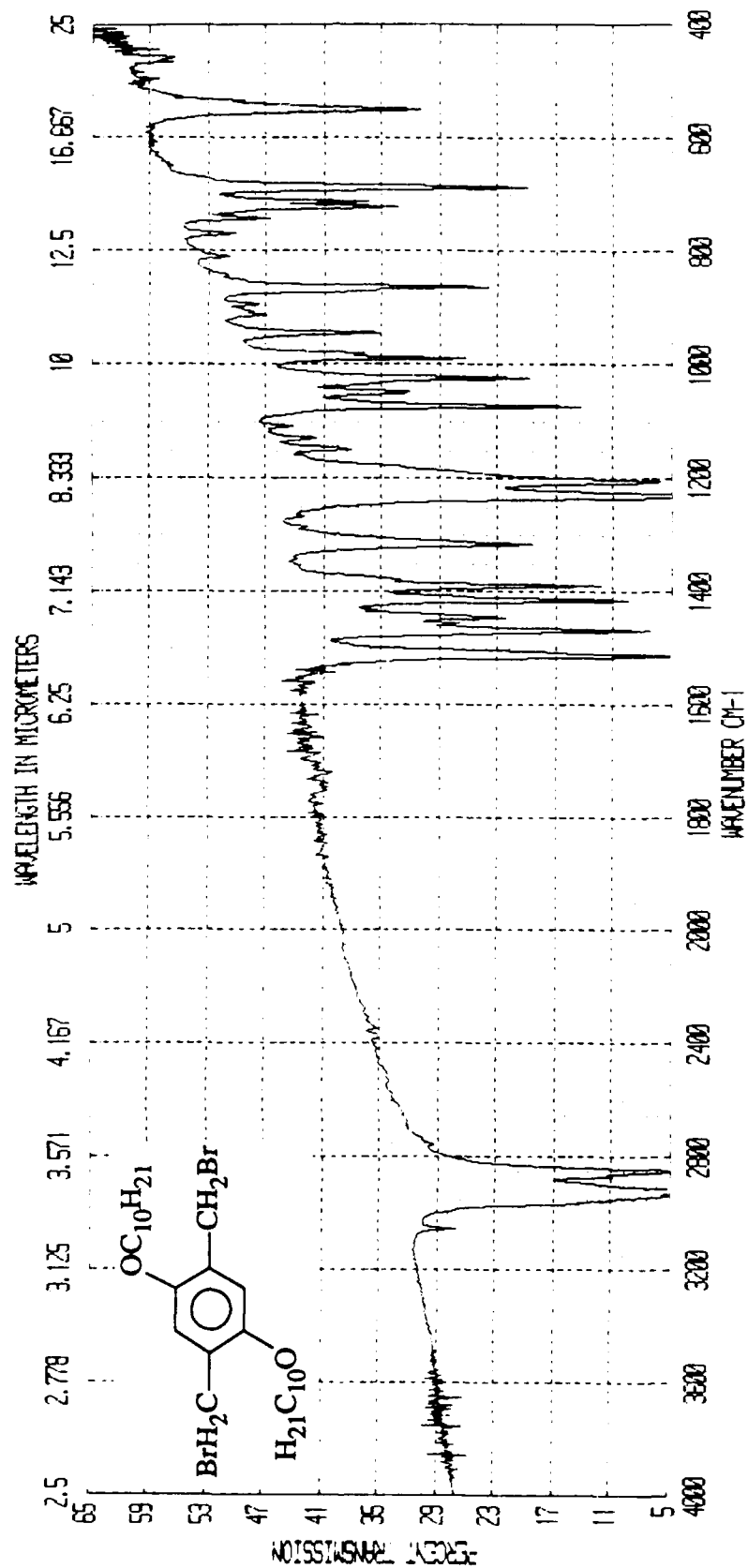


Figure 7. FTIR Spectrum of Compound 3.

