

1998

# Preparation and characterization of porous polyimides

Elena Lebedeva  
*San Jose State University*

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**PREPARATION AND CHARACTERIZATION OF  
POROUS POLYIMIDES**

**A Thesis**

**Presented to**

**The Faculty of the Department of Chemistry**

**San Jose State University**

**In Partial Fulfillment**

**of the Requirements for the Degree**

**Master of Science**

**by**

**Elena Lebedeva**

**December 1998**

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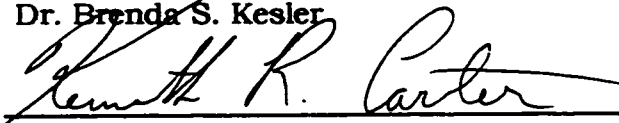
**Elena Lebedeva**

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APPROVED FOR THE DEPARTMENT OF CHEMISTRY



Dr. Brenda S. Kesler



Dr. Kenneth R. Carter  
(IBM, Almaden Research Center)




Dr. Daniel A. Straus



Dr. Leon S. Yengoyan

APPROVED FOR THE UNIVERSITY



## ABSTRACT

### PREPARATION AND CHARACTERIZATION OF POROUS POLYIMIDES

by Elena Lebedeva

Polyimides are currently used as interlayer dielectrics in microelectronics applications due to their excellent thermooxidative and mechanical stabilities. However, the lowest possible dielectric constant is required for the material in such an application. Modification of the polymer in one desired direction can often compromise some of the existing properties. Preparation of porous polyimides allows retention of all of the desired properties of polyimides while significantly decreasing the dielectric constant. Foam preparation was achieved by using a graft copolymer approach, where the thermally labile block, polypropylene oxide, became evenly distributed in the polyimide matrix and was later selectively degraded by heating, leaving voids filled with air. The decrease in dielectric constant is effected in this case because air has a dielectric constant of 1. Subsequent steps of functional macromonomer synthesis, preparation of poly(amic alkyl ester) graft copolymers, their thermal imidization and subsequent foaming, as well as the characterization of the products of all these steps, are described in the present thesis.



## **Acknowledgments**

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## **Chapter 1. Introduction**

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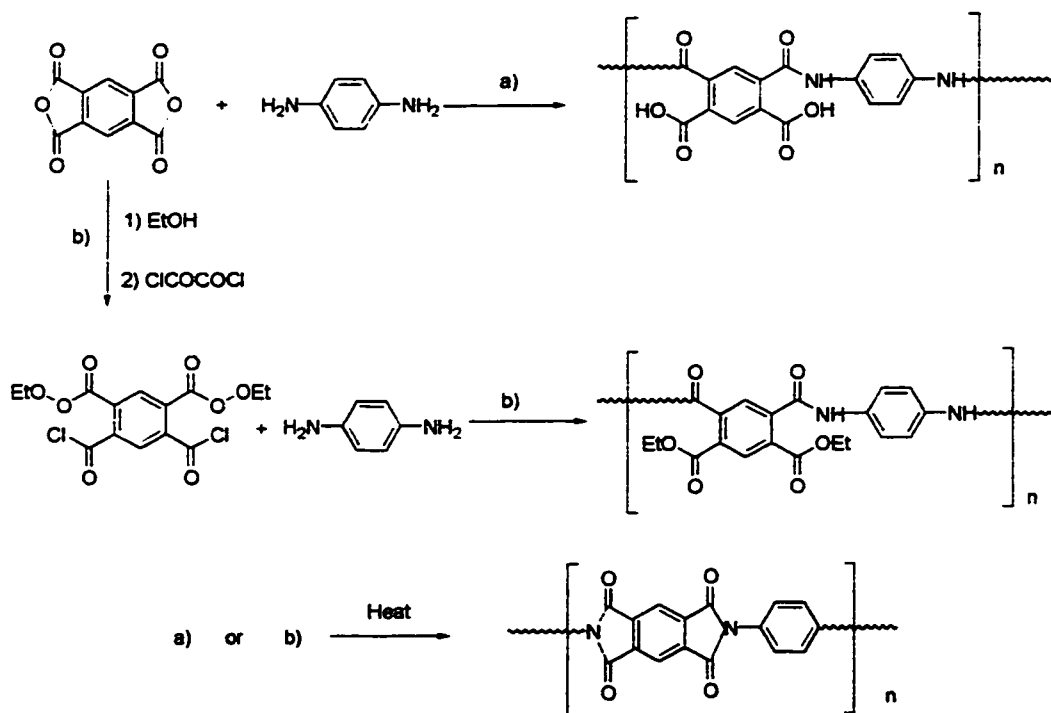
Polyimides are high performance polymers originally developed for wire coating and free standing film application because of their high thermal and oxidative stability. As research on polyimides has progressed, other valuable properties have been discovered: dimensional stability, crack and solvent resistance, high resistivity and low dielectric constant. All these properties have satisfied some of the material requirements for microelectronic applications. Polyimides not only are used as packaging materials in the manufacture of microelectronic devices, they also work as interlayer dielectrics for thin film wiring in multichip packages and chip interconnection.

Aromatic polyimides are commonly prepared in a two-stage synthesis first developed at the DuPont laboratories.<sup>1,2</sup> First, polycondensation between any aromatic diamine and dianhydride yields poly(amic acid) as shown in reaction a) (Scheme 1). Second, a thermal imidization of poly(amic acid) affords the polyimide. However, poly(amic acid), a polyimide precursor, exhibits a number of undesired characteristics such as the side reaction of isoimide formation or hydrolysis into starting materials.<sup>3</sup>

An alternative approach involves chemical modification of the poly(amic acid) into the poly(amic alkyl ester), which has eliminated side reactions.<sup>4,5</sup> Even though esterification of the poly(amic acid) backbone is possible,<sup>6</sup> the best

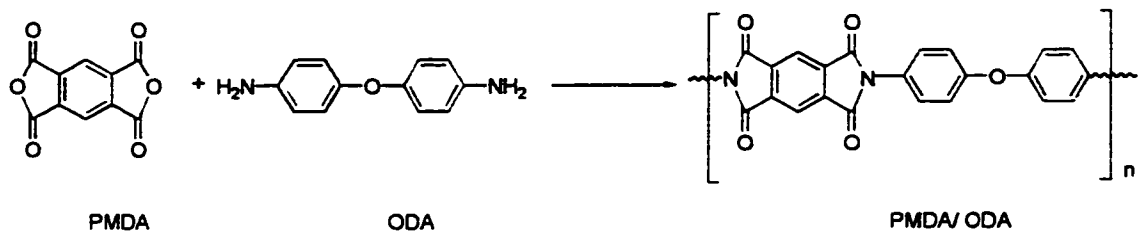
results are obtained when the monomer, for example pyromellitic dianhydride, is modified with an alcohol prior to polycondensation.<sup>7</sup> This dialkyl dihydrogen pyromellitate<sup>8</sup> then can be activated with oxalyl chloride in order to further react with aromatic diamine (route b) in Scheme 1). Not only is the poly(amic alkyl ester) much more hydrolytically stable and a more soluble polyimide precursor than poly(amic acid), but it also offers great synthetic flexibility by the ability to vary alcohol and activating agents.<sup>9</sup> All of this results in a better imidization behavior of poly(amic alkyl esters), for example, higher imidization temperature and molecular weight than the corresponding poly(amic acid). Taking advantage of synthetic opportunity, the present research utilizes a poly(amic alkyl ester) route to the polyimide.

**Scheme 1**



Chemical names of polyimides usually do not follow IUPAC rules because of the complexity of their structures; rather their names are derived from the names of the corresponding dianhydride and diamine for both, poly(amic acid) and poly(amic alkyl ester) polyimide methods. For example, one of the most common polyimides, PMDA/ODA (Scheme 2), is based on pyromellitic dianhydride, PMDA, and 4,4'-oxydianiline, ODA.

**Scheme 2**



One of the crucial properties of the material in microelectronics applications is a low dielectric constant. Since the velocity of pulse propagation is inversely proportional to the square root of the dielectric constant of the medium, a decrease in the dielectric constant of insulating material results in a faster traveling signal and shorter device cycle times.

$$V=C/\epsilon^{1/2}$$

V-propagation velocity of a pulsed signal

$\epsilon$ -dielectric constant

C-propagation medium

Furthermore, lowering of the dielectric constant of the insulator allows decrease in "crosstalk", noise arising from current induced in conductors adjacent to active signal lines. Thus, low dielectric constant insulators allow a closer spacing between the signal lines and, therefore, denser circuit patterns and smaller microelectronic devices.<sup>10</sup>

Even though dielectric constants of most polyimides (3.2-3.0) are lower than that of silicon dioxide (4.0), the currently used material, the goal is to modify polyimides to further decrease their dielectric constants. One approach has been to incorporate pendant perfluoroalkyl groups,<sup>11,12</sup> which allow the dielectric constant to be lowered to 2.6, but this approach is limited by synthetic difficulties. The second approach includes preparation of a block copolymer of polyimide and a lower dielectric constant polymer, for example, perfluoroalkylene aryl ether.<sup>13</sup> However, dielectric constants of such block copolymers can not be decreased significantly because of the limiting choice of low dielectric constant oligomers. The third, and very efficient approach, is to introduce pores into the polyimide material, filling the polyimide with air, material with the lowest dielectric constant equal to 1.0. For example, polyimides derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) have dielectric constants of approximately 3.2; the incorporation of 25% porosity would decrease the dielectric constant to 2.65. The relationship between porosity and dielectric constant of material was first described by Maxwell Garnett.<sup>14</sup>

Preparation of porous materials can be achieved by adding foaming agents,<sup>15</sup> inclusion of glass, or carbon hollow microspheres,<sup>16,17</sup> or partial

degradation generating foaming agents.<sup>18</sup> All of these methods yield materials with the pore size  $>1\mu\text{m}$ , which are good for aerospace and transportation applications but unsuitable in microelectronics, where nanometer size voids are required. It is very important to have pores much smaller than the polymer film thickness to prevent open pore structure. Interconnected porous dielectric is incompatible with current manufacturing processes.

Nanofoams, materials with voids nanometer in size, can be synthesized by utilizing a block copolymer approach where a thermolabile polymer is dispersed in the matrix of a thermally stable polymer. Subsequent thermal treatment degrades the thermally unstable component leaving pores with size and shape corresponding to the original morphology of the phase separated block copolymer.

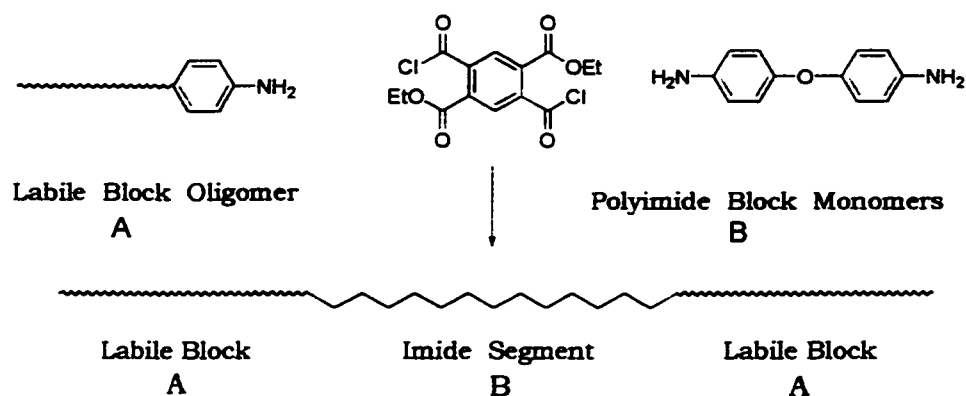
One of the first successful polymer nanofoams was prepared by Hedrick et. al.,<sup>19</sup> where -ABA-triblock copolymers were composed of a thermally stable poly(phenylquinoxaline) (PPQ) matrix with either poly(propylene oxide) (PPO) or poly(methyl methacrylate) (PMMA) as the thermally labile coblocks.

Carter et. al.,<sup>20</sup> have synthesized polyimide nanofoams using both poly(amic acid) and poly(amic alkyl ester) approaches to polyimide synthesis as well as a variety of aromatic diamines and dianhydrides. ABA-triblock copolymer consisted of thermostable matrix, polyimide, and thermally labile oligomer, polypropylene oxide (PPO). Scheme 3 shows one of examples of PPO-Polyimide-PPO triblock polyimide before thermal degradation of polypropylene oxide.



An alternative approach, other than the ABA-triblock copolymer, is graft copolymer synthesis. This approach is characterized by the fact that “the sites

**Scheme 3**

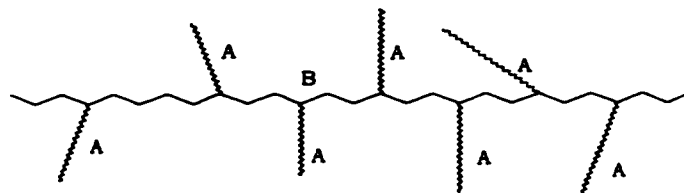


at which the second and subsequent blocks are attached to the first are no longer terminal units but are at positions along the backbone of the first chain”.<sup>21</sup> There are a number of methods for graft copolymer synthesis, including grafting “from”, grafting “into”, and grafting via macromonomers. Grafting via macromonomers yields comb-branch structures similar to the one presented in Scheme 4, where branches of thermally labile oligomer A are attached to the matrix polymer backbone B. This approach is amenable to creating block copolymers necessary for the generation of polyimide foams.

The present Master’s thesis describes the first attempt to synthesize polyimide nanofoams using a graft copolymer approach with polypropylene

oxide as thermally degradable block and polyimide, prepared by a poly(amic alkyl ester) route, as the thermally stable matrix.

**Scheme 4**



## Chapter 2 Research Goals

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The entire project “Preparation and Characterization of Porous Polyimides” can be divided into three main parts: preparation of novel functional macromonomer, polyimide graft copolymer synthesis, and foam preparation. Each subsequent part is a logical continuation of the previous.

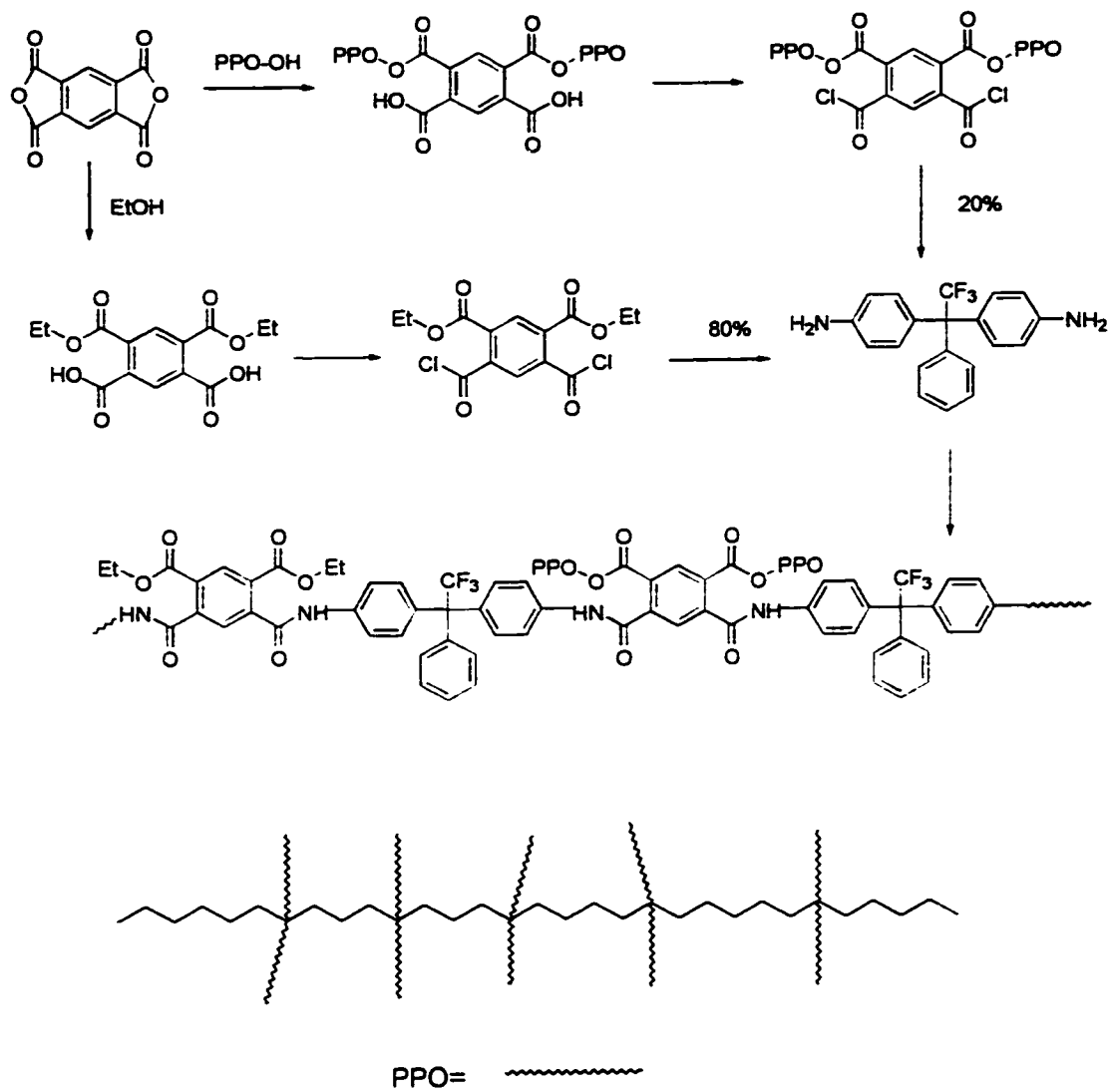
There are two diester dichloride monomers competing with the diamine to form poly(amic alkyl ester), one is meta- or para- pyromellitic dianhydride diester dichloride (PMDA (OEt)); and the other is macromonomer pyromellitic dianhydride diester (polypropylene) dichloride (PMDA-PPO). PMDA (OEt) diester dichloride is prepared by an esterification reaction of pyromellitic dianhydride with ethanol, followed by activation of the resulting diester-diacid with oxalyl chloride. The macromonomer is obtained in the similar way, but pyromellitic dianhydride is esterified with freshly prepared polypropylene oxide, which is synthesized so that each polymer chain has one terminal hydroxyl group.

Varying amounts of the macromonomer (5% to 35%) can be added along with the PMDA (OEt) monomer in the reaction with diamine to yield poly(amic alkyl ester) as a graft copolymer with polypropylene oxide. Because two polypropylene oxide chains are attached to each macromonomer, resultant graft copolymer can be described as “two-sided comb”. Scheme 5 shows an example of such a synthesis with 20% of functional macromonomer added to 80% of

of such a synthesis with 20% of functional macromonomer added to 80% of “regular” PMDA (OEt) diester dichloride monomer. Upon thermal cyclimidization, the ester bonds of the ethoxy groups and PPO get broken and are no longer connected to the polyimide backbone. If imidization is conducted under the argon atmosphere, with no oxygen in the system, the ethanol evolved is evaporated but the polypropylene oxide block remains and is locked in its original phase separated morphology within the polyimide matrix.

Thermal treatment in the presence of oxygen (air) at 260-280 °C causes degradation of the polypropylene oxide into low molecular weight volatile products leaving voids of size and shape of thermally labile copolymer morphology. Optimal temperature and time of foaming must be found since the prepared porous polyimide can collapse during excessive heating.

**Scheme 5**



## **Chapter 3 Monomer Synthesis**

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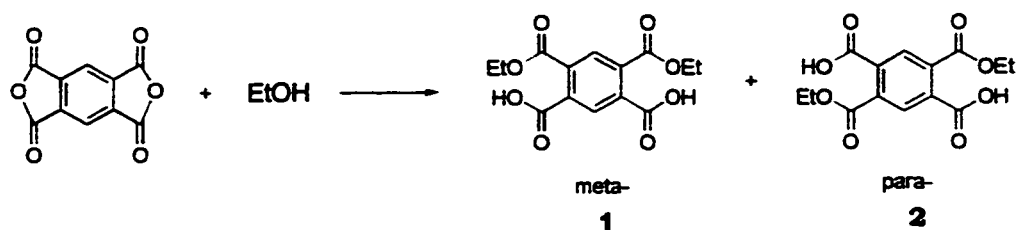
### **3.1. Preparation of PMDA-OEt-diethyl dichloride**

#### **3.1.1. Esterification of PMDA with Ethanol**

Nomenclature in polyimide chemistry can be quite confusing. There are several commonly used names for the product of esterification between pyromellitic dianhydride, PMDA, and ethanol: dicarboethoxyisophthalic acid, diethyl dihydrogen pyromellitate,<sup>9</sup> bis(ethoxycarbonyl)phthalic acid,<sup>21</sup> or the name traditionally used in our group, PMDA (OEt) diester diacid. The standard procedure described by Bell and Jewell <sup>7</sup> has been used in many other polyimide syntheses.<sup>8,9,22</sup>

PMDA was refluxed in an excess of the ethanol under Ar slowly dissolving during 4-6 hours (scheme 6). After the excess of ethanol was vacuum distilled, the mixture of para-PMDA (OEt) diester diacid, 2,5-dicarboethoxyterephthalic acid, and meta-PMDA (OEt) diester diacid, 4,6-dicarboethoxyterephthalic acid, isomers (1:1) were obtained as white crystalline solid. The isomer mixture thus prepared was supplied by Rick Dipietro at the IBM Almaden Research Center.

### Scheme 6



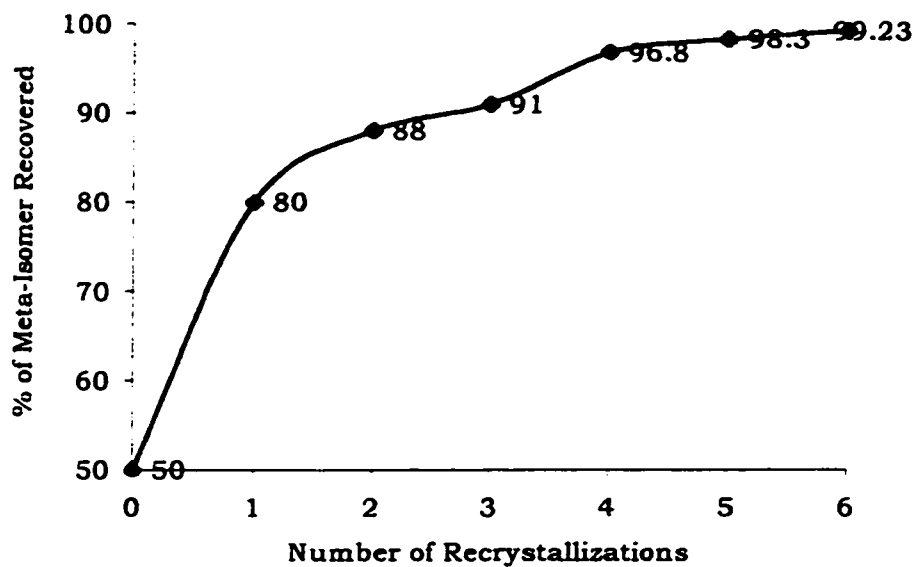
#### 3.1.2. Isomer Separation

Because of the vastly different solubility of the meta- and para- isomers, the meta-isomer of PMDA diester (OEt)-diacid **1** was separated from the initial 1:1 isomer mixture by performing six subsequent fractional recrystallizations with an overall yield of 20%. The lower solubility of the para- isomer caused it to preferentially precipitate from the initial 1:1 solution. However, after several subsequent recrystallizations, the concentration of the para- isomer was low enough to allow for the crystallization of the meta- isomer.

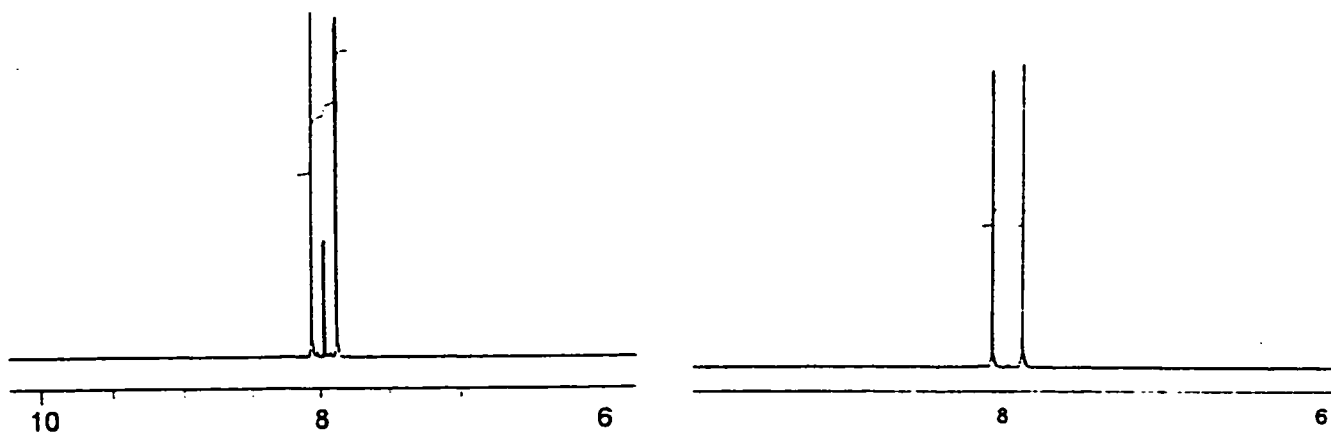
As is seen from Figure 1, the first two recrystallizations resulted in good enhancement of the meta-/para-isomer ratio; while the last four gave only small gains. Recrystallizations were performed from hot ethyl acetate with hexane added to initiate crystallization. Isomer ratio of each subsequent precipitate/filtrate was analyzed by  $^1\text{H}$  NMR spectroscopy and HPLC chromatography.

In the case of  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ), integration of two singlets at 7.88 ppm and 8.07 ppm corresponding to the meta-isomer steadily increased over integration of the singlet at 7.97 ppm corresponding to the para-isomer (Figure 2). Middle peak for para-isomer gradually gets smaller (9% in Figure 2a) after

**Figure 1.** Results of Subsequent Recrystallizations of 1:1 meta/para PMDA Diester Diacid Mixture.



**Figure 2.**  $^1\text{H}$  NMR spectra of aromatic regions of PMDA diester diacid isomer mixture: 90/10 meta/para ratio (to the left) and 99.23/0.77 meta/para ratio (to the right).

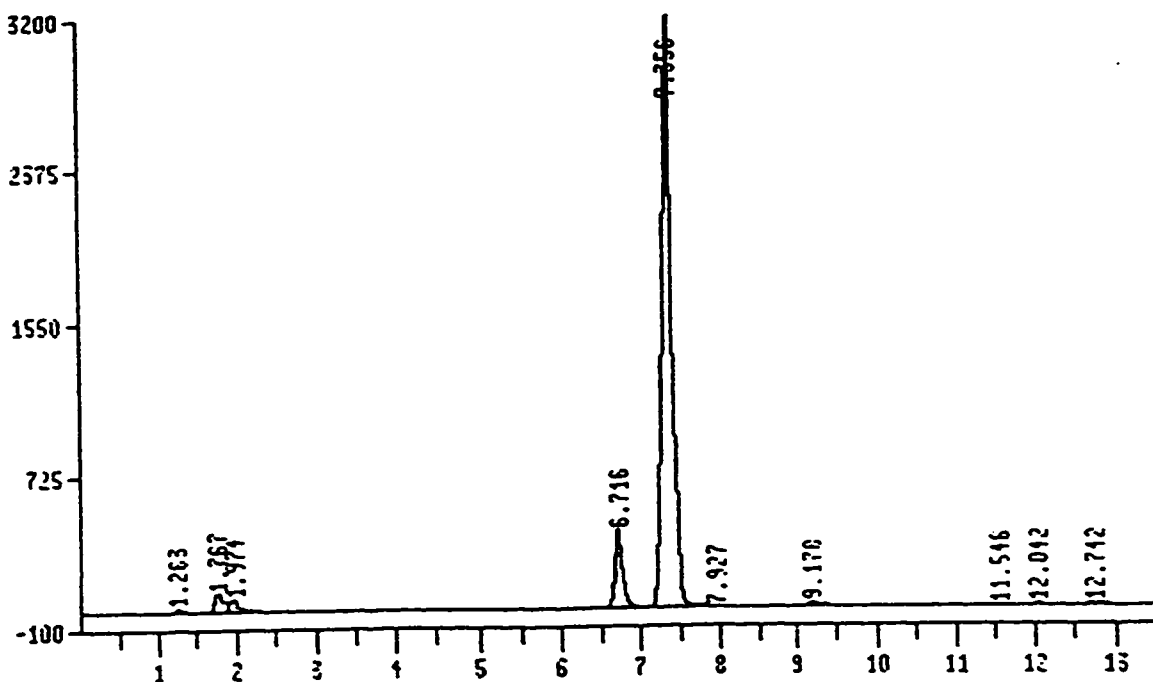




the third recrystallization and almost disappears (0.8%, figure 2b) after the last recrystallization.

HPLC analysis yielded the same numbers for the isomer ratio as  $^1\text{H}$  NMR spectroscopy, indicating the same sensitivity of both methods. Figure 3 shows the chromatogram of the third consecutive recrystallization: 91% and 9% of meta- and para-isomer. The peak with the retention time 6.716 corresponds to the para-isomer, whereas, the peak at 7.356 minutes corresponds to the meta-isomer.

**Figure 3.** HPLC Results of 9/91% Ratio of Meta/Para PMDA Diester Diacid Mixture.



### 3.1.3. Activation of PMDA Diester-Diacid with Oxalyl Chloride

Activation of the acid groups in PMDA diester diacid enables the monomer to enter a polymer forming reaction with diamine. The most widely used activation process is conversion of the diacid derivative into diacyl chloride,<sup>4,5,23</sup> though the other milder reagents have been reported.<sup>24,25</sup> Scheme 7 presents the activation process with an excess of oxalyl chloride as the chlorinating agent.

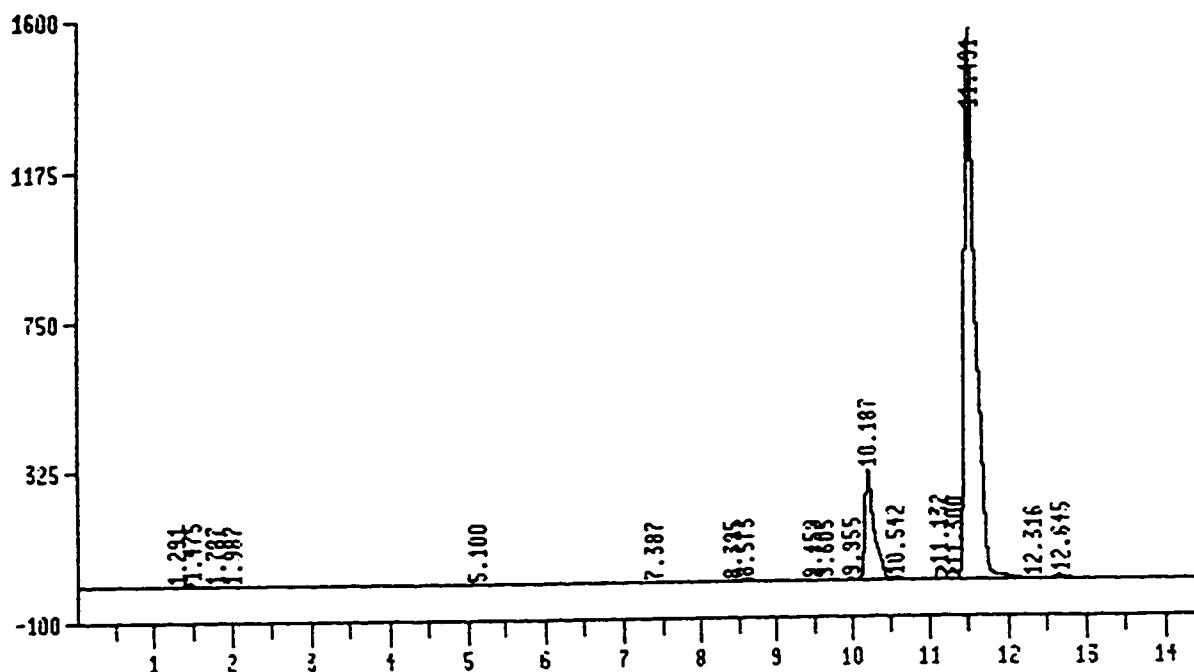
Scheme 7



Completion of the reaction was monitored by HPLC (Figure 4) in THF-water after product 3 was converted into diamide by reaction with dipropylamine. Reaction was judged complete when only two peaks were observed, corresponding to the residual oxalyl chloride at retention time 10.187 and diethyldiamide pyromellitate at retention time 11.101.

Additionally, <sup>1</sup>H NMR confirmed the purity of the product 3, and the completion of the activation reaction. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum shows only two peaks for the two aromatic hydrogens of PMDA diester (OEt) dichloride at 7.89 and 8.36 ppm, each with integration for one proton (Figure 5). If the starting material, PMDA diester diacid were still present, there would be more than two aromatic single peaks.

**Figure 4.** Results of HPLC Analysis Confirming the Completion of the Conversion of PMDA Diester Diacid into PMDA Diester Dichloride.

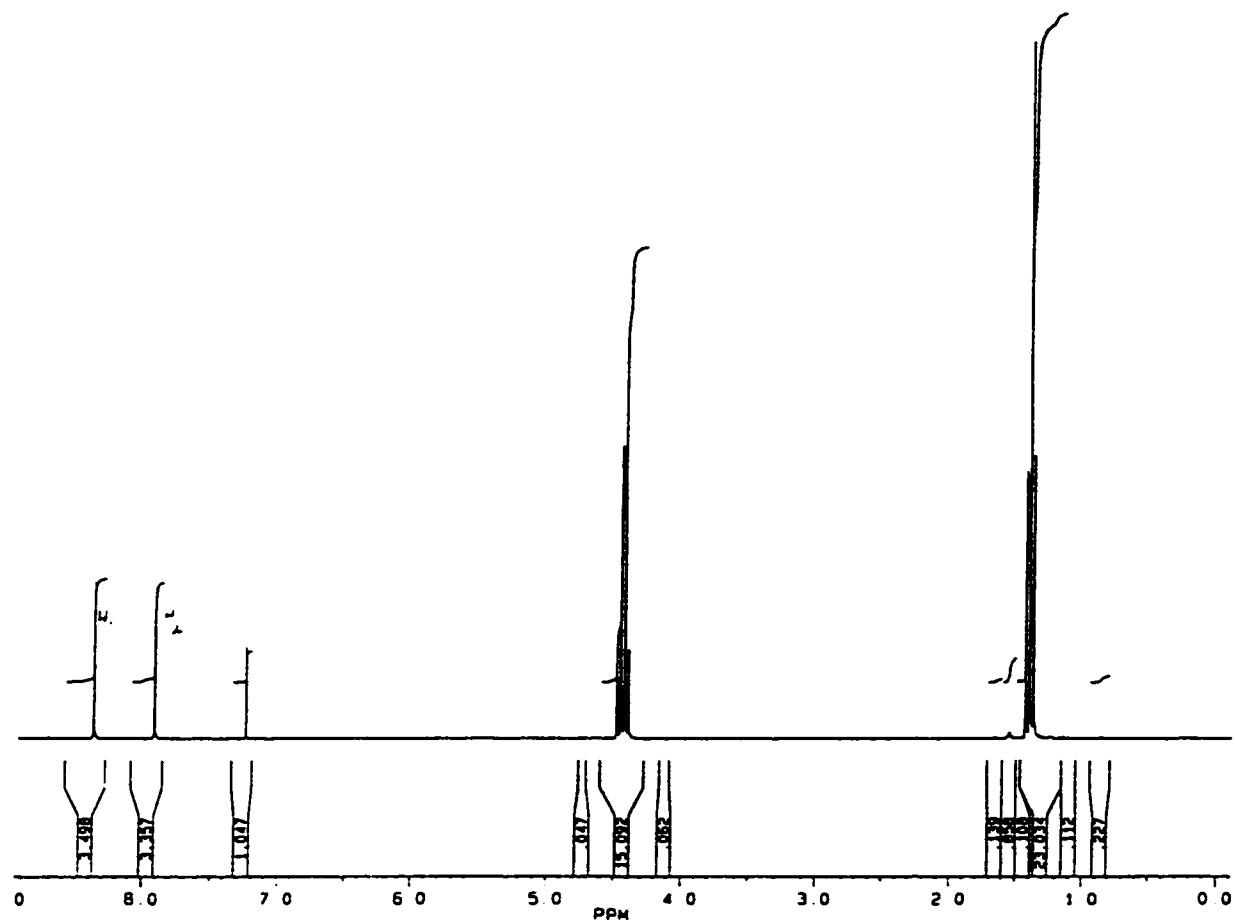


## **3.2. Preparation of the PPO-Containing Functional Macromonomer**

### **3.2.1 Polypropylene Oxide Preparation**

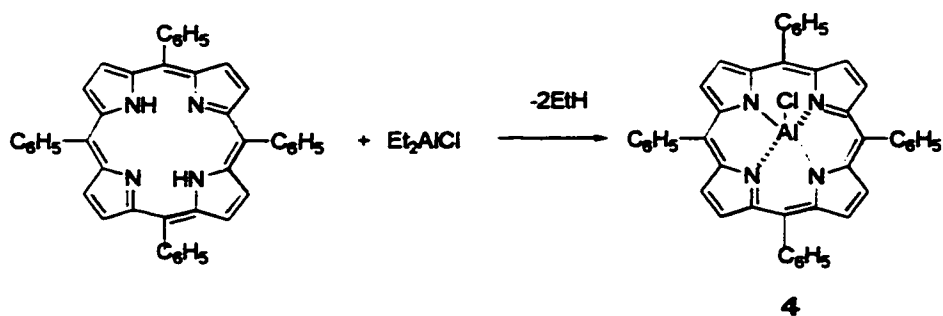
Synthesis of polypropylene oxide as a product of “living polymerization” of propylene oxide in the presence of metalloporphyrin was well researched and described by Inoue et al<sup>26,27</sup>. The method included two steps: catalyst preparation and catalytic polymerization. The catalyst system was obtained by equimolar reaction of diethylaluminum chloride,  $\text{Et}_2\text{AlCl}$ , with 5,10,15,20-tetraphenylporphyrin,  $\text{TPPH}_2$ .

**Figure 5.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of *m*-PMDA (OEt) diester dichloride (**3**).



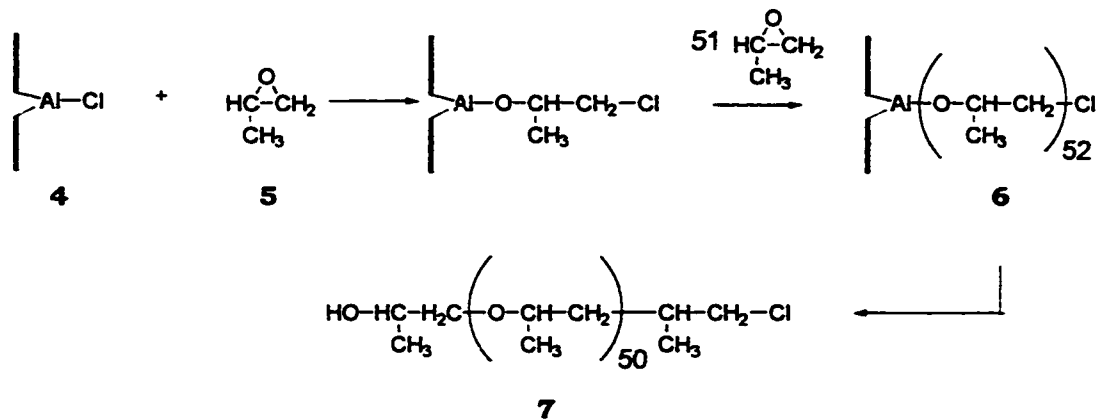
In our research, 20% excess of  $\text{Et}_2\text{AlCl}$  was added slowly to the  $\text{TPPH}_2$  dissolved in methylene chloride in a dry box (Scheme 8) to yield the catalyst, tetraphenyl-porphinato aluminum chloride (4).

**Scheme 8**



To the ice cold solution of the catalyst (4),  $(\text{TPP})\text{AlCl}$ , propylene oxide (5) was added with molar ratio 1:52 so that final polymer (6) had degree of polymerization  $n=52$  and estimated molecular weight of 3000 g/mol (Scheme 9). Those calculations were based on the properties of “living polymers.” Tetraphenylporphinato aluminum chloride (4) is a type of coordination initiator, each molecule of which initiates a chain. Therefore, all polymer chains were initiated at the same instant and grew at the same rate until all monomer was consumed. Such polymerization conditions resulted in the narrow molecular weight distribution. Chain growth would continue if more monomers were added, thus producing the term “living polymer.”

### Scheme 9



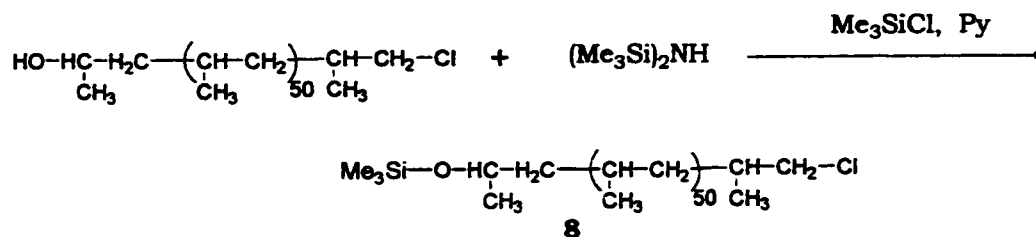
Addition of methanol to **6** cleaved and separated the catalyst from the polymer **7**. At this point all solvent was evaporated and weight of the mixture of the catalyst and PPO was measured. Subtracting the catalyst weight, the corrected value of the molecular weight of the prepared PPO was calculated (2800 Daltons). Because of numerous acid, water, and base washings and filtering through celite, only 66% of PPO was recovered.

Polypropylene oxide **7**, analyzed by gel permeation chromatography (GPC), showed a very narrow molecular weight distribution, with a polydispersity of 1.13, and molecular weight of 3,010 Daltons (Figure 6).

Since polypropylene oxide was to be further reacted with pyromellitic dianhydride, it was important to know the exact molecular weight of the PPO.  $^1\text{H}$  NMR spectrum of the pure PPO could not provide such information, but derivatized polypropylene oxide could. The challenge was to find such a reagent, which could provide 100% yield of the product in a reaction with PPO.

If the yield of the derivative was less than theoretical, it would erroneously increase the calculated molecular weight of PPO. Acyl chloride or benzoyl chloride were tried at different conditions but proved unsuitable. Finally, trimethylsilyl ether was prepared according to the procedure of Sweeley et al.<sup>28</sup> They reported 100% yield in the reaction between carbohydrates and hexamethyldisilazane, where hydroxy groups were silylated at room temperature in 5 minutes in pyridine solution. This reaction worked well for polypropylene oxide, giving reasonable yield and molecular weight close to that expected (Scheme 10).

**Scheme 10**



<sup>1</sup>H NMR spectrum of **8** presented in Figure 7 gave molecular weight value of 3140 Daltons. The value was calculated as follows:

Integration of the PPO methyl protons (1 ppm)=143.9

Integration of one PPO methyl proton=143.9/3=47.97

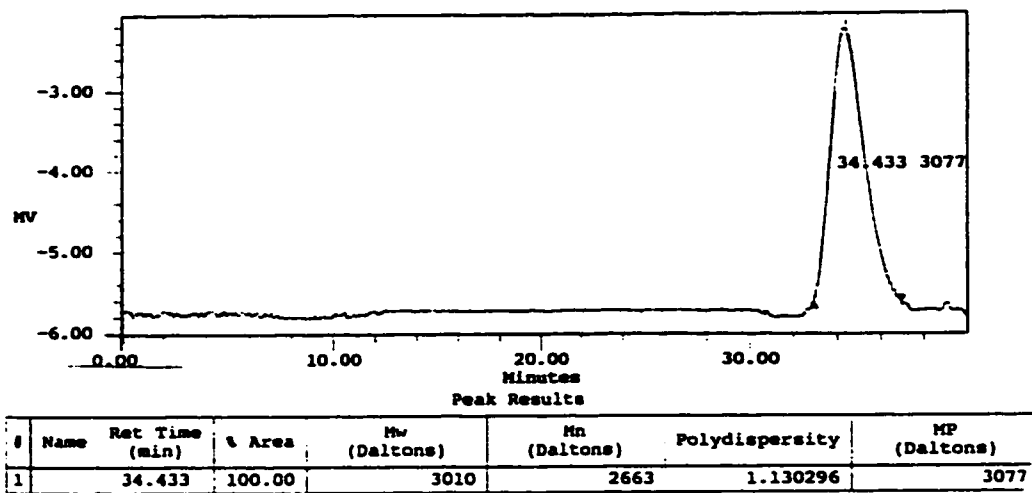
Integration of the trimethylsilyl group protons (0.05 ppm)=7.98

Integration of one trimethylsilyl hydrogen=7.98/ 9=0.887

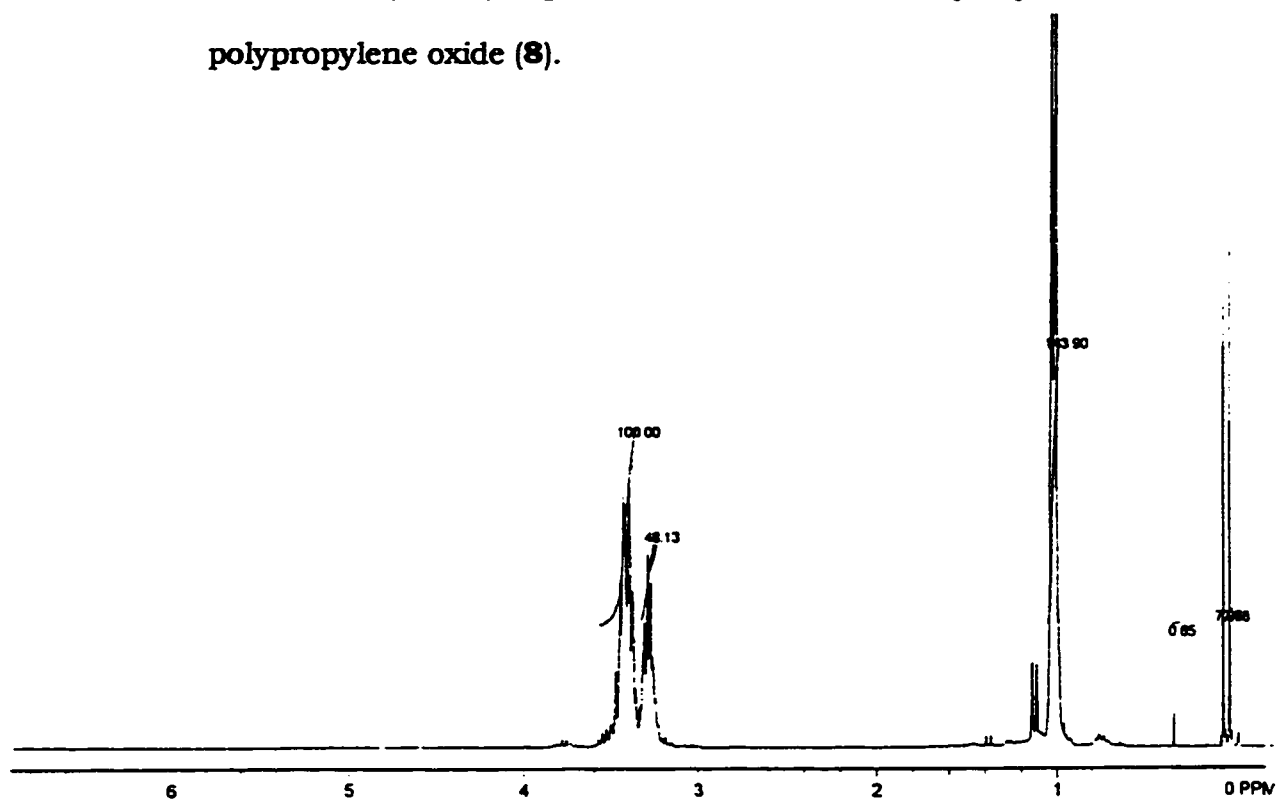
Ratio of PPO/trimethylsilyl hydrogens=47.97/0.887=54.08 (number of repeating units in polymer chain)

Molecular weight of the PPO=54.08\*58.08 (weight of one unit)=3140

**Figure 6.** Results of GPC analysis of polypropylene oxide (7)



**Figure 7.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of the trimethylsilyl ether of polypropylene oxide (8).

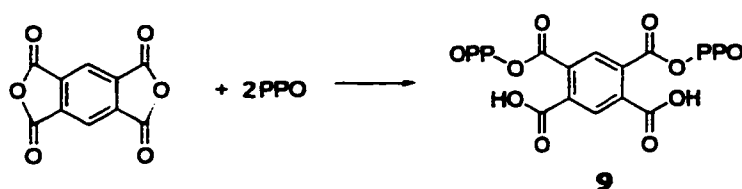




### 3.2.2. Synthesis of the Functional Macromonomer

Functional macromonomer **9** was prepared by reaction esterification (Scheme 11) between PMDA and hydroxy-terminated PPO (**7**) in ethyl acetate with 48 hour reflux.

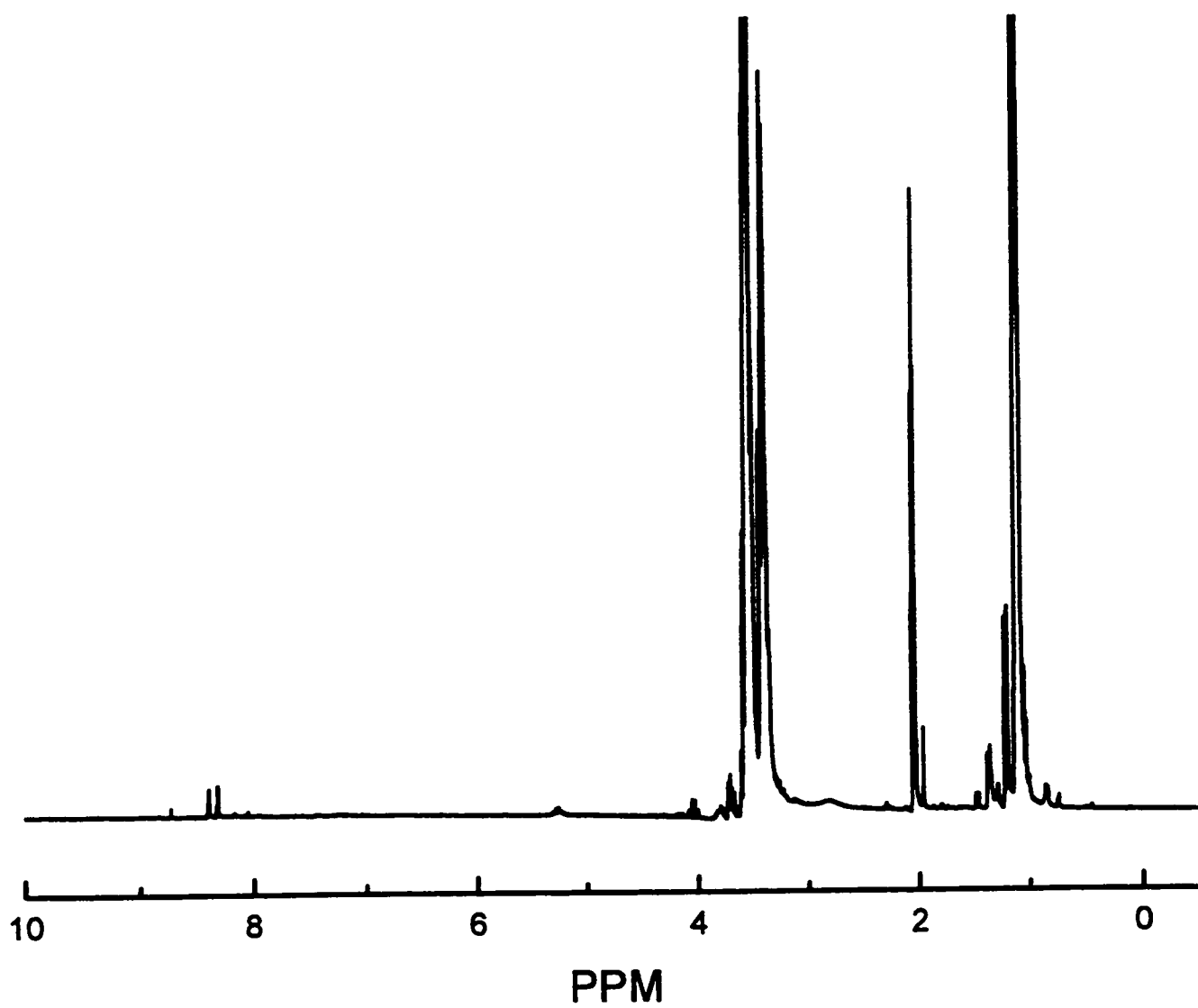
Scheme 11



Unexpectedly, only one of the two possible isomers, meta-, was obtained as was indicated from  $^1\text{H}$  NMR (acetone- $d_6$ ) spectrum of the product **9**. The aromatic region (Figure 8) consisted of the two single peaks: at 8.39 ppm, integration 1.00, and 8.31 ppm, integration 0.99. Equal integrations and the absence of the middle, para-, peak with double integration argued for the presence of only meta- isomer. Although, there was one more very small peak at 8.72 ppm, but it was obviously residual PMDA, whose  $^1\text{H}$  NMR in acetone- $d_6$  is well-known. The integration 0.09 of starting material, PMDA, in the spectrum of the product **9** could give an estimation of completion of the reaction. Indeed, ratio  $0.09/(1.0+0.99+0.09)=0.043$  gave 4.3% unreacted PMDA and 95.7% yield of the functional macromonomer **9**.

Additional molecular weight information can be gained from the  $^1\text{H}$  NMR spectrum of compound **9**. Comparing integrations of aromatic meta-hydrogens

**Figure 8.**  $^1\text{H}$  NMR (acetone- $d_6$ ) spectrum of functional macromonomer **9**.

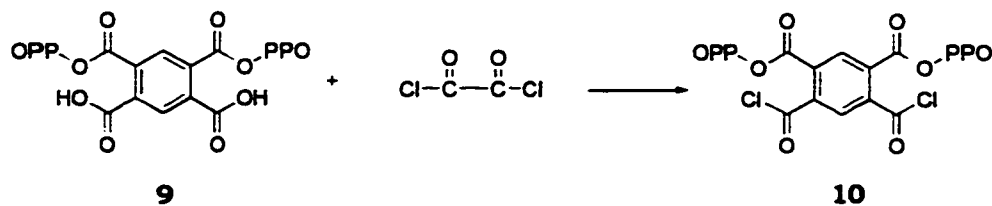


and integrations of PPO hydrogens one can calculate the number of repeating units in the PPO chain. The calculated molecular weight was 5300 g/mol. Since the macromonomer consists of two PPO units, a rough approximation of the PPO molecular weight is 2650 g/mol.

### 3.2.3. Activation of the Functional Macromonomer

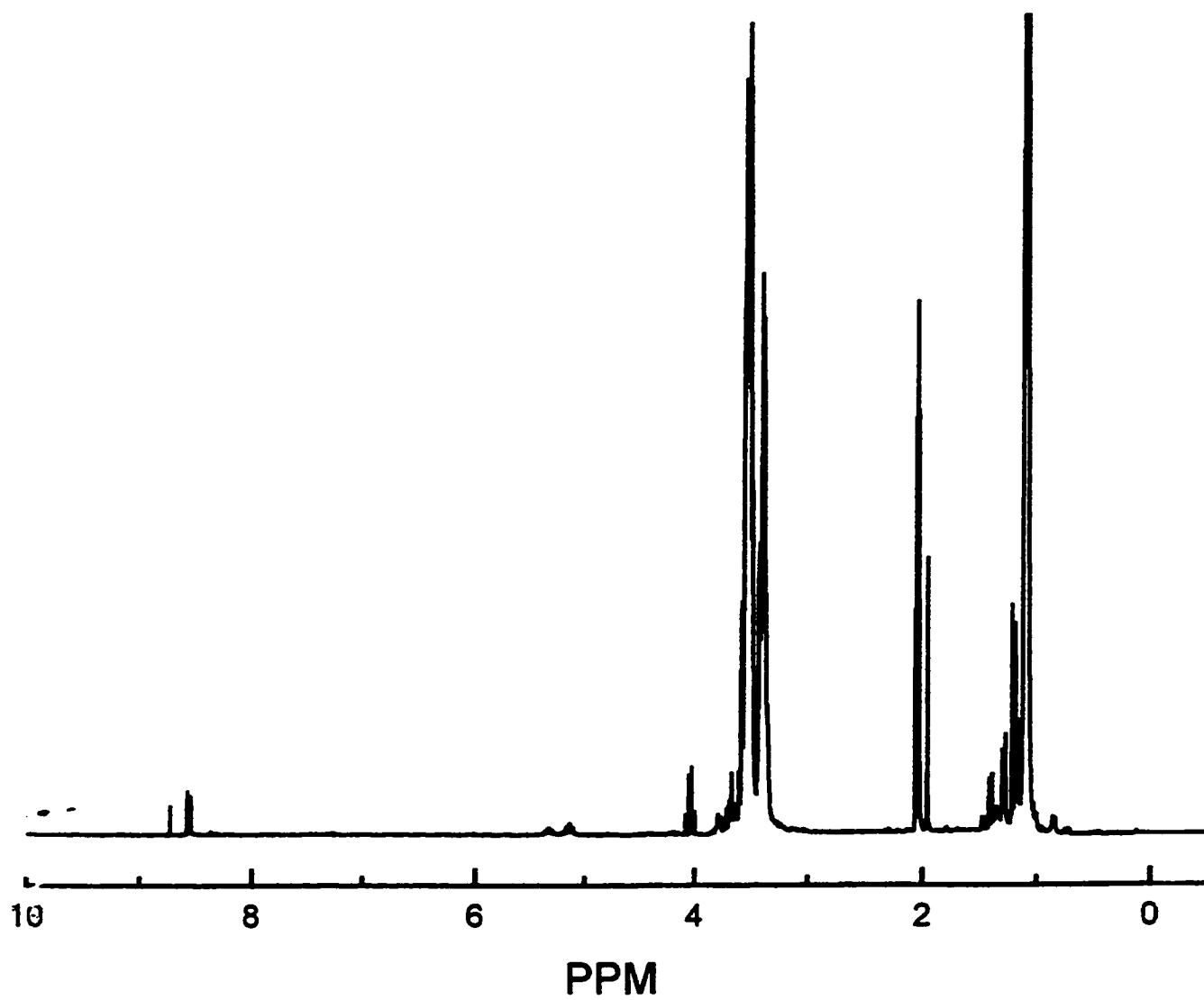
Similar to section 3.1.3, where the “regular” monomer, PMDA (OEt) diester diacid, was activated and converted into the diacyl chloride, this section deals with diacylation of functional macromonomer **9**, PMDA (OPPO) diester diacid. Even though the starting material is much more complicated, the same experimental conditions (Scheme 12) were employed: 24 hours of heating at 57 °C and a 20-fold excess of oxalyl chloride.

Scheme 12



Aromatic protons of meta-PMDA (OPPO) diester dichloride (**10**) appeared shifted downfield to the values 8.57 and 8.54 ppm, confirming synthesis of the new compound (Figure 9). Analogous to Figure 8, integration provides some useful information. First, the yield of this reaction is 92%. Second, the number of repeating units is 91, and the molecular weight of the activated functional monomer is 5300 g/mol. The last number gives the value of molecular weight of the PPO somewhere around 2600.

**Figure 9.**  $^1\text{H}$  NMR (acetone- $d_6$ ) spectrum of the activated functional macromonomer **10**.



The importance of knowing exact molecular weights of PPO and the functional monomer prepared from PPO is clear if one understands how the functional macromonomer is to be used. Since high molecular weight polymers can be achieved only by carefully using the equimolar ratio of diamine and dianhydride (or diester dichloride), it is important to know the exact molecular weight and purity of all monomer reactants. The use of incorrect molecular weights would certainly result in wrong equivalents calculated and in poor quality of low molecular weight poly(amic alkyl ester) and resulting polyimide.

PMDA diester (PPO) dichloride undergoes hydrolysis in the presence of water, forming acidic hydroxyl groups. Therefore, its molecular weight can be determined by titration with a base (a standardized tetrabutylammonium hydroxide solution in methanol). An automatic titrator, Metrohm 736 GP Titrino, gave an average value over five titrations of 6380g/mol for functional macromonomer **10**. If we are interested in knowing molecular weight of PPO before it reacted with pyromellitic dianhydride, division by two would provide approximate value. Of course, we disregard weight of PMDA moiety in such a calculation. A sample of **10**, 0.2-0.8 g, was dissolved in 30-40 mL of methanol, 3 drops of water were added and titrated with 44.4 mmol/L titrant.

All of the results for all the methods of molecular weight determination of PPO, were placed in one table for comparison (Table 1). Average MW of PPO was found to be 2865 Daltons. The results shown are for only one of several prepared batches of PPO. All other batches were analyzed with the same methods and gave values of molecular weight somewhat close.

**Table 1.** Methods of PPO Molecular Weight Determinations.

Number	Method used	Section in the thesis	M.W. of PPO determined, g/mol
1	Theoretical M.W. assuming "living" polymerization	3.2.1.	3000
2	Estimation from polymerization yield	3.2.1	2800
3	Gel permeation chromatography	3.2.1.	3010
4	Derivatization (trimethylsilyl ether of PPO), <sup>1</sup> H NMR	3.2.1.	3140
5	Synthesis of the functional macromonomer, <sup>1</sup> H NMR	3.2.2.	2650
6	Activation of the functional monomer, <sup>1</sup> H NMR	3.2.3.	2600
7	Titration (Acid M.W. method)	3.2.3.	2855

## **Chapter 4. Polymer Synthesis**

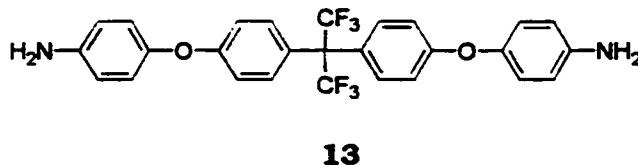
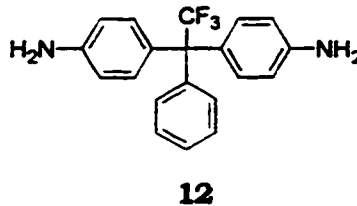
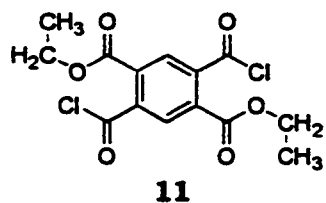
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### **4.1. Poly(amic Alkyl Ester) Graft Copolymer Preparation**

Poly(amic alkyl ester), being a condensation polymer, can be obtained with high molecular weight only if the materials are pure, and functional groups ( $\text{NH}_2$  and  $\text{COCl}$ ) are present in exactly equal amounts. If the requirement of the 1:1 ratio is not followed, low molecular weight polymer results. Low molecular weight polyimides have unsuitable characteristics and bad performance. That is why exact calculations and precise measurements are crucial in polyimide synthesis.

In the present research, the goal was to prepare not just poly(amic alkyl esters) but poly(amic alkyl ester) graft copolymers. There are three types of monomers in the reaction, complicating the situation. Two monomers having the same functional group, “regular” monomer PMDA (OEt) diester dichloride and functional macromonomer PMDA (PPO) diester dichloride have to be present in the same molar ratio as the diamine, the third monomer. For simplicity, words ‘diester dichloride’ will be omitted in this chapter.

We used different monomers for the graft copolymer synthesis: para-PMDA (OEt) (**11**), meta-PMDA (OEt) (**3**), PMDA (PPO) (**10**), and diamines 3FDA (**12**), 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane, and 4-BDAF (**13**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.

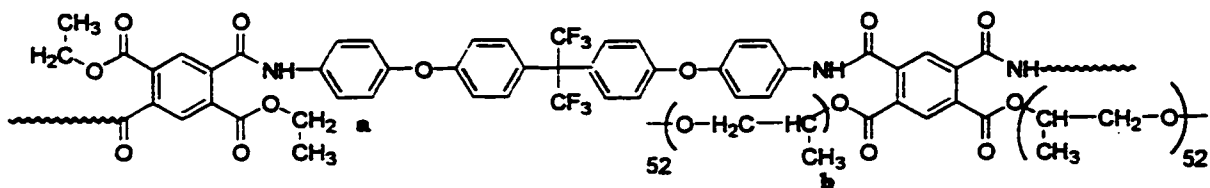


Several batches of macromonomer PMDA (PPO) were prepared, each with slightly different molecular weight. Total amount of the polymer to be prepared was usually 3.5g, but for some preparations it was 2.5g. All of these differences will be reflected in the tables of reagents. The general procedure for poly(amic alkyl ester) graft copolymer synthesis, which was used for all 13 prepared copolymers, is described in the experimental part of the thesis in section 6.3.

#### **4.1.1. Synthesis of para-PMDA (OEt) / PMDA (PPO)/ 4-BDAF Copolymers**

Starting materials for this graft copolymer were para-PMDA (OEt) diester dichloride (**11**), the functional macromonomer **10**, PMDA (PPO) diester dichloride, and 4-BDAF (**13**). Five copolymers were prepared with different weight percent of PPO incorporated in it: 5%, 10%, 15%, 20%, 35% of general formula **14**.





14

General calculations for the amounts of reagents used in each particular copolymer were obtained using equations (1) and (2).


$$\text{mol PMDA (PPO)} + \text{mol PMDA (OEt)} = \text{mol BDAF} \quad (1)$$

$$\text{mol PMDA(PPO)} + \frac{3.5\text{g-PMDA(PPO)} - \text{g(BDAF)}}{\text{M.W. PMDA(OEt)}} = \frac{\text{g BDAF}}{\text{M.W. BDAF}} \quad (2)$$


For 3.5 g total of the polymer, 5% incorporation of polypropylene oxide by weight would be  $0.05 \times 3.5 = 0.175\text{g}$ . Thus, weight of PMDA (PPO) is known. Also, molecular weight of PMDA (PPO) was determined (see Table 1). Therefore, mol PMDA (PPO) in the equation (2) can be calculated. Further, M.W. PMDA (OEt) is known (347.15 g/mol) as well as M.W. BDAF (518.45 g/mol). Putting all the numbers in the equation (2), the equation can be solved for the only unknown g BDAF. Table 2 includes all information necessary for the synthesis of 5% PMDA (PPO)/para-PMDA (OEt)/ BDAF poly(amic alkyl ester) graft copolymer.

Calculations for other percents of PPO incorporated were made using the same equation (2) and the same considerations as was described for the 5% PPO case. Results for 10%, 15%, 20%, and 35% are presented in Tables 3, 4, 5, 6 accordingly.


**Table 2.** Reagents and Their Amounts for the Preparation of 5% PMDA (PPO)/para-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	p-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.175	1.3271	1.997906	0.8535
Molec. Weight	5710	347.15	518.45	79.10
# of mmols	0.030639	3.822825	3.853465	10.789
# of equiv.	 1		1	2.8


**Table 3.** Reagents and Their Amounts for the Preparation of 10% PMDA (PPO)/para-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	p-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.35	1.2505	1.89946	0.811414
Molec. Weight	5710	347.15	518.45	79.10
# of mmols	0.06123	3.602	3.6636	10.25
# of equiv.	 1		1	2.8


**Table 4.** Reagents and Their Amounts for the Preparation of 15% PMDA (PPO)/para-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	p-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.525	1.1740	1.8022	0.7694
Molec. Weight	5710	347.15	518.45	79.10
# of mmols	0.091917	3.381789	3.473706	9.726
# of equiv.	 1		1	2.8

**Table 5.** Reagents and Their Amounts for the Preparation of 20% PMDA (PPO)/para-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	p-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.7000	1.0974	1.7026	0.7273
Molec. Weight	5710	347.15	518.45	79.10
# of mmols	0.1226	3.1612	3.2838	9.195
# of equiv.			1	2.8

**Table 6.** Reagents and Their Amounts for the Preparation of 35% PMDA (PPO)/para-PMDA (OEt)/4BDAF Poly(amic Alkyl Ester) Graft Copolymer.

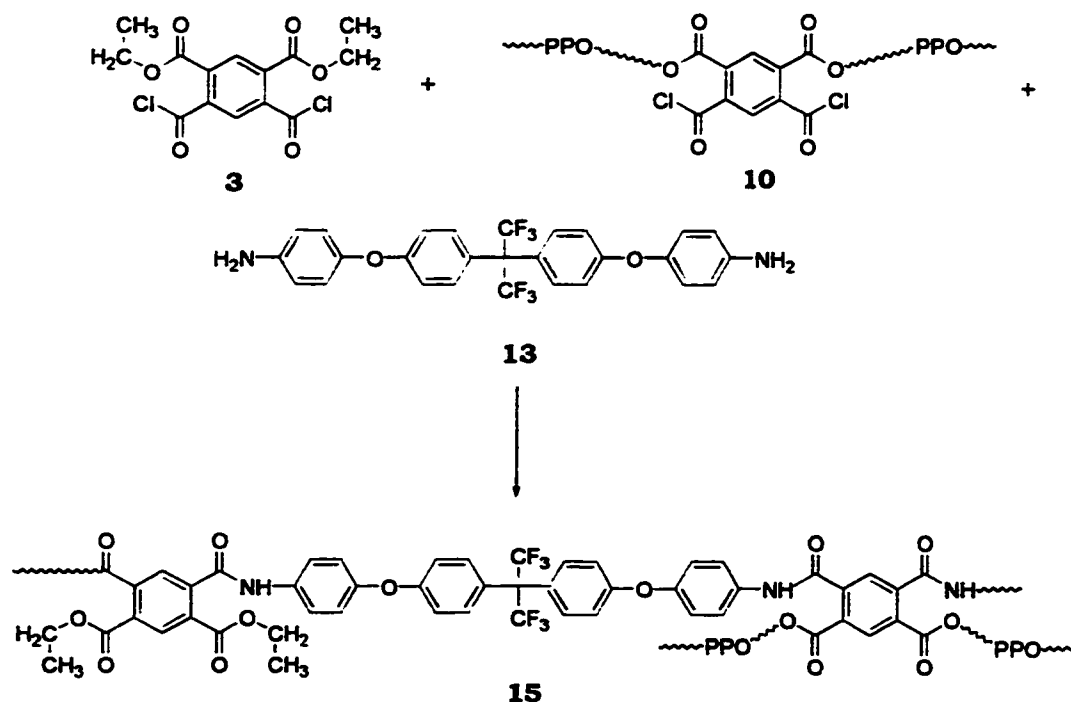
	PMDA (PPO)	p-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	1.2250	0.8679	1.4071	0.6011
Molec. Weight	5710	347.15	518.45	79.10
# of mmols	0.214	2.500	2.714	7.599
# of equiv.			1	2.8

#### 4.1.1. Synthesis of meta-PMDA (OEt)/ PMDA (PPO)/ BDAF Copolymers


Following the same calculations of reagents amounts as in section 4.1.1 and the same experimental procedure (section 6.3), meta- PMDA (OEt)/PMDA (PPO)/ BDAF graft copolymers (**15**) were prepared with 5, 10, 15, and 20% by

weight of PPO incorporated into the poly(amic alkyl ester) backbone. Reactions in all four cases proceeded as shown in Scheme 13. Calculated amounts of starting materials for graft copolymers are presented in Tables 7, 8, 9, 10. For these syntheses a new batch of polypropylene oxide was prepared, molecular weight of which was 6000 g/mol. NMP (1-methyl-2-pyrrolydone) solutions of the prepared copolymers were precipitated into a methanol/water blender, filtered and washed again several times. That resulted in the loss of some lower molecular weight fractions and, therefore, lower yields. The yields were 67%, 86%, 86%, and 78% in accordance with increased PPO weight percent incorporated.

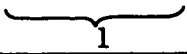
**Scheme 13**




**Table 7.** Reagents and Their Amounts for the Preparation of 5% PMDA (PPO)/meta-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	m-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.175	1.3275	1.9976	0.8534
Molec. Weight	6000	347.15	518.45	79.10
# of mmols	0.0292	3.824	3.853	10.8
# of equiv.			1	2.8


**Table 8.** Reagents and Their Amounts for the Preparation of 10% PMDA (PPO)/meta-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	m-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.3500	1.2497	1.8988	0.8102
Molec. Weight	6000	347.15	518.45	79.10
# of mmols	0.058	3.60	3.658	10.24
# of equiv.			1	2.8

**Table 9.** Reagents and Their Amounts for the Preparation of 15% PMDA (PPO)/meta-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	m-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.525	1.2451	1.8001	0.7685
Molec. Weight	6000	347.15	518.45	79.10
# of mmols	0.0875	3.3844	3.47	9.716
# of equiv.			1	2.8

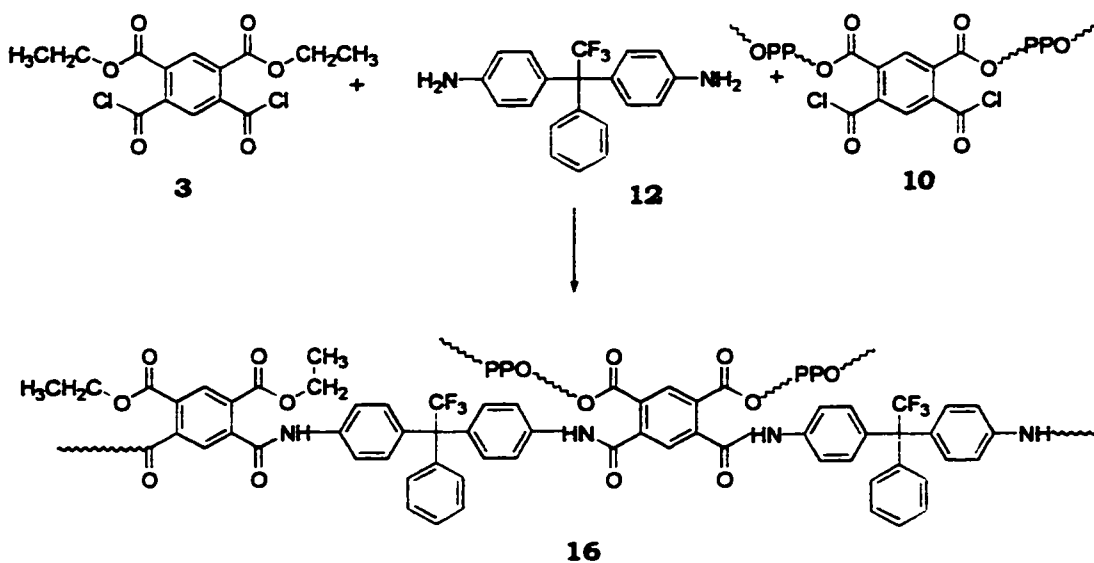
**Table 10.** Reagents and Their Amounts for the Preparation of 20% PMDA (PPO)/meta-PMDA (OEt)/ BDAF Poly(amic Alkyl Ester) Graft Copolymer.

	PMDA (PPO)	m-PMDA (OEt)	4-BDAF	Pyridine
Weight, g	0.7000	1.0986	1.7013	0.7265
Molec. Weight	6000	347.15	518.45	79.10
# of mmols	0.1167	3.16	3.28	9.184
# of equiv.			1	2.8


### 4.1.3. Synthesis of meta-PMDA (OEt)/ PMDA (PPO)/ 3-FDA Copolymers

Following the same calculations of reagents amounts as in section 4.1.1 and the same experimental procedure (section 6.3), meta-PMDA (OEt)/PMDA (PPO)/3-FDA graft copolymers (**16**) were prepared with 5, 10, 15, and 20% by weight of PPO incorporated into the poly(amic alkyl ester) backbone. Reactions in all four cases proceeded as shown in Scheme 14. Calculated amounts of starting materials for graft copolymers are presented in Tables 11, 12, 13, 14. The yields were 78%, 72%, 50%, and 80% for the 5%, 10%, 15%, and 20% PPO copolymers.


Scheme 14



**Table 11.** Reagents and Their Amounts for the Preparation of 5% PMDA (PPO)/meta-PMDA (OEt)/3-FDA Poly(amic Alkyl Ester) Graft Copolymer.


3.5 g total	PMDA (PPO)	m-PMDA (OEt)	3-FDA	Pyridine
Weight, g	0.175	1.6689	1.6559	1.0712
Molec. Weight	6000	347.15	342.37	79.10
# of mmols	0.0292	4.8074	4.8366	13.542
# of equiv.			1	2.8

**Table 12.** Reagents and Their Amounts for the Preparation of 10% PMDA (PPO)/meta-PMDA (OEt)/3-FDA Poly(amic Alkyl Ester) Graft Copolymer.

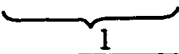
2.5 g total	PMDA (PPO)	m-PMDA (OEt)	3-FDA	Pyridine
Weight, g	0.25	1.1256	1.1244	0.7273
Molec. Weight	6000	347.15	342.37	79.10
# of mmols	0.0416	3.2426	3.2842	9.2
# of equiv.			1	2.8



**Table 13.** Reagents and Their Amounts for the Preparation of 15% PMDA (PPO)/meta-PMDA (OEt)/3-FDA Poly(amic Alkyl Ester) Graft Copolymer.

2.5 g total	PMDA (PPO)	m-PMDA (OEt)	3-FDA	Pyridine
Weight, g	0.3750	1.0591	1.0659	0.6895
Molec. Weight	6000	347.15	342.37	79.10
# of mmols	0.0625	3.0508	3.1133	8.72
# of equiv.			1	2.8

**Table 14.** Reagents and Their Amounts for the Preparation of 20% PMDA (PPO)/meta-PMDA (OEt)/3-FDA Poly(amic Alkyl Ester) Graft Copolymer.

2.5 g total	PMDA (PPO)	m-PMDA (OEt)	3-FDA	Pyridine
Weight, g	0.5000	0.9926	1.0074	0.6516
Molec. Weight	6000	347.15	342.37	79.10
# of mmols	0.0833	2.8591	2.9424	8.24
# of equiv.			1	2.8

## **4.2 Characterization of Poly(amic Alkyl Ester) Graft Copolymers**

Poly(amic alkyl ester) copolymers were characterized by  $^1\text{H}$  NMR spectroscopy, gel permeation chromatography, and measurements of intrinsic viscosity.

*$^1\text{H}$  NMR Spectroscopy.*  $^1\text{H}$  NMR spectra of copolymers **14**, **15**, and **16** were taken to control incorporation of PPO into the poly(amic alkyl ester) backbone. Percent (by weight) of polypropylene oxide incorporated was obtained as integration ratio of methyl hydrogens of PPO (**b**) and methylene hydrogens of ethoxy group (**a**) (see formula **14**). Results for PPO incorporation are presented in Table 15. Example of such calculations for 10% PMDA (PPO)/p-PMDA (OEt)/BDAF poly(amic alkyl ester) follows (see also Figure 10):

$$\text{Weight of PPO} = 3.13/3 \times 58.08 = 60.57$$

$$\text{Weight of poly(amic alkyl ester)} = 4.02/4 \times 792.62 = 792.62$$

$$\% \text{PPO (weight)} = 60.57 \times 100\% / (60.57 + 792.62) = 7.1\%$$

Where, 3.13 is integration of methyl hydrogens of PPO (**14b**)

4.02 is integration of methylene hydrogens of the ethoxy group of the poly(amic alkyl ester) (**14a**)

58.08 g/mol is the weight of repeating unit of PPO

792.62 g/mol is the weight of repeating unit of poly(amic alkyl ester)

*Gel Permeation Chromatography.* Samples of all the copolymers were prepared by dissolving 0.010 g of the polymer in 2.5 ml of THF and filtering (0.45 microns). Results of GPC analysis are presented in Table 16.

**Figure 10.**  $^1\text{H}$  NMR spectrum of the compound 14-II, 10% PMDA (PPO)/p-PMDA (OEt)/BDAF poly(amic alkyl ester) graft copolymer.



Since GPC was calibrated with polystyrene standards, the values obtained for both the poly(amic esters) and polypropylene oxide are not absolute values. We used these relative values to compare prepared graft copolymers between each other.

Some trends can be noticed. For example, copolymers of group **14** have higher molecular weight than copolymers of group **15** and **16**. Their main difference is that group **14** polymers have para-PMDA diacid dichloride **11**, while **15** and **16** copolymers are prepared from meta-PMDA diester dichloride **3**. Para-PMDA based poly(amic esters) are rod-like, while meta-PMDA based poly(amic esters) are more flexible.<sup>21</sup> Therefore their hydrodynamic volume is different. That may be why the GPC results show higher molecular weight for para-PMDA based poly(amic esters) **14**, whose hydrodynamic volume is presumably higher than for meta-PMDA based polymers.

**Table 15.** Results of Incorporation of the PPO from <sup>1</sup>H NMR Spectra of Poly(amic Alkyl Ester) Graft Copolymers.

Entry	Polymer	PMDA (OEt) isomer	Diamine	% (PPO) in reaction (planned)	% PPO by NMR (weight)	%PPO by NMR (volume)
1	14-I	para	4-BDAF	5	3.4	4.7
2	14-II	para	4-BDAF	10	7.1	9.9
3	14-III	para	4-BDAF	15	9.0	12.2
4	14-IV	para	4-BDAF	20	13	17.7
5	14-V	para	4-BDAF	35	26	33.5
6	15-I	meta	4-BDAF	5	2.9	4.2
7	15-II	meta	4-BDAF	10	9.1	12.4
8	15-III	meta	4-BDAF	15	13.6	18.3
9	15-IV	meta	4-BDAF	20	16.7	22.2
10	16-I	meta	3-FDA	5	4.5	5.8
11	16-II	meta	3-FDA	10	7.4	9.5
12	16-III	meta	3-FDA	15	7.25	9.3
13	16-IV	meta	3-FDA	20	23	28.2

The polydispersity of the polymers **14-16** ranged from 1.3 to 2.2 which is consistent with these types of condensation polymers.

**Table 16.** Results of GPC Analysis of Poly(amic Alkyl Ester)s 14-16.

Entry	Polymer	% Area	Mw (Daltons)	Polydispersity
1	14-I	97.44	28,480	1.81
2	14-II	93.76	28,646	1.80
3	14-III	98.72	22,906	1.86
4	14-IV	98.13	25,954	1.77
5	14-V	100.00	19,214	1.70
6	15-I	99.54	12,419	1.73
7	15-II	93.92	11,886	1.65
8	15-III	96.45	15,085	1.83
9	15-IV	97.58	6,381	2.21
10	16-I	96.13	6,362	1.67
11	16-II	97.91	4,824	1.49
12	16-III	100.00	3,811	1.31
13	16-IV	90.62	3,560	1.46

*Intrinsic Viscosity.* Viscosities of dilute solutions of all the copolymers were measured using Cannon-Fenske capillary viscometer at 30.0 °C and intrinsic viscosities were calculated in each case. Intrinsic viscosity  $[\eta]$  can be related to molecular weight ( $M_w$ ) by the Mark –Houwink -Sakurada equation<sup>29</sup>:

$$[\eta]=K M_w^a,$$

where K and a are coefficients, whose values depend on the nature of the polymer, temperature and solvent. Even though there are tabulated values of those coefficients for several of the most wide spread polymers, our poly(amic

alkyl ester) graft copolymers with a different percent of labile copolymer incorporated could not be in those tables. It was therefore decided to use values of intrinsic viscosity not for exact molecular weight determination but for comparison between the copolymers. Intrinsic viscosity can be a measure of higher or lower molecular weight in the group of similar copolymers (see Table 17). Also, materials with intrinsic viscosities of less than 0.1 dL/g tend to be

**Table 17.** Intrinsic Viscosities for All Prepared Poly(amic Alkyl Ester) Graft Copolymers.

Entry	Polymer	% PPO planned	Intrinsic Viscosity, dL/g
1	14-I	5	0.3242
2	14-II	10	0.3146
3	14-III	15	0.2794
4	14-IV	20	0.3194
5	14-V	35	0.2730
6	15-I	5	0.2799
7	15-II	10	0.4187
8	15-III	15	0.2540
9	15-IV	20	0.2279
10	16-I	5	0.1760
11	16-II	10	0.0967
12	16-III	15	0.0902
13	16-IV	20	0.1056

very low molecular weight and yield poor film upon processing.

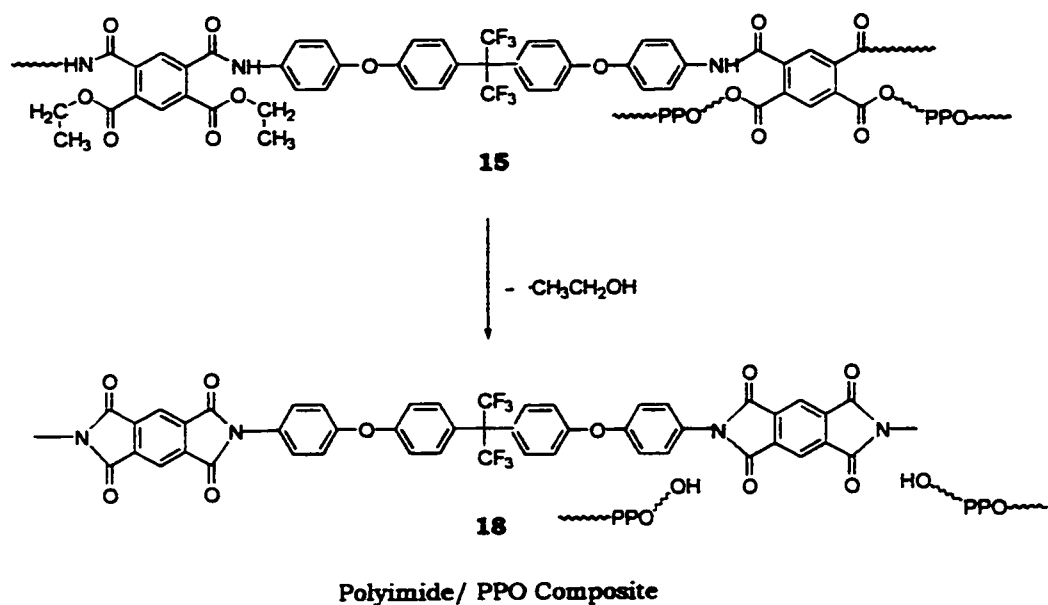
Measurements of intrinsic viscosity confirmed the data obtained from GPC analysis. In fact, copolymers **14**, para-PMDA (OEt)/PMDA (PPO)/4-BDAF have much higher values for intrinsic viscosities than copolymers **15** and **16**. These results again can be explained by the different hydrodynamic volumes in the case of similar molecular weight polymers with the different degree of rigidity.

### **4.3 Imidization of Poly(amic Alkyl Ester) Graft Copolymers.**

Poly(amic alkyl ester) graft copolymers were thermally imidized as thick films (10-40  $\mu\text{m}$ ) by casting from solution on glass slides and or spinning from solution onto glass, quartz and silicon wafers as thin films (0.5-2.5  $\mu\text{m}$ ). For thick film preparation of the copolymers **14** (I-V), 25% solutions in NMP were prepared; whereas, for lower viscosity copolymers **15** (I-IV) and **16** (I-IV) more concentrated solutions (30%) had to be prepared. Because thin films are generally prepared from less concentrated solutions, 20% solutions of polymers for group **14** and 25% for groups **15** and **16** were obtained for spin-coating. While NMP provides good coating on the glass surface, all samples spun on quartz and silicon dewetted resulting in poor coatings. A solvent mixture of 1:1 cellosolve acetate and DMF, suitable for spinning of some polyimides on quartz and silicon surfaces has been described earlier.<sup>30</sup> This solvent mixture was found to give a good coatings in the case of PPO-poly(amic alkyl ester) graft copolymers **14-16** on quartz and silicon wafers.

During imidization, ethoxy and PPO ester bonds get broken and ethanol and polypropylene oxide get released from the imide chain. While ethanol penetrates to the surface and evaporates, PPO stays confined inside the polyimide structure yielding a polyimide/PPO composite. Poly(amic alkyl ester)s **14**, **15**, and **16** were transformed into the corresponding polyimide/PPO composites **17**, **18**, **19**. Because the imidization processes are identical for all samples, an example of imidization reaction is given for copolymer **15** in the Scheme 15:

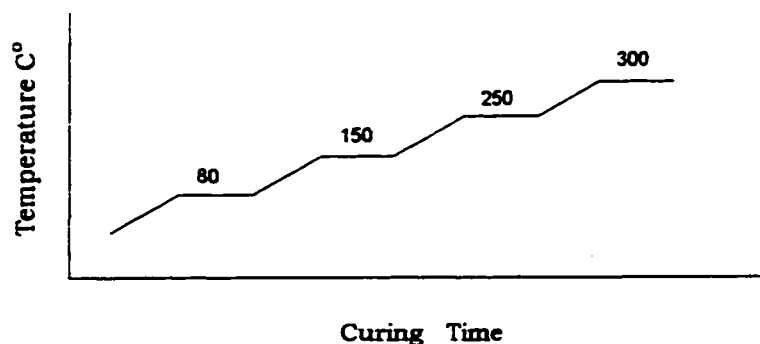
**Scheme 15**



The thermal curing process must be conducted in an argon atmosphere to assure that only proper solvent removal and imidization happens, but not polypropylene oxide degradation induced by the presence of oxygen. A



thermally controlled hotplate was regulated in a ramp and soak mode, with the ramp rate being 5 °C per minute and holds for an hour each at designated temperatures:



In the case of thin films, two temperature modes were tried. The first was the one described for the thick films, and the other was fast curing, with only one hour hold for solvent removal at 80 °C followed by 5 °C per minute ramp up to 300 °C and gradual cooling down. The second method for curing was designed because thin films cured with the first temperature regime seemed partially foamed and/or collapsed.

#### 4.4. Characterization of Polyimide/PPO Composites.

Thick films were characterized by TGA (thermal gravimetric analysis), DSC (differential scanning calorimetry), and DMTA (dynamic mechanical thermal analysis). In contrast, thin films were subjected to refractive index, film thickness measurements, and QCM (quartz crystal microbalance).

The isothermal TGA method continually measures the weight of a polymer, placed on a sensitive balance, as a function of time at constant temperature in air. Weight loss in the polyimide/PPO composites can arise for several reasons. First, evaporation of solvent or absorbed moisture can be noticed in the first several minutes. Weight loss due to the evolution of volatilities from PPO degradation is a second reason. Finally, thermal degradation of the imide matrix can be observed if isothermal TGA is performed at high enough temperatures.

Two first sources for weight loss were observed on thermograms of all thirteen polyimide /PPO composites. Figure 11 depicts TGA data for composite **18-II**, 10% PMDA (PPO)/ meta-PMDA (OEt)/ 4-BDAF. One can see 0.4% weight loss in first five minutes due to absorbed water on the film surface, followed by loss of 9.1% of weight during polypropylene oxide degradation. Because isothermal analysis was conducted at a temperature of 300 °C, which is significantly lower than degradation temperature of the imide component, the isothermal TGA does not show the weight loss due to the imide matrix degradation.

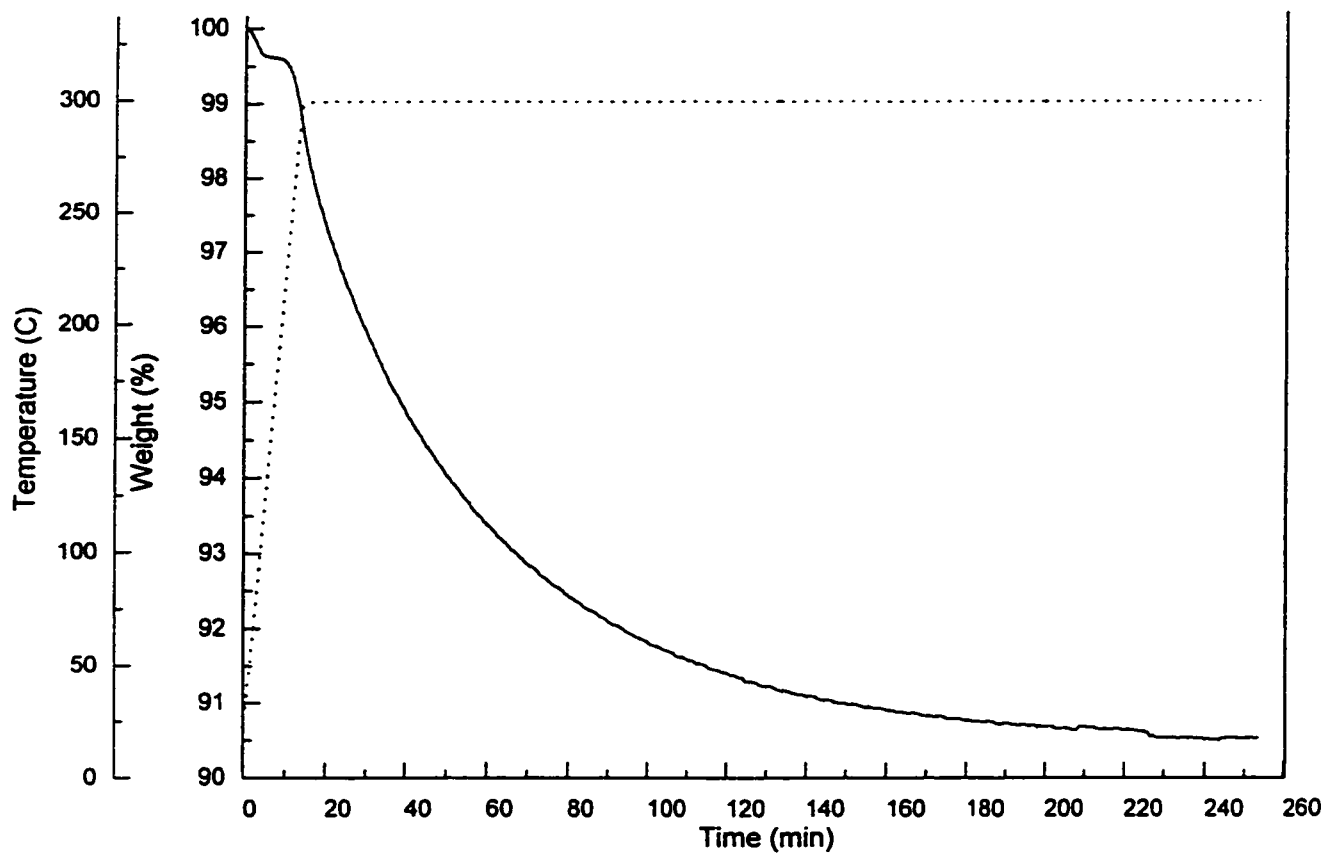
The purpose of isothermal TGA analysis of polyimide/PPO composites **17-19** was to confirm the presence of PPO in the composites after imidization occurred. If the value for PPO content in the composites had been significantly lower than that determined by <sup>1</sup>H NMR spectroscopy of copolymers before imidization, one could conclude that the composites partially lost polypropylene oxide during thermal curing. Therefore, thermal conditions of imidization would need some adjustment.

A very good correlation was found between the PPO percent in the copolymers before ( $^1\text{H}$  NMR spectra of poly(amic alkyl ester) graft copolymers) and after (thermal gravimetric analysis data) imidization (see Table 18). The values for TGA are the same or a little higher than those from  $^1\text{H}$  NMR spectra. Thus, a certain percent of PPO was proven to be incorporated into the structure of the graft copolymers. Also, the data indicates that there was no loss of PPO during imidization.

**Table 18.** Results of Isothermal TGA for Composites **17-19**, Compared to  $^1\text{H}$  NMR Spectral Data for Poly(amic Alkyl Ester) Graft Copolymers **14-16**.

Entry	PMDA (OEt) isomer	Diamine	%PPO in reaction	% PPO) Weight ( $^1\text{H}$ NMR)	% PPO Weight (TGA)
1	Para	4-BDAF	5	3.4	4
2	Para	4-BDAF	10	7.1	11.1
3	Para	4-BDAF	15	9	10.2
4	Para	4-BDAF	20	13	13.8
5	Para	4-BDAF	35	26	27
6	Meta	4-BDAF	5	2.9	3.4
7	Meta	4-BDAF	10	9.1	9.1
8	Meta	4-BDAF	15	13.6	13.5
9	Meta	4-BDAF	20	16.7	17.5
10	Meta	3-FDA	5	4.5	5.25
11	Meta	3-FDA	10	7.4	9.75
12	Meta	3-FDA	15	7.25	8.7
13	Meta	3-FDA	20	23	20.5

**Figure 11.** Results of isothermal TGA of 10% (PPO) / Polyimide composite (18-II).



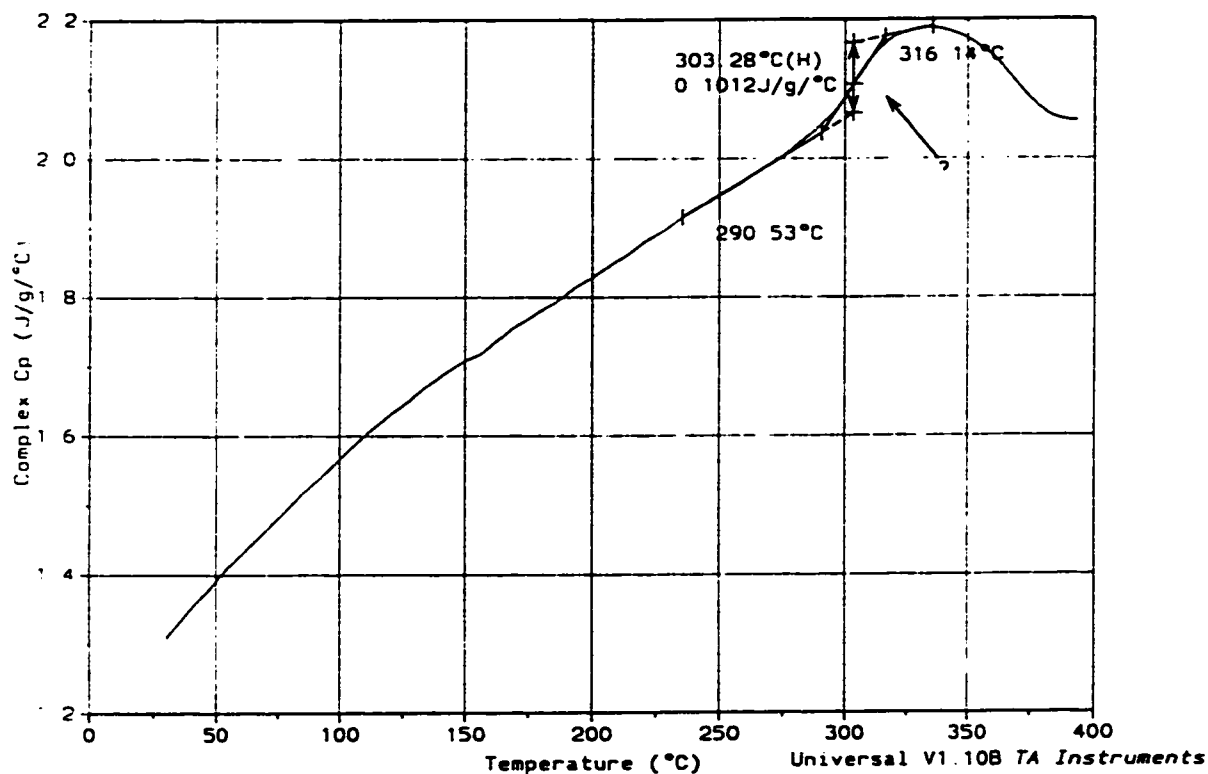
Differential scanning calorimetry (DSC), one of the thermal analysis methods, reflects enthalpic changes such as melting point or glass transition temperature. The glass transition causes an endothermic shift in the initial baseline because of the sample's increased heat capacity.

The objective of our research did not include tracking the changes in the glass transition temperature ( $T_g$ ) with the change in the composite content (meta- or para- PMDA (OEt) diester dichloride, different diamine, or PPO percent). It is rather difficult to measure the glass transition temperature in the case of composites. In fact, out of four samples submitted for DSC analysis, two (**18-IV** and **19-IV**) did not give noticeable shifts in the heat capacitance. Those samples that had an observable  $T_g$  belonged to the same group of polyimide/PPO composites, **17-IV** (see figure 12) and **17-V**. A transition temperature 290 °C was observed for this material.

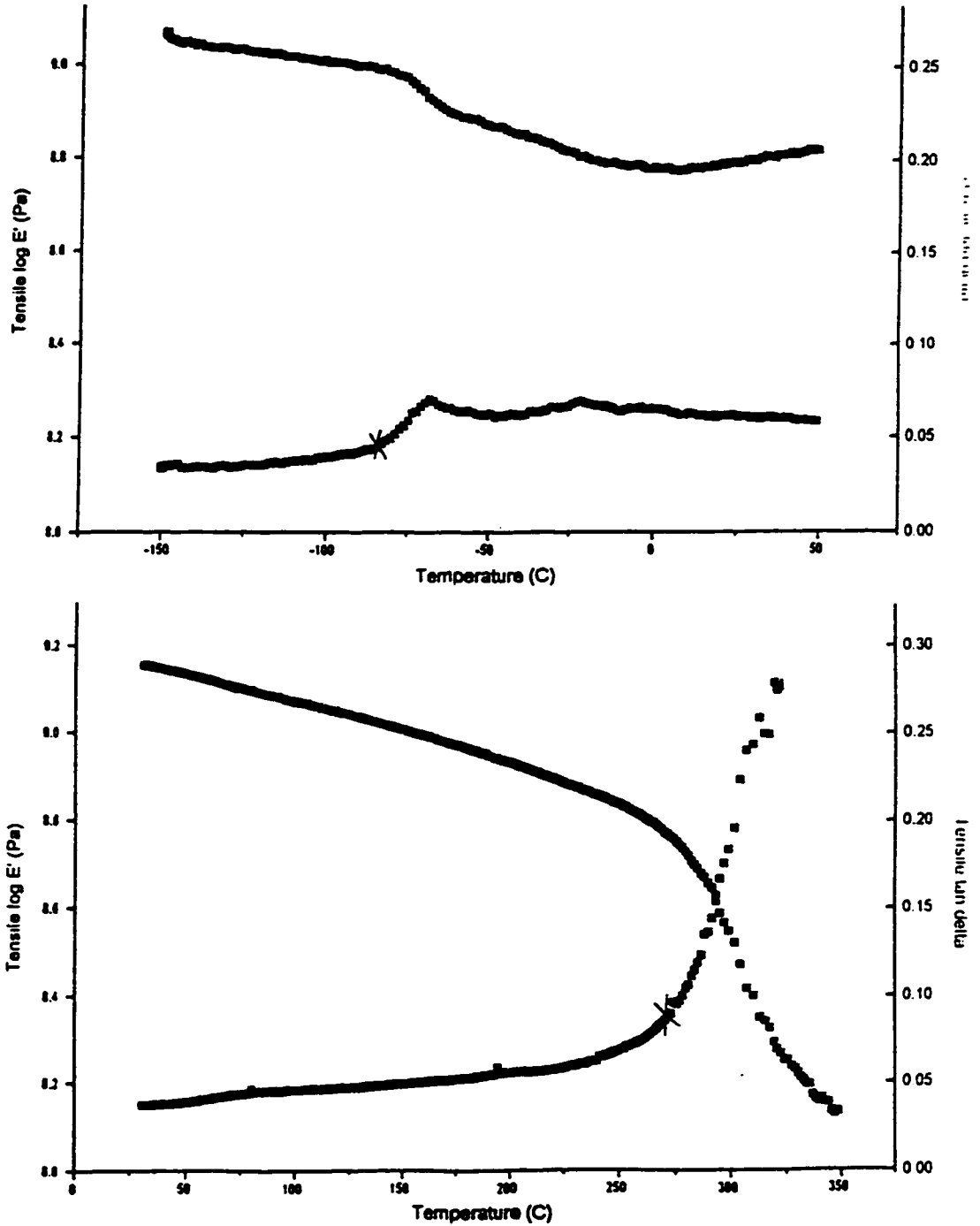
In dynamic mechanical thermal analysis (DMTA), the sample is perturbed by a sinusoidal force, and the response of the material is measured over a range of temperatures and at different frequencies of applied force. A forced vibration-non-resonance instrument, most suitable for rigid polymers, was used for tensile mode measurement of polyimide/PPO copposites. DMTA technique was applied only to two samples from which several strong and thick films were prepared. Figure 13 shows two DMTA runs for the sample **18-IV** made in the two different temperature intervals. The first run started at temperature as low as -150 °C and indicated glass transition temperature for polypropylene oxide at -80 °C. The second, high temperature run was started

at room temperature and continued until 350 °C presenting polyimide glass transition shift at 275 °C.

**Figure 12.** Differential scanning calorimetry thermogram for 17-IV polyimide/PPO composite.



**Figure 13.** DMTA –tensile runs for the 20% PMDA (PPO)/meta-PMDA (OEt)/4-BDAF polyimide/PPO composite (18-IV). The low temperature run is on the top, and the high temperature run is on the bottom.



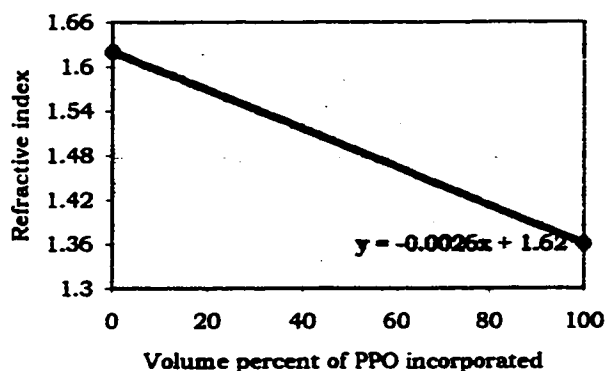
Results of DMTA analysis of the other composite (17-IV) film were identical. The fact that a measured sample had two different glass transition temperatures indicates that the sample is, indeed, a phase separated composite material containing two different substances, not a homogeneous blend.

Thermal conditions for thick film imidization, 'ramp and soak' temperature mode with holds for an hour at 80, 150, 250, and 300 °C, were found to be too strong for imidization of thin films (0.5-2.5 microns). Measurements of refractive index of all samples revealed complete or partial polypropylene oxide decomposition and in some cases film collapse during imidization. The refractive index values were very similar for different polymer groups and within each group. It was expected to obtain a correlation between a decrease in refractive index and an increase in PPO content in each group. Indeed, refractive index of polyimides is 1.62, whereas the value for polypropylene oxide is 1.36. Therefore, the more PPO incorporated into a polyimide copolymer, the lower refractive index of a sample. Figure 14 presents such a correlation.

When it became obvious that imidization conditions, which worked for thick films, did not work for thin films, different thermal conditions were designed. Samples spun on the silicon wafers would be held for an hour at 80 °C for solvent removal and then heated without stops up to 300 °C with the rate of 5 °C per minute. This thermal curing cycle can be called 'fast' or 'mild'. Results of refractive index measurements performed after 'mild' imidization



**Figure 14.** Ideal, or by theory predicted, relationship between volume percent of PPO incorporated into the structure of the polyimide/PPO composite and refractive index.

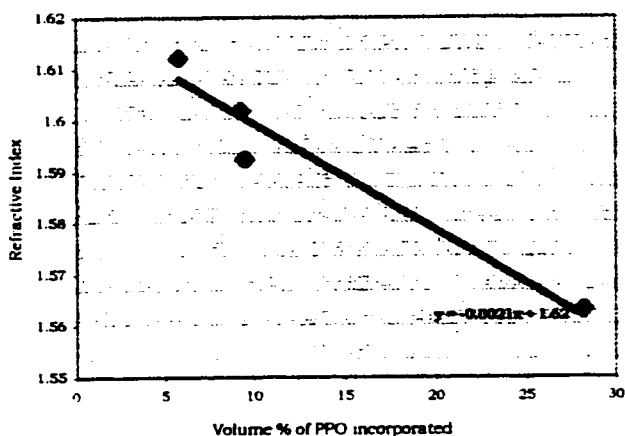


PMDA (OEt)/3-FDA. Data points (Figure 15 and Table 19) of refractive index versus volume percent of PPO incorporated are fit to the equation

$$y = - 0.0021x + 1.62.$$

Refractive index of a polymer can be used as a crude measurement of the dielectric constant of that material. It has been shown<sup>31</sup> that the measured dielectric constant is approximately the square of the refractive index at 633 nm wavelength with corrections for frequency dispersions [the actual relationship is roughly  $\epsilon \cong (\text{refractive index})^2 + 0.2$ ]. The polyimide PMDA/3-FDA has a measured dielectric constant of  $\sim 2.9$  at 70 °C.<sup>32</sup> Results presented in Table 19 indicate significant decrease in dielectric constant for polypropylene oxide/polyimide composites. A 20% PMDA (PPO)/meta-PMDA (OEt)/3-FDA showed a drop in calculated dielectric constant to  $\sim 2.64$ .

**Figure 15.** Correlation between volume percent of polypropylene oxide in composites group **19**, PMDA (PPO)/meta-PMDA (OEt)/ 3-FDA, and refractive index of the composite.



**Table 19.** Data Obtained from Refractive Index Measurements of PMDA (PPO)/meta-PMDA (OEt)/ 3-FDA Composite **19** Thin Film under 'Fast' Curing Conditions.

Entry	Polymer	Weight % PPO charge	Volume % PPO ( <sup>1</sup> H NMR)	Refractive Index	Thickness $\mu\text{m}$	Calculated Dielectric Constant
1	19-I	5	5.8	1.6122	2.0431	2.80
2	19-II	10	9.5	1.5925	1.6309	2.74
3	19-III	15	9.3	1.6019	1.7740	2.77
4	19-IV	20	28.2	1.5632	1.8145	2.64

Similar trends were noticed in the two other groups of composites. Without presenting charts and tables of data, a great deal of information can be obtained from the linear equations of the best fit to the data for composites **17** and **18**. Within the group of **17**, PMDA (PPO)/para-PMDA (OEt)/4-BDAF, the relationship between volume % of PPO and refractive index was  $y = - 0.0017 x + 1.62$ . Composites PMDA (PPO)/meta-PMDA (OEt)/4-BDAF (**18**) had the following equation:  $y = - 0.0014 x + 1.62$ .

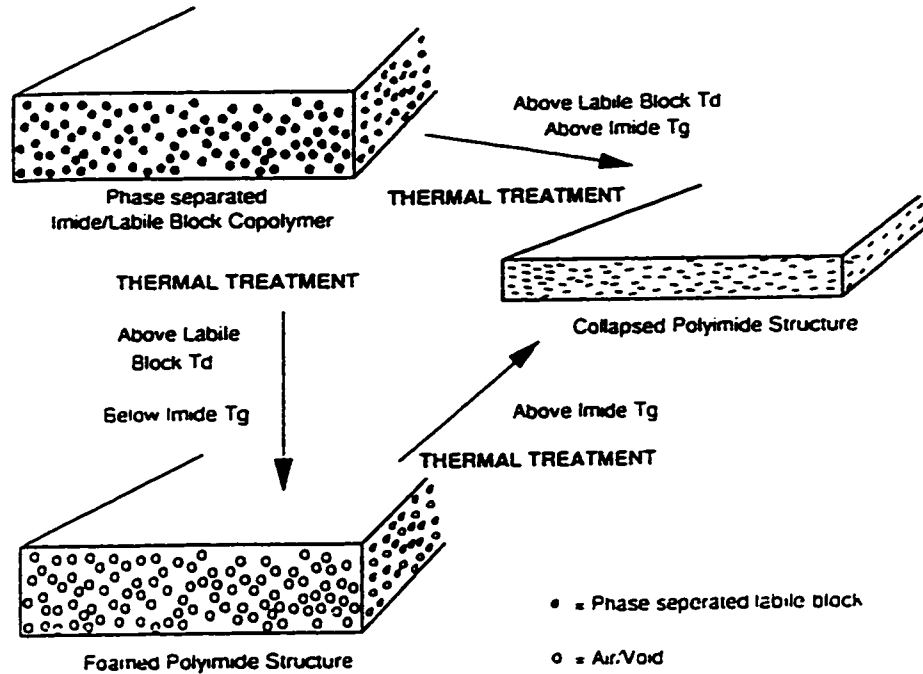
Measured refractive indexes for these samples are 65% and 54% of the theoretical values predicted on the basis of original PPO content. In other words, retention of PPO in the cured composites always occurs at less than 100% efficiency. The current results can be an indication that the 'mild' thermal conditions are the most appropriate for the copolymers of group 19 (81% of theory); while, the other two groups because of their different composition might require a little different imidization schemes.

Polypropylene oxide is one of the most attractive thermally labile polymer blocks for the use in the preparation of porous polyimides. It easily degrades at 250 °C if heated in air. Conversely, when heated to 300 °C in an inert atmosphere, it stays stable. The ability of the labile block to withstand temperatures up to 300 °C is crucial for polyimide/PPO composite synthesis since this is the temperature which is needed to achieve imidization. Therefore, there is a “processing window”, 250-300 °C, for copolymer to be thermally cured to 300 °C or above and at any time later for the PPO to be degraded at the lower temperature (250 °C) without causing destruction of the polyimide. Additionally, these properties of PPO allow for the identification of specific temperature conditions for each particular composite to prepare foamed polymer structure without collapsing. If foaming has been done at temperatures higher than  $T_g$  of the polyimide matrix material, any porous structure collapses (Figure 16).

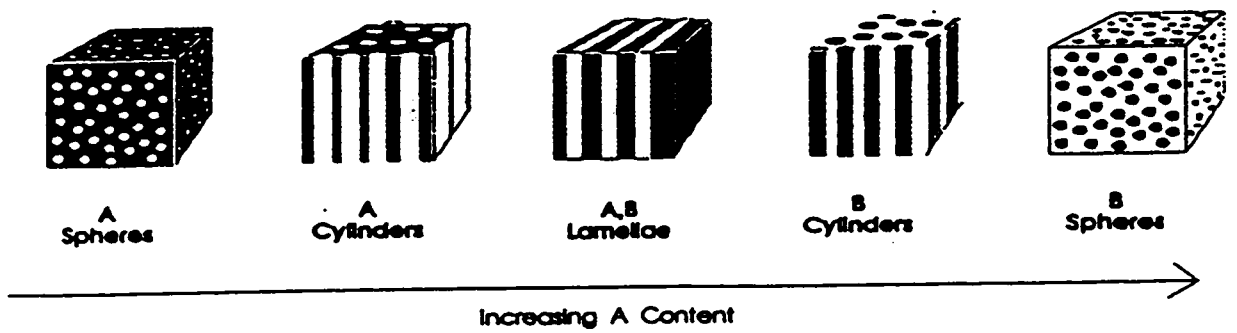
During the thermolysis, labile block degrades and leaves voids in the polymer matrix structure. Size and shape of these pores would depend on initial morphology of the labile component in the composite. In the event of a high concentration of labile block (higher than 30% by volume) polymer physics dictates a new morphology of cylindrical or lamellar domains, which would result in formation of an open pore structure (scheme 16).<sup>20</sup> When trying to

develop a foamed material for microelectronic applications, then achieving spherical domains in the submicron size is thought to be essential.

**Figure 16.** Formation and collapse of polyimide foam.



**Scheme 16**



### **5.1. Preparation and Characterization of Thick Film Foamed Polyimides.**

Polyimide composites as thick films (15-25  $\mu\text{m}$ ) coated on glass slides were foamed by heating at 280  $^{\circ}\text{C}$  for six hours in air. Foamed films with low content of PPO, 5%, 10%, 15%, cracked; while, foams with 20 or 35% of PPO formed strong, tough films. Table 20 shows the composition of the copolymers (14-16), composites (17-19) and foams (20-22). Roman numbers correspond to the percent of PPO so that I is 5%, II is 10%, III is 15%, IV is 20%, and V is 35%. Those percent values are weight percents of PPO charged initially in the reactions to afford copolymers 14-16.

The density of the polymer can show if formation of the foam occurred or not. If the density of the homopolymer is known and the density of the copolymer was measured, one can easily calculate percent porosity in the copolymer. Densities of foamed polyimides 20-22 were measured using gradient density column calibrated with standard glass floats in the density range 1.07-1.41  $\text{g}/\text{cm}^3$ . The calibration graph is given in Figure 22 (Chapter 6.5).

The density values for the foams together with the polyimide homopolymers are presented in Table 21. For the polyimide nanofoams of group 20 the density value were in the range 1.40-1.34 which correspond to about 9% porosity in the best case. Considering data from initial PPO composition (volume %) and volume fraction of voids formed, the conclusion of

**Table 20.** Numeration of Polyimide Copolymers, Their Precursors and Foamed Polyimides.

Entry	Diamine	PMDA (OEt) Isomer	Poly(amic alkyl ester) Copolymer	Polyimide Copolymer	Foamed Polyimide
1	4-BDAF	Para	14 (I-V)	17 (I-V)	20 (I-V)
2	4-BDAF	Meta	15 (I-IV)	18 (I-IV)	21 (I-IV)
3	3-FDA	Meta	16 (I-IV)	19 (I-IV)	22 (I-IV)

inefficient foam formation can be made. One reason for that might be incomplete degradation of PPO and, therefore, different thermal conditions are required. The second reason of poor porosity of polyimides **20** might be a collapse of the completely foamed film as a consequence of too high temperature. Finally, some polyimides just do not form foamed structures because of their specific molecular ordering and orientation of the matrix macromolecules. That was a case with PMDA/ODA-based systems which possess a characteristic in-plane molecular orientation.<sup>32</sup> Relaxation in such a system was found to be enhanced in the presence of pores.

Good foaming was observed for polyimides of group **21** which is derived from the meta-isomer of PMDA (OEt) diester dichloride as opposed to the para-isomer in group **20**. Here it can be seen that all of the PPO, which was incorporated into the polyimide precursor (<sup>1</sup>H NMR data), survived imidization (TGA data), and was subsequently degraded. The film did not collapse, and this

is an example of efficient foaming. The highest value of porosity among the polyimides of group **21** is 22.5%. Taking into account that dielectric constant of non-foamed polyimide is 2.82, the decrease in calculated dielectric constant to 2.1 for sample **21-IV** is quite significant. Maxwell Garnett<sup>14</sup> described the non-linear relationship between porosity and dielectric constant (Figure 17).

Densities of foamed polyimides of group **22** have lower values because of the lower density of the matrix material, polyimide PMDA/3FDA. The density of homopolymer PMDA/3FDA is 1.35 g/cm<sup>3</sup>. As it is seen from Table 21, only the first sample (**22-I**) was not foamed efficiently. The other density measurements and percent of porosity calculated are in good agreement with actual amount of PPO incorporated. Foam **22-IV** was floating on the water surface indicating the density of ~1.0. That value translates into 26 % of porosity and a calculated dielectric constant of ~ 2.0 (Maxwell Garnett theory).

Thermal gravimetric analysis gave weight % of thermally degraded PPO for each copolymer (see Table 18). Here, the volume fraction of PPO was needed for comparison with the volume fraction of PPO by <sup>1</sup>H NMR and volume fraction of voids (Table 21).

An example of calculations for conversion of the weight percent of polypropylene oxide into the volume percent are given as follow for **20-IV**:

PPO weight % (TGA): 13.8%

PPO weight = 13.8 g

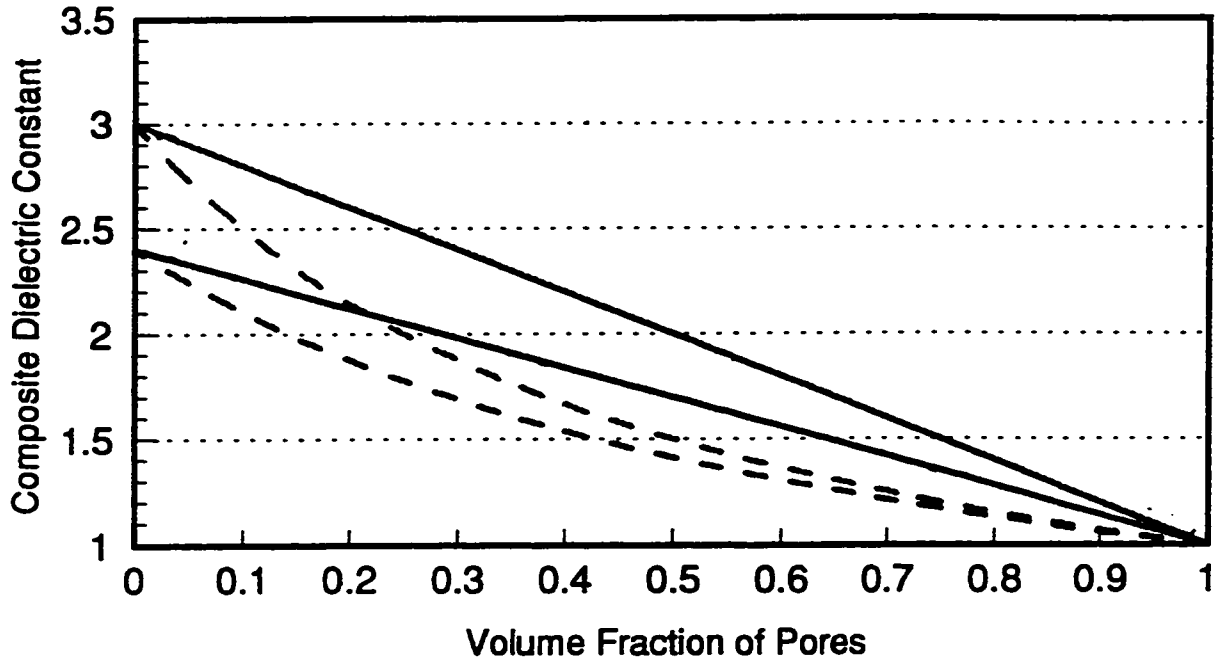
Polyimide weight = 86.2 g

PPO density = 1.032 g/cm<sup>3</sup>

Polyimide density = 1.41 g/cm<sup>3</sup>



**Figure 17.** Maxwell Garnett theory used for the prediction of dielectric constant of the porous material.



$$\text{PPO volume} = 13.8 \text{ g} / 1.032 \text{ g/cm}^3 = 13.37 \text{ cm}^3$$

$$\text{Polyimide volume} = 86.2 \text{ g} / 1.41 \text{ g/cm}^3 = 61.13 \text{ cm}^3$$

$$\text{PPO volume \% (TGA)} = \text{PPO weight} \cdot 100\% / (\text{PPO weight} + \text{Polyimide weight}) = 17.9\%$$

**Table 21.** Results of Density Measurements for Foamed Polyimides and Calculations of Their Porosity.

Entry	Polyimide	Density	PPO Incorporated Volume %		Volume Fraction of Voids (Porosity) %
			<sup>1</sup> H MNR	TGA	
1	PMDA/4BDAF	1.47	-	-	-
2	20-I	1.40	4.7	5.4	4.76
3	20-II	1.36	9.9	14.6	7.48
4	20-III	1.34	12.2	13.4	8.84
5	20-IV	1.34	17.7	17.9	8.84
6	20-V	1.38	33.5	33.6	6.1
7	21-I	1.41	4.2	4.6	4.1
8	21-II	1.27	12.4	12.0	13.6
9	21-III	1.21	18.3	17.6	17.7
10	21-IV	1.14	22.2	22.5	22.5
11	PMDA/3FDA	1.35	-	-	-
12	22-I	1.34	5.8	6.8	0.7
13	22-II	1.21	9.5	12.4	10.4
14	22-III	1.23	9.3	11.1	8.9
15	22-IV	1.00	28.2	25.2	26

## **5.2. Preparation and Characterization of Thin Films Foamed Polyimides.**

There has not been much reported research done on conditions for imidization and foaming of thin (0.5-2.5  $\mu\text{m}$ ) films. As was the case with

imidization, the optimal temperature and time had to be found for the foaming of thin films.

Processes of imidization and foam formation were monitored by refractive index measurements as well as by QCM (quartz crystal microbalance) measurements. Quartz crystal microbalance is a technique which allows for the determination of mass of thin polymer films and small changes in mass. QCM works by measuring the oscillating frequency of crystalline quartz. The frequency of this oscillation is dependent upon the mass of the crystal or any thin film coating on the crystal. The relation between frequency of the quartz crystal and added mass for small loads is given<sup>33</sup> by equation (3):

$$\Delta m/A = - \rho_Q V_Q \Delta v / 2v_0^2 \quad (3)$$

Where  $\Delta m$  is the change in mass;  $A$  is the “active area” of the crystal;  $\rho_Q$  is the density of quartz, 2.65 g/cm<sup>3</sup>;  $V_Q$  is the shear wave velocity for quartz, 3.34×10<sup>5</sup> cm/s;  $\Delta v$  is the change in frequency induced by the mass change; and  $v_0$  is the initial frequency of the crystal. For the determination of mass loss by the thin film, there is no need to determine the active area  $A$ ; the mass per unit area determined experimentally is simply divided by the film thickness to yield a mass per unit volume change. This technique was used to measure the mass of the polyimide/PPO copolymer/composite films, and to measure the weight changes as a function of curing and foaming conditions.

Four samples, two of **20-IV**, **21-IV** and **22-IV** were spun on 5 MHz gold polished quartz crystals and left for 20 hours at 80 °C for complete solvent removal. At this point, “the soft bake”, the first measurements of refractive index, thickness of film and exact film weight by QCM were taken. Then, “mild”

curing was performed on all the samples, and the second measurements of the same parameters were made. Finally, a foaming as a function of foaming temperature and time was studied by QCM, and the final products, foams, were subjected to refractive index and thickness measurements.

It was important first to compare some characteristic features of films before imidization, on the stage of being poly(amic alkyl ester) graft copolymers, and after imidization in order to answer the question if our “mild” imidization conditions indeed caused complete imidization. We wanted to make sure that only weight loss happening during thermal curing was caused by evolution of ethanol but not by degradation of polypropylene oxide.

Table 22 shows the weight changes during imidization for three samples as results of QCM analysis. There is a good correlation between predicted and experimental values of weight losses, indicating that all the ethanol is driven off and high degree of imidization is obtained. Two of these data, for sample **21-IV** and **22-IV**, are slightly higher than their expected values. Possible explanation of this fact can be removal of adsorbed moisture or residual solvent. The same was observed in literature<sup>21</sup> and explained as possible end-group effect or potential chain breakage.

Calculations of expected weight losses were done using the values of PPO % incorporated from Table 22. An example of such a calculation for sample **20-IV** follows:

Weight of poly(amic ethyl ester) repeating unit = 793.6 g/mol

Weight of polyimide repeating unit = 701.46 g/mol

The difference (loss of two ethanol molecules per unit) = 92.14 g/mol or 11.61%

**Table 22.** QCM Analysis of Weight Loss during Imidization.

Entry	Sample	PPO % Charge	PPO % Incorporated*	Predicted Weight Loss %	QCM Weight Loss %
1	20-IV	20	13.4	10.05	9.47
2	21-IV	20	17.1	9.62	13.62
3	22-IV	20	21.8	11.73	16.19

\* Here, % of incorporated PPO is given as an average between results of <sup>1</sup>H NMR spectroscopy and TGA. For results of each method see Table 18.

PPO % incorporated =13.4%

Therefore, 13.4 % of repeating units have PPO and 86.6% ethanol.

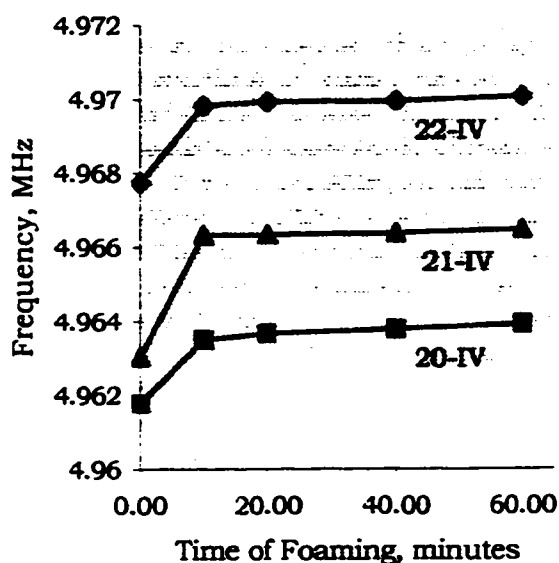
Weight loss during imidization= 11.61%\*0.866= 10.05%.

The next step was to find the best foaming conditions. Foaming rate was studied at 240 °C for samples of all three groups using QCM technique (Figure 18). Knowing that increase in frequency indicates loss of weight, it is easy to see that the most significant drop in weight happened in the first 10 minutes of foaming for all the samples. This was in some ways surprising since previous studies utilizing thin films showed that longer periods of time (hours) were required for PPO removal.<sup>19</sup> Sample **20-IV** has lost 81% of its overall weight loss in the first 10 minutes, while the same parameter for samples **21-IV** and **22-IV** were 96% and 89% respectively. There was not weight change after 60 minutes of foaming at 240 °C.

To examine the influence of different foaming temperatures, processing at two different temperatures for the same type of polyimide was performed and monitored by refractive index measurements. In-plane refractive indexes at 633 nm wavelength were measured on a Metricon Prism Coupler (PC-2010). Figure 19 reflects the difference in the thin film properties of two 20-IV polymers, which were spun on silicon wafers, soft baked and cured at the same conditions, but foamed separately at 240 °C and 260 °C.

Successful foam formation results in the decrease of the refractive index of the foamed polyimide comparing to the non-foamed polyimide-PPO copolymer.<sup>19</sup> Indeed, in the course of foam formation, PPO with the refractive index 1.36 gets substituted with air (refractive index =1.00). The 260 °C

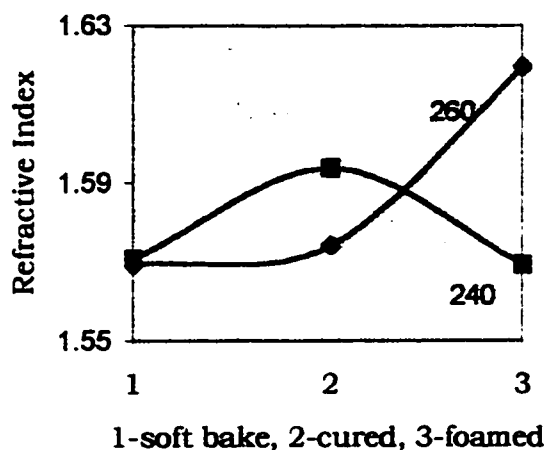
**Figure 18.** Change in frequency during QCM measurements as a function of time for samples 20-IV, 21-IV and 22-IV.



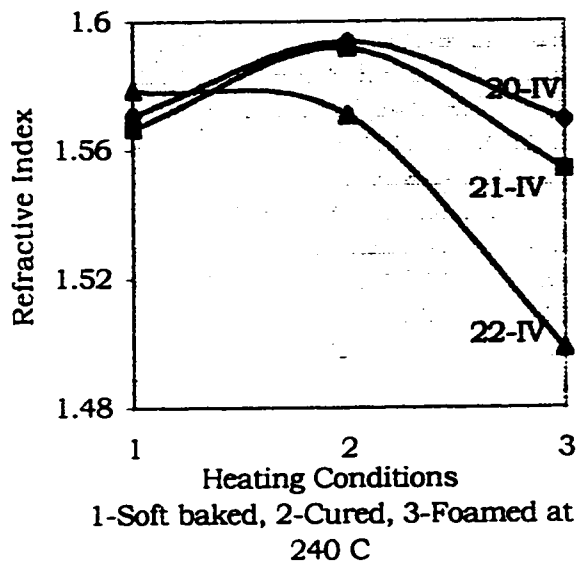
foamed sample had refractive index much higher than it was before foaming, indicating that the foam collapsed because of too high temperature. Conversely, the 240 °C foam had a decrease in refractive index. Subsequently, all the samples were foamed at 240 °C and showed much more significant decrease in refractive index (Figure 20 and Table 23). Therefore, one hour or less at 240 °C was adopted as the best foaming conditions for thin film foam preparations.

As mentioned before, refractive index can be used for dielectric constant calculations using formula  $\epsilon = (\text{R.I.})^2 + 0.2$  (Chapter 4.4). Results of refractive index measurements of thin films **20-IV**, **21-IV**, and **22-IV** after foaming at 240 °C are given in Table 24 as well as the calculated dielectric constants.

**Figure 19.** Refractive index measurements for two **20-IV** samples, which were foamed at different temperatures, 240 and 260 °C.



**Figure 20.** Refractive index change at various heating conditions for the samples from three different polymer groups.



**Table 23.** Refractive Indexes of Foamed Foams and Their Calculated Dielectric Constants.

Entry	Polymer	Foaming temperature °C	Refractive index after foaming	Dielectric Constant
1	20-IV	260	1.62	2.82
2	20-IV	240	1.57	2.66
3	21-IV	240	1.55	2.61
4	22-IV	240	1.50	2.44

Finally, analogous to the QCM data of weight loss during imidization (Table 24), the results of the weight loss during 240 °C foam formation were



obtained for three different polyimide samples, **20-IV**, **21-IV**, and **22-IV**. Foam efficiencies were excellent (92 and 99%) and good (63%).

**Table 24.** QCM Data for Weight Loss during Foam Formation at 240 °C.

Entry	Polymer	Initial PPO Charge %	Expected Weight Loss at Foaming* %	QCM Weight Loss at Foaming %	Foam Efficiency %
1	20-IV	20	13.4	8.43	62.9
2	21-IV	20	17.1	17.03	99.6
3	22-IV	20	21.8	20.01	91.8

\* Here, % of expected weight loss at foaming is given as an average between results of <sup>1</sup>H NMR spectroscopy and TGA for incorporated PPO. For results of each method see Table 18.

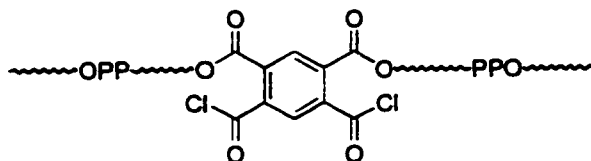
Here with the thin films again as in the case with thick films (Table 21), the same polyimide samples showed the best foam efficiency, **21** and **22**. Thus, the best foams were prepared from copolymers, which derived from meta-PMDA (OEt) diester dichloride and 4BDAF and 3FDA diamines. Combination of para-PMDA (OEt) diester dichloride and 4BDAF gave lower foaming efficiency.

## Conclusions

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Porous polyimide materials with low dielectric constants were prepared as the result of several subsequent steps:

1. A new functional macromonomer PPO-PMDA-PPO was synthesized:



2. A new type of graft copolymer, a “two-sided comb” poly(amic alkyl ester)/PPO, was designed. Thirteen variations of this copolymer were prepared with different aromatic amines, the isomers of PMDA diester dichloride, and different content of PPO. They were characterized by  $^1\text{H}$  NMR, GPC and intrinsic viscosity measurements.
3. Polyimide/ PPO composites were prepared and characterized by TGA, DMTA and DSC.
4. Porous polyimides were prepared in the form of thick (15-25  $\mu\text{m}$ ) and thin (0.5-2.5  $\mu\text{m}$ ) films and characterized by density, QCM and refractive index measurements. Low dielectric constants ( $\epsilon = 2.00$  and  $\epsilon = 2.44$ ) were obtained for meta-PMDA (OEt)/ PMDA (PPO)/3-FDA for thick and thin films accordingly.

## **Chapter 6. Experimental**

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### **6.1 Reagents, Suppliers, and Purification**

#### **Commercially Available Materials:**

Acetic acid, glacial	J.T. Baker
2,2-bis[4-(4-aminophenoxy)phenyl]	Chriskev, sublimed
Hexafluoropropane (4-BDAF)	
Calcium nitrate, tetrahydrate	Aldrich
Charcoal	Mallinckrodt
Celite	J.T. Baker
Chloroform, deuterated	Cambridge Isotope Laboratory
Dichloromethane	J.T. Baker
Diethyl ether, anhydrous	EM Science
Diethylaluminum chloride, 1M in heptane	Aldrich
N,N-Dimethylformamide (DMF)	Aldrich
Dimethyl sulfoxide-d <sub>6</sub> (DMSO)	Cambridge Isotope Laboratory
2-Ethoxyethyl acetate (cellusolve acetate)	Aldrich
Ethyl acetate	J.T. Baker
1,1,1,3,3,3,-Hexamethyldisilazane (HMS)	Aldrich
Hydrochloric acid, 36.5-38%	EM Science

Magnesium sulfate, anhydrous	EM Science
Methanol, semiconductor grade	Pacific Pac International Incorporated
1-Methyl-2-pyrrolydone, 99.5% anhydrous	Aldrich
Oxalyl chloride, 98%	Aldrich
Propylene oxide	Aldrich, distilled over CaH <sub>2</sub>
Pyridine	Aldrich
Pyromellitic dianhydride (PMDA)	Criskev
Sodium hydroxide, 50% solution	J.T. Baker
Sodium bicarbonate, powder	J.T. Baker
Tetrabutylammonium hydroxide, 4.44 mmol/L in Methanol	Metrohm
Tetrahydrofuran (THF)	J.T. Baker
5,10,15,20-Tetraphenylporphyrin	Midcentury
Toluene	EM Science
Triethylamine	EM Science
Trimethylchlorosilane (TMS)	Aldrich

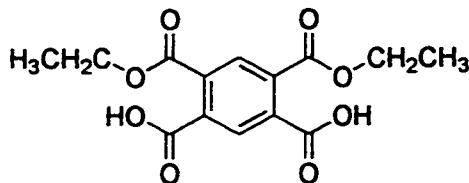
**Noncommercial reagents used in the research:**

1,1-bis(4-aminophenyl)-1-phenyl- 2,2,2-trifluoroethane (3-FDA)	Prepared according to the literature procedure of Rogers et al. <i>Mater. Plast. Soc. Symp.</i> 1992, 277, 23.
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4,6-Dicarbethoxyisophthalic acid, Prepared according to the procedure of meta/para (meta/para PMDA(OEt) Diester Diacid) Bell V.L. and Jewell, *J. Polym. Sci.*, 1967, Part A-1, vol. 5, 3043.

## 6.2 Experimental Procedure for Monomer Preparation

### Preparation of meta-PMDA (OEt) Diester Diacid (1)



354 g of PMDA diester (OEt)-diacid isomeric mixture (80/20% meta/para isomers) was dissolved in 1.5 L of ethyl acetate with heating and stirring. After half of the solvent was evaporated, 75 mL of hexane was added to the hot solution to cause precipitation at cooling. The precipitate was filtered from the mother liquid, washed twice with hexane, and dried (55% yield). HPLC analysis and  $^1\text{H}$  NMR indicated 90/10% composition of meta/para mixture. After six subsequent recrystallizations, ratio meta/para had been increased up to 99.23% of meta isomer and 0.77% of para with overall yield 37 g (20 %).

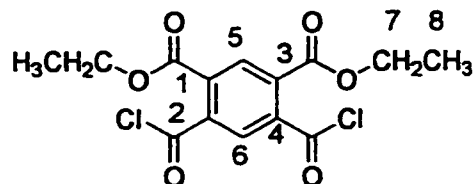
#### Analytical data for 1

M.W.: 310.26

$^1\text{H}$  NMR: (250 MHz, DMSO- $d_6$ )

8.06 (s, 1H, aromatic H), 7.88 (s, 1H, aromatic H), 4.30 (q, 4H, CH<sub>2</sub>), 1.27 (t, 6H, CH<sub>3</sub>).

### Preparation of meta-PMDA (OEt) Diester Dichloride (**3**)



A 250 mL flask equipped with a stirrer, chilled water reflux condenser, addition funnel, and heating mantle was charged with the meta diester(OEt)-diacid of PMDA (23.3 g, 0.075 mol) and ethyl acetate (100 mL) and heated to 55-58° C. Oxalyl chloride (27.3 g, 0.215 mol) was slowly added to the reaction mixture over 3 hours; reaction was maintained at 55-58° C for additional 12 hours. After reaction completion (HPLC), the excess oxalyl chloride was removed by performing six subsequent solvent evaporations in vacuo (80 mL of fresh ethyl acetate was added each time). The open flask was left for a night under the strong nitrogen flow for complete oxalyl chloride removal. The product was twice recrystallized from hexane to yield sparkling light-weight crystals of **2** in 80% yield.

#### Analytical data for **3**

M.W.: 347.15

<sup>1</sup>H NMR: (250 MHz, CDCl<sub>3</sub>)

8.35 (s, 1H, aromatic H), 7.91 (s, 1H, aromatic H), 4.35-4.46 (q, 4H,

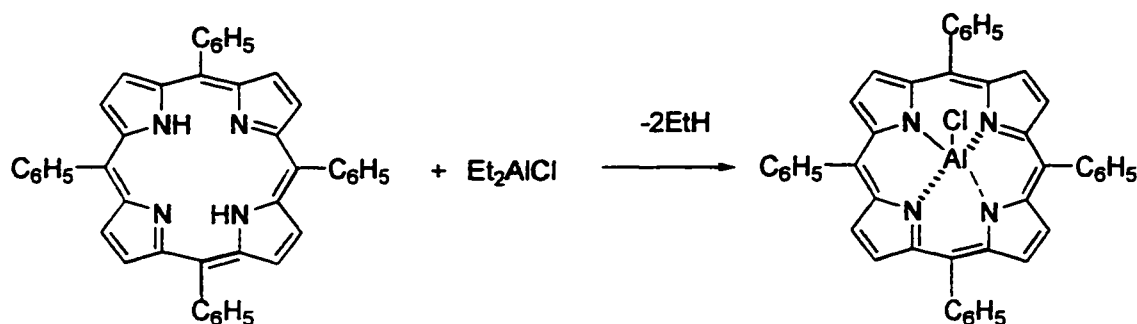
CH<sub>2</sub>), 1.30-1.47 (t, 6H,CH<sub>3</sub>).

<sup>13</sup>C NMR: (62.9 MHz, CDCl<sub>3</sub>)

166.56 (C1), 163.68 (C2), 139.75 (C3), 132.16 (C4), 131.58 (C5), 126.83 (C6), 63.24 (C7), 13.82 (C8).

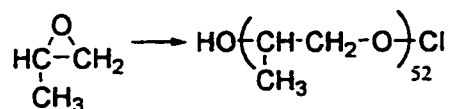
### Preparation of Polypropylene Oxide (PPO) (7)

a) Catