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SYNTHESIS OF AROMATIC POLYBENZOXAZOLES IN TRIMETHYLSILYL POLYPHOSPHATE (PPSE)

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Polymer Branch
Nonmetallic Materials Division

September 1990

Final Report for the Period May 1987 to December 1988

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A series of five 6F-polybenzoxazoles were synthesized by the trimethylsilyl-polyphosphate (PPSE) condensation of various aromatic dicarboxylic acids with 4,4'-hexafluoroisopropylidene bis(2-aminophenol). Glass transition temperatures (Tg) were measured by differential scanning calorimetry (DSC). Thermogravimetric analysis and isothermal aging results are also reported for the polybenzoxazoles.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 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. R. C. Evers as the Materials Laboratory Project Scientist. The author was Bruce A. Reinhardt, Materials Laboratory (WRDC/MLBP).

This report covers research conducted from May 1987 to December 1988. The author wishes to thank Ann G. Dillard for help with the polymer scale up, Marlene D. Houtz and Edward J. Soloski for the thermal analytical data and finally the personnel of the Materials Integrity Branch, WRDC/MLSA, for mass spectrum and elemental analysis determinations.

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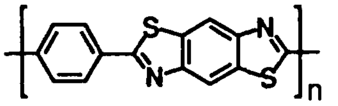
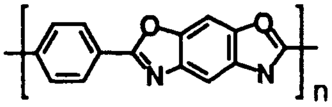
SECTION I

INTRODUCTION

The synthesis of aromatic heterocyclic rigid rod polymers has been a continuing area of investigation in this laboratory for the last decade (References 1-5). Attempts to obtain understanding of polymer solution properties, processing parameters, and polymer mechanical properties have led Air Force synthetic chemists to synthesize a variety of structurally modified analogs of poly(p-phenylenebenzobis-thiazole) (PBT) and poly(p-phenylenebenzobis-oxazole) (PBO) (References 3-5). The most successful method to date for producing these materials has involved the use of poly-phosphoric acid (PPA) as a polymerization media. In cases where structural modifications are desired which involve the incorporation of large, highly organic pendants along the polymer backbone, polyphosphoric acid may not solubilize monomers or the resulting polymers adequately. For example, PBT polymers containing pendant phenyl groups could only be prepared in a mixture of PPA and sulfolane (Reference 3). PBT polymers containing pendants longer than phenyl could only be kept in solution in PPA if the polymerization was run at low concentration and acid soluble benzothiazole moieties were incorporated into the pendants themselves (Reference 5).



PBT



PBO

It was postulated that it would be necessary to find an alternate polymerization media for aromatic heterocyclic rigid rod polymer formation in order to incorporate a greater number of structurally varied pendants into such systems. This is no simple task as thermodynamic considerations make it necessary to have specific interactions between the rigid rod polymer molecules and the solvent to attain solubility.

The objective of the current research was, as a first step, the investigation of an alternate non-acidic polymerization media which could be used to form *coil-like* polybenoxazoles of high molecular weight . If this research were successful, it would provide evidence that high molecular weight *coil-like* aromatic heterocyclic polymers could be prepared in nonacidic solvents, thus making the extension of the method feasible for the preparation of rigid rod polymers.

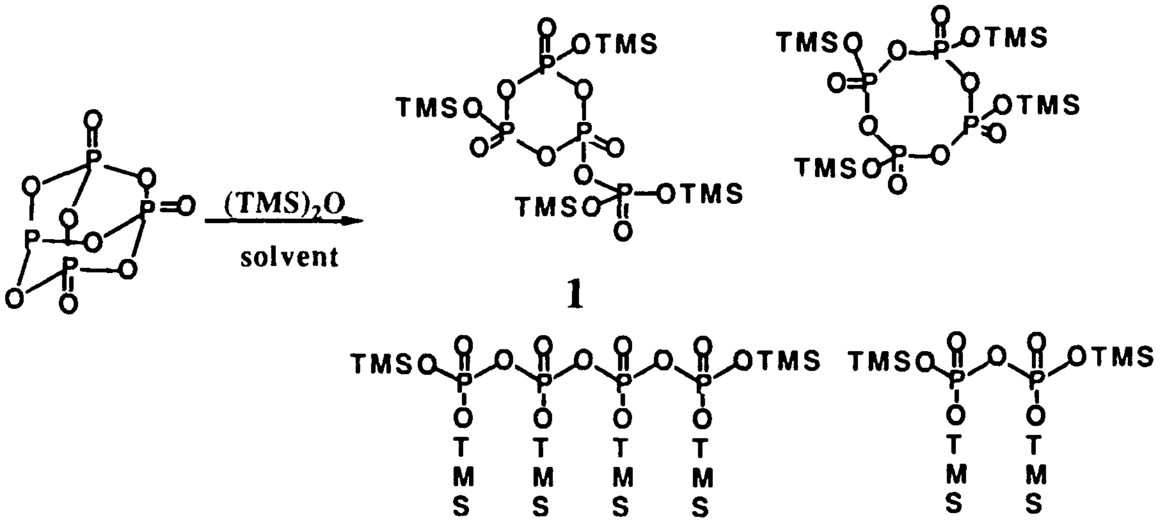
The synthetic method chosen for the investigation was the condensation of *o*-aminophenols with aromatic acids catalyzed by a trimethylsilyl polyphosphate (PPSE) / chlorinated aromatic solvent system previously reported in the literature for the synthesis of simple molecules containing the benzoxazole nucleus (Reference 6).

SECTION II

RESULTS AND DISCUSSION

1. Synthesis of Trimethylsilyl Polyphosphate (PPSE)

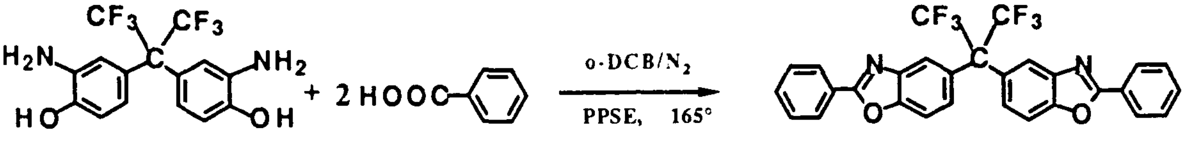
The synthesis of trimethylsilyl polyphosphate (PPSE) was carried out using a method similar to that described in the literature (Reference 7). The reaction of phosphorus pentoxide with hexamethyldisiloxane in refluxing methylene chloride or nonalcohol stabilized chloroform under a nitrogen atmosphere gave colorless PPSE upon removal of the organic solvent. The composition of PPSE is postulated to be a complex mixture of trimethylsilated polyphosphates with the cyclic oligomer **1** postulated as possessing the greatest dehydrating ability (Reference 8).



1

2. Synthesis of Model Compounds

The reaction of 4,4'-hexafluoroisopropylidene bis(2-aminophenol) (2) with benzoic acid in o-dichlorobenzene / PPSE at elevated temperature gave the model benzoxazole 3 in quantitative yield.



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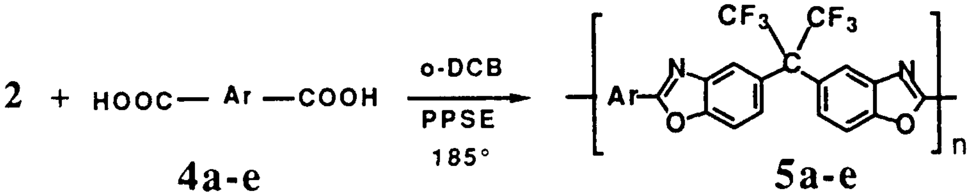
3. Synthesis of Polybenzoxazoles

The polycondensation of 2 with the appropriate difunctional aromatic acid 4a-e using experimental conditions similar to those established for the synthesis of the model compounds gave essentially quantitative yields of the polymers 5a-e. The aromatic diacid structures chosen where generally those which would not be easily prepared in polyphosphoric acid.



4a-e

5a-e

The polymers 5a-d precipitated from solution during the latter stages of the polymerization. Polymer 5e remained in solution during the entire polymerization.

4. Polymer Properties

a. Solubility and Viscosity

The polybenzoxazoles 5a-d were soluble in both methane sulfonic acid (MSA) and concentrated sulfuric acid. The same polymers were also soluble in a 3:1 mixture of

1,1,2,2-tetrachloroethane : phenol, and tough flexible films could be cast at 60°C in a vacuum oven from 2% solutions of the polymers in this solvent. Polymer **5e** was soluble in MSA and organic solvents such as chloroform, dichlorobenzene, and tetrahydrofuran (THF). Tough, flexible films of this polymer could be cast from 2% solutions of the polymer in chloroform or THF.

Inherent viscosities ranged from 1.82 to 2.82 dl/g (0,15g/dl @ 30°C) in MSA for polymers **5a-d**. Polymer **5e** exhibited inherent viscosities, at the same concentration, of 0.90 and 0.52 dl/g in MSA and **o**-dichlorobenzene respectively.

b. Thermalanalytical Properties

The viscosity and thermalanalytical data for polymers **5a-e** are summarized in Table 1. Polymers **5a-e** exhibit a base line shift in the DSC thermogram characteristic of a glass transition ranging from 94° to 382°C. Thermogravimetric analyses of the polybenzoxazoles **5a-d** exhibited onsets of their respective major weight losses between 530° and 540°C in air. The same polymers showed onsets of major weight loss in helium between 524° and 547°C. The polymer **5e** showed an onset of weight loss in air at 414°C with major weight loss in helium commencing at 426°C.

Isothermal aging of polymers **5a-c** showed excellent thermooxidative stability by retaining 92 to 95 percent of their weight after 200 hours at 650° F (346°C) in circulating air. Polymer **5d** retained only 59 percent of its weight after 200 hours under the same conditions. This reduction in thermooxidative stability of the 2,5-pyridyl linked polymer when compared to the 2,6-pyridyl linked is not fully understood and is still under investigation.

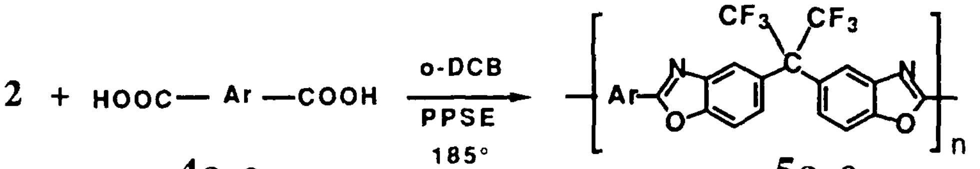
The isothermal aging of polymer **5e** showed a 50 percent weight retention after only 50 hours at 650°F. This decreased thermooxidative stability was expected due to the presence of the more thermally labile oxydecyl pendants.

5. Conclusions and Future Work

The subject polymerization method as investigated thus far shows exceptional promise for the synthesis of aromatic polybenzoxazoles. The major benefits of such a method are its

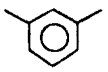
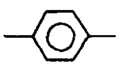
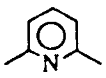
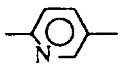
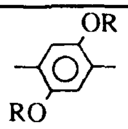
TABLE 1

Viscosities and Thermal Properties of Polybenzoxazoles



4a-e

5a-e

Polymer	Ar	η_{inh}[a] (dl/g)	T_g[b] (°C)	TGA[c] (°C)	ITA[d] %
5a		2.82	300	532(air) 524(He)	95
5b		2.23	382	533(air) 525(He)	94
5c		1.82	329	539(air) 528(He)	92
5d		2.18	352	530(air) 547(He)	59
5e	 R = $C_{10}H_{21}$	0.92 0.52[f]	94	414(air) 425(He)	50[e]

(a) Inherent viscosity in methane sulfonic acid (0,15g/dl) at 30°C.
(b) Glass transition temperature determined by DSC (ΔT= 10° C / min.
(c) Decomposition temperature determined by thermogravimetric analysis in air and helium.
(d) Isothermal aging, weight retained after 200 hrs at 650° F (346°C) in air.
(e) Weight retained after 50 hrs at 650°F (346°C) in air.
(f) Inherent viscosity in o-dichlorobenzene (0.15g/dl) at 30°C.

simplicity and the convenience of using nonderivitized dicarboxylic acids and o-aminophenols directly in the polymerization. Recently, a novel method to synthesize thermoplastic polybenzoxazoles has appeared in the literature (Reference 9). This method involves not only a costly trimethylsilylated o-aminophenol monomer but also requires a two-step polymerization process. The PPSE polymerization method appears to produce much higher molecular weight polymers than the method described in Reference 9 when inherent viscosities are compared.

Future work to refine the polymerization procedure and the investigation of various cosolvents needs to be carried out in order to optimize the purity of the polymers produced. Research involving other cosolvents could also lead to a reaction medium which would allow a greater number of polymer structures to remain soluble during the course of the polymerization, thus generalizing the procedure to an even greater extent. This research is currently underway.

SECTION III

EXPERIMENTAL

The o-dichlorobenzene used in this study was Aldrich HPLC grade. It was dried for 48 hours over 4A molecular sieves prior to use. All other solvents were used as received. The phosphorus pentoxide (99.99%) was purchased from Alpha Chemical Company and used without further purification. Terephthalic acid was purchased from Aldrich Chemical Company and purified by sublimation. Isophthalic acid was purchased from Aldrich Chemical Company and recrystallized from 9:1 ethanol : water prior to use. Pyridine 2,5-dicarboxylic acid and pyridine 2,6-dicarboxylic acid were also purchased from Aldrich and recrystallized from water prior to use. Monomer grade 4,4'-hexafluoroisopropylidene bis(2-aminophenol) was purchased from Daychem Laboratories Inc. and used without further purification.

1. Preparation of trimethylsilyl polyphosphate (PPSE)

The preparation of PPSE was carried out using a procedure similar to that described in the literature (Reference 7). A mixture of 10.0g (0.070 mol) of P_2O_5, 19.1g (0.117mol) (25ml) of hexamethyldisiloxane, and 50 ml of alcohol free chloroform were heated at reflux under N_2 until all the P_2O_5 had dissolved (approx 1 hr). The reaction mixture was cooled to room temperature and the chloroform removed under vacuum.

2. Preparation of 5,5'-(hexafluoroisopropylidine)bis(2-phenyl-benzoxazole) (3)

A mixture of 1.83 g (0.005 mol) of 4,4'-(hexafluoroisopropylidine)bis(2-aminophenol) (2), and 1.34g (0.011 mol) of benzoic acid, was placed in a combination of 6.0g of PPSE (made as described above) and 10 ml of o-dichlorobenzene. The reaction mixture was heated under nitrogen to 110°C for 2 hrs. The temperature was then slowly raised over a period of 3 hrs to

180°C and maintained there for 4 hrs. The reaction mixture was allowed to cool to room temperature poured into 250 ml of H_2O and extracted with 100ml of methylene chloride. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate and evaporated under vacuum. The resulting solid was recrystallized from n-propanol /water to give 2.43g (90%) of white crystals, mp 173°-175° C. Analysis calc'd for $C_{29}H_{16}F_6N_2O_2$: C, 64.69 ; H, 3.00 ; N, 5.20 . Found : C, 64.48 ; H, 3.00; N, 5.20 . Mass Spectrum (EIMS) : m/z = 538 (M+ , 19.5), 207 (100) . The FTIR Spectra for model compound **3** is illustrated in Figure 1.

3. General Procedure for Synthesis of Polymers (**5a-d**)

A mixture of 1.8313g (0.005 mol) of 4,4'-(hexafluoroisopropylidene) bis(2-aminophenol), (0.005 mol) of the appropriate acid, and 6.0g of PPSE in 15ml of o-dichlorobenzene was heated by means of an oil bath to 135° C under nitrogen and maintained there for 24 hrs. The temperature of the polymerization mixture was then raised to 165°C for an additional 24 hrs. At the end of this period, the temperature was again increased to 180° C for 24 hrs. During the final heating period, the polymer precipitated from the reaction mixture. The polymerization mixture was allowed to cool to room temperature and poured into stirring methanol (500 ml). The precipitated polymer was filtered, chopped in a Waring blender with methanol, filtered and air dried. Further purification was carried out by extracting the polymer with 33% aqueous ammonium hydroxide in a Soxhlet extractor for 18 hrs. The polymer was then washed extensively with water and dried at 140° (1 mm Hg) for 18 hrs.

Poly[2,5-benzoxazolediyl][2,2,2,-trifluoro-1-(trifluoromethyl)ethylidene]-5-2-benzoxazolediyl-1,3-phenylene] (5a): Inherent viscosity = 2.79 dl/g (0.15 g/dl @ 30° C). Analysis calc'd for $(C_{23}H_9F_6N_2O_2)_n$: %C, 60.01; %H, 2.19; %N, 6.09; %F, 24.77. Found: %C, 59.58; %H, 2.38; %N, 5.79; %F, 23.60. The FTIR spectra for polymer **5a** is illustrated in Figure 2.

Poly[2,5-benzoxazolediyl[2,2,2,-trifluoro-1-(trifluoromethyl)ethylidene]-5-2-benzoxazolediyl-1,4-phenylene] (5b): Inherent viscosity = 2.23 dl/g (0.15 g/dl @ 30° C).

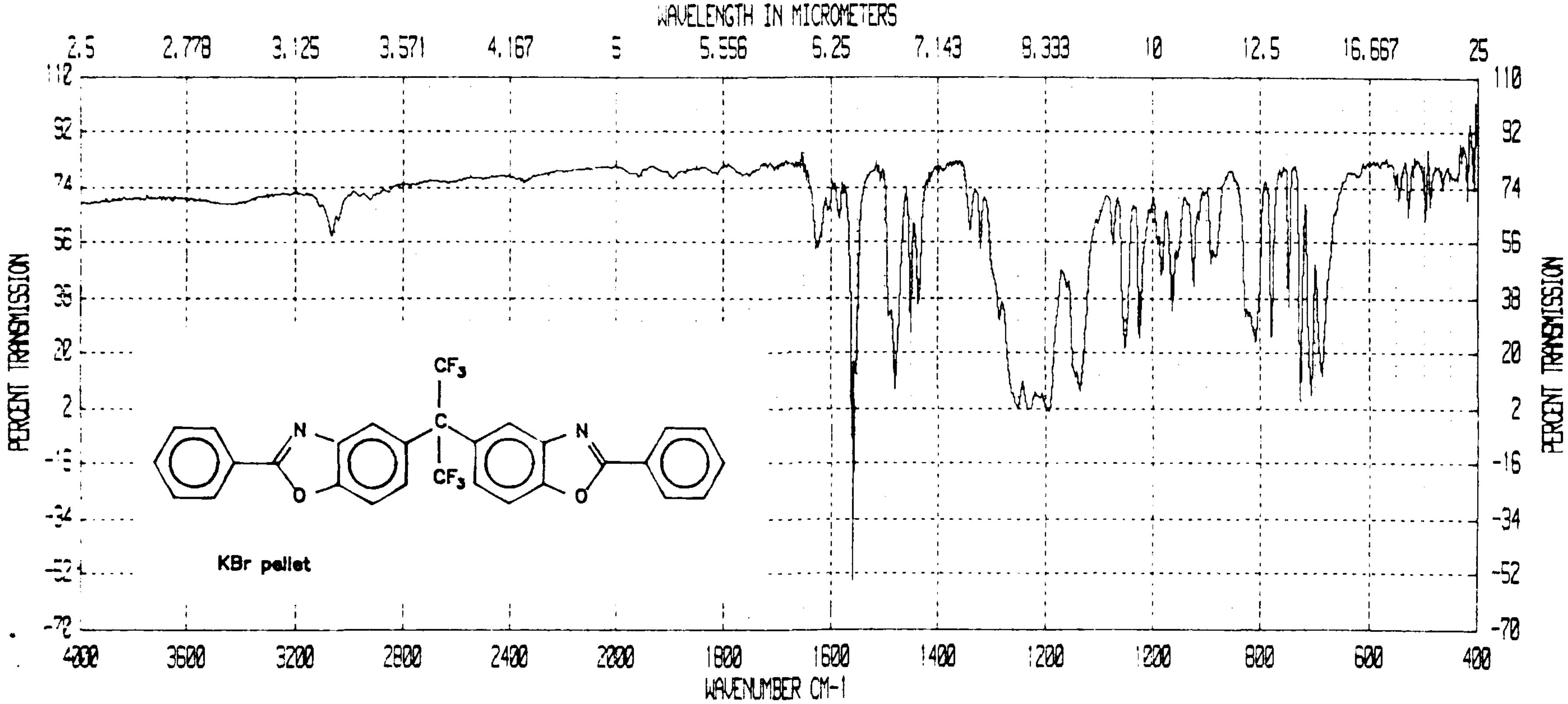


Figure 1. FTIR Spectrum of Model Compound 3

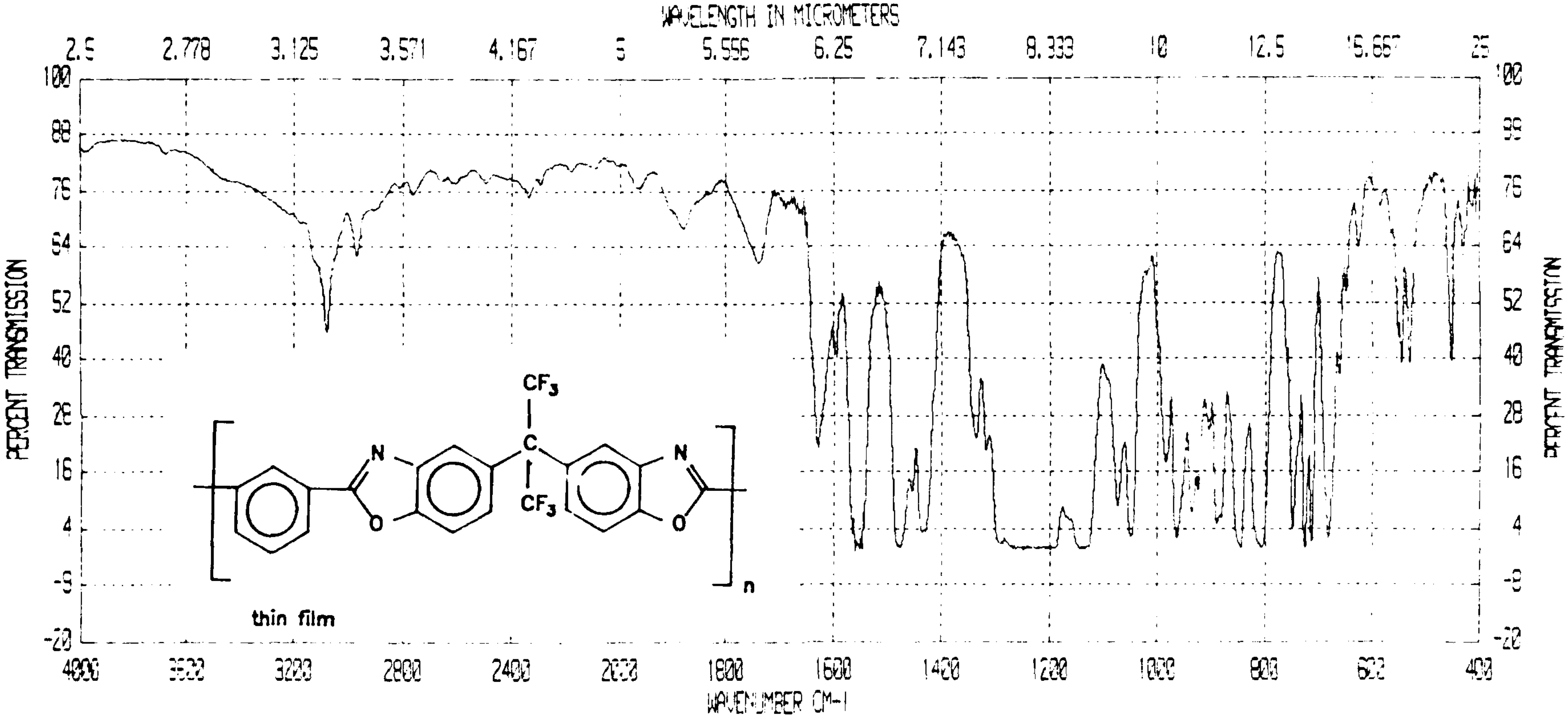


Figure 2. **FTIR Spectrum of Polymer 5a (film cast from 3:1 1,1,,2,2-tetrachloroethane:phenol)**

Analysis calc'd for $(C_{23}H_9F_6N_2O_2)_n$: %C, 60.01; %H, 2.19; %N, 6.09; %F, 24.77.

Found : %C, 59.55; %H, 2.53; %N, 5.80; %F, 23.60.

Poly[2,5-benzoxazolediyl[2,2,2,-trifluoro-1-(trifluoromethyl)ethylidene]-5-2-benzoxazolediyl-2,6-pyridinediyl] (5c): Inherent viscosity = 1.82dl/g (0.15g/dl @ 30° C)

Analysis calc'd for $(C_{22}H_9F_6N_3O_2)_n$:.%C, 57.28; %H, 1.97; %N, 9.11; %F, 24.71.

Found : %C, 56.75; %H, 2.13; %N, 8.93; %F, 23.59.

Poly[2,5-benzoxazolediyl[2,2,2,-trifluoro-1-(trifluoromethyl)ethylidene]-5-2-benzoxazolediyl-2,5-pyridinediyl] (5d): Inherent viscosity = 2.18dl/g (0.15g/dl @ 30° C)

Analysis calc'd for $(C_{22}H_9F_6N_3O_2)_n$: %C, 57.28; %H, 1.97; %N, 9.11; %F, 24.71.

Found : %C, 56.00; %H, 2.29; %N, 8.54; %F, 23.40.

4. Synthesis of Poly[2,5-benzoxazolediyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-5,2-benzoxazolediyl[2,5-bis(decyloxy)-1,4-phenylene]] (5e)

A mixture of 1.8313g (0.005 mol) of 4-4'-(hexafluoroisopropylidene) bis(2-aminophenol), 2.3933g (0.005 mol) of 2-5-bis(oxy-n-decyl)terephthalic acid, and 6.0g of PPSE in 15 ml of o-dichlorobenzene was heated by means of an oil bath to 135°C under nitrogen for 24 hrs. The temperature was then increased to 160°C for 48 hrs. The temperature was further increased to 185°C and maintained there for 24 hrs. Upon completion of the final heating period, the polymer solution was allowed to cool and was precipitated by pouring into 500 ml of stirring methanol. The polymer was filtered and dried at 110°C (1 mm Hg) for 24 hrs to give 2.91g (75%) with an inherent viscosity of 0.90 dl/g (0.17g/dl @ 30°C). The FTIR spectra of polymer 5e is illustrated in Figure 3.

Analysis calc'd for $(C_{43}H_{50}F_6N_2O_4)_n$: %C, 66.82; H, 6.52; N, 3.63; F, 14.75.

Found : %C, 66.14; %H, 6.56; %N, 3.37; %F, 14.27.

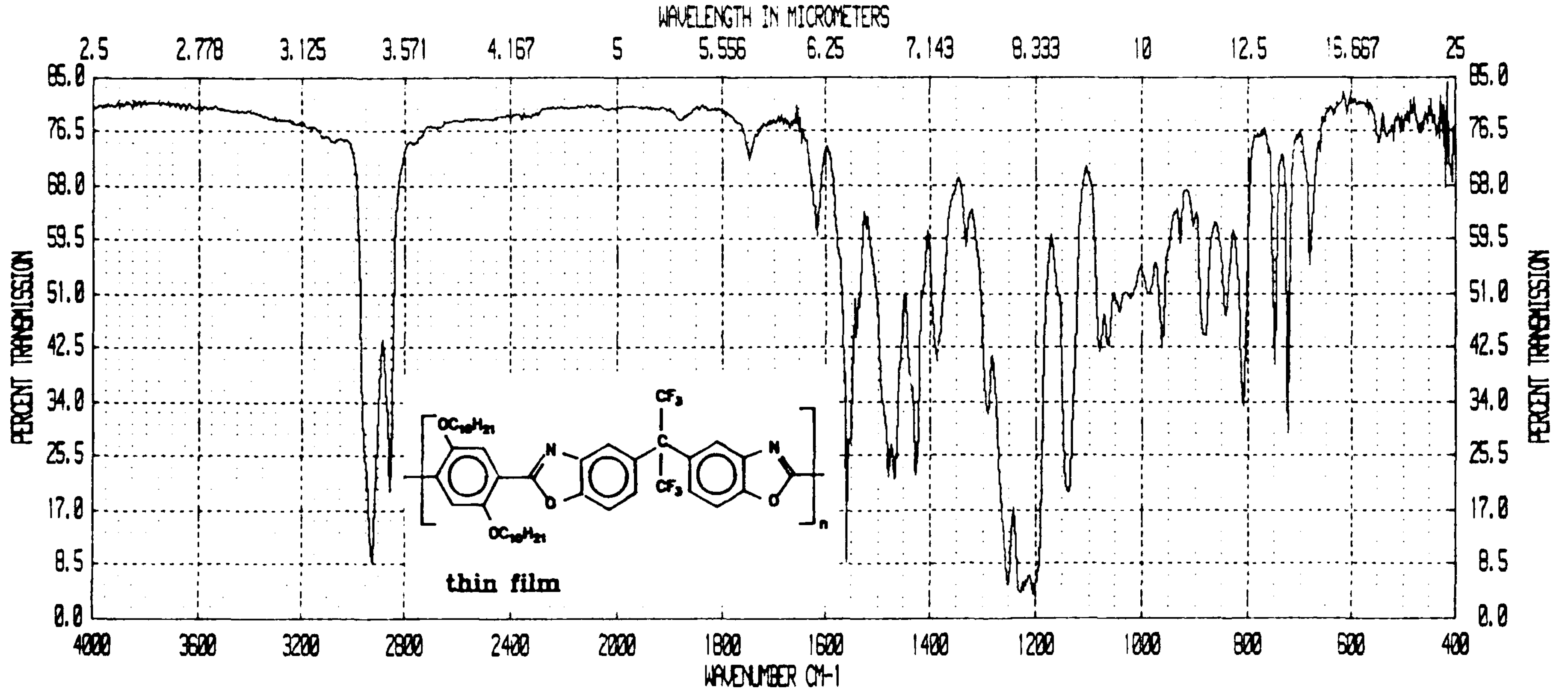


Figure 3. FTIR Spectrum of Polymer 5e (film cast from chloroform).

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