Preparation of 2,5-Didecyloxyterephthaldehyde From 3 Using a Bisammonium Salt (Reference 15)

Compound **3** (1.5 g, 2.6 mmol), hexamethylene tetraamine (MCB, 0.8 g, 5.72 mmol) and chloroform (20 mL) were refluxed for 2 h after which a bisammonium salt precipitated from solution. TLC of the reaction on a silica gel strip (4:1 cyclohexane: methylene chloride) indicated that no starting material remained. The reaction was allowed to cool to room temperature and the precipitate was filtered. Anhydrous diethyl ether (80 mL) was added to the filtrate to precipitate additional product. The solids were collected and air dried to give a white powder (0.98 g, 34%). The salt was immediately added to 50% glacial acetic acid (50 mL) and the solution was heated to reflux for 2 h. The flask was allowed to cool to room temperature and was poured into saturated sodium bicarbonate solution (150 mL) and extracted with diethyl ether (2 X 50 mL) after bubbling had ceased. The ethereal layers were combined and washed with water (100 mL). After drying over anhydrous magnesium sulfate the solvent was distilled by rotary evaporation to give a yellow oil (0.22 g, 56%). TLC of the oil on a silica gel strip with known standards indicated the presence of little dialdehyde and mostly half product.

Preparation of 2,5-Didecyloxyterephthaldehyde From 3 Using Bis(tetrabutylammonium)dichromate (Reference 16)

Compound **3** (1.81 g, 3.14 mmol), bis(tetrabutylammonium)dichromate (Aldrich, 8.8 g, 12.6 mmol) and chloroform (120 mL) were heated to reflux in the absence of light for 20 h at which time TLC on a silica gel strip (hexane; 4:1 cyclohexane:ethyl acetate) indicated no starting material remained. The dark green-brown solution was filtered over silica gel (52.18 g) packed in a coarse porosity fritted funnel and eluted with diethyl ether (25 mL). An

iridescent yellow-green eluate was afforded which was distilled to dryness. The residue was chromatographed on a silica gel column (Woelm DCC, 5 cm dia X 40 cm H) using 2:1 petroleum ether:methylene chloride to remove the product and leave the residual chromium salts at the top of the column. The eluate was evaporated to dryness and recrystallized from cyclohexane (25 mL) to afford a yellow powder (0.79 g, 56%): mp 69-73°C. Mass spectrum indicated the presence of dialdehyde and an impurity with the tentative assignment of structure of 2,5-didecyloxy-1-(hydroxyethyl)-4-benzenethanal.

Mass spectrum (EIMS): m/z = 477 (3, M^+), 446 (9, M^+), 166 (100, $M - 2 C_{10}H_{20}$). FTIR (KBr): ν = 2919, 2851, 1683, 1470, 1214, 1030 cm^{-1} .

Modification of this procedure for use of a stoichiometric and two equivalent excess of the bis(tetrabutylammonium)dichromate under the conditions previously described afforded yields of the contaminated dialdehyde of 58% each for both adjustments of dichromate.

1,4-Didecyloxybenzene (4)

A solution of hydroquinone (MCB, 10.00 g, 90.8 mmol), 1-bromodecane (Aldrich, 40.17 g, 181.6 mmol) and sulfolane (70 mL) were stirred under a nitrogen purge for 0.5 h before the addition of potassium carbonate (MCB, 26.36 g, 190.7 mmol). The flask was heated to an internal temperature of 160°C for 48 h under nitrogen until TLC on a silica gel strip (3:1 hexane:methylene chloride) indicated reaction completion. The dark brown solution was poured while still hot into ice water (1500 mL) to precipitate a tan solid. The solid was recrystallized twice from boiling methanol (650 mL) to give colorless plates (25.70 g, 78%): mp 67-68°C. Elem. Anal. calcd for $C_{26}H_{46}O_2$: C, 79.94; H, 11.87. Found: C, 79.92; H, 11.85. Mass spectrum (EIMS): m/z = 390 (25, M^+), 110 (100, $M - 2C_{10}H_{20}$). 1H -NMR ($CDCl_3$): δ = 6.8 (s, 4 H_{arom}), 3.9 (t, 4 H_{-OCH_2-}), 2.2-0.6 (m, 38 H_{alkyl}) ppm (Figure 8).

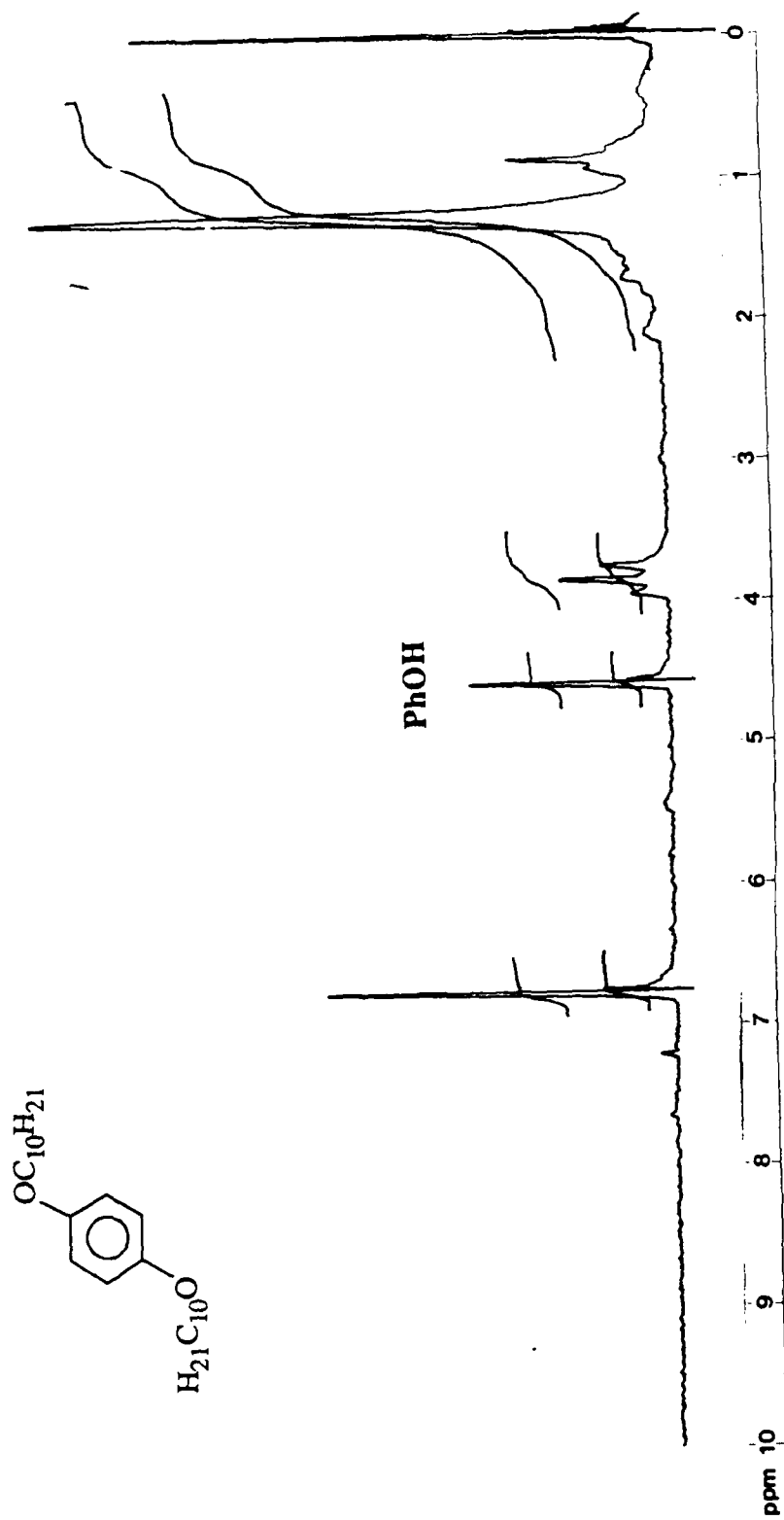


Figure 8. ^1H -NMR Spectrum of 1,4-Didecyloxybenzene.

Preparation of 2,5-Didecyloxyterephthaloyl Dichloride Using a Polymer Supported Catalyst System (Reference 23)

To a 50-mL three-necked roundbottom flask fitted with reflux condenser, drying tube and thermometer were added 2,5-didecyloxyterephthalic acid (Reference 22) (0.53 g, 1.11 mmol), polystyrene supported triphenylphosphine (Aldrich, 0.72 g, 2.21 mmol; 3.06 mmol triphenylphosphine/g polymer), and carbon tetrachloride (25 mL). The solution was refluxed at 80°C for 19 h as a layer of triphenylphosphine oxide formed at the top of the solution.

TLC on a silica gel strip (4:1 cyclohexane:ethyl acetate; 1:1 cyclohexane:ethyl acetate) at 2, 3, and 4 h reaction showed only starting material present. TLC after 19 h of heating showed only starting diacid present.

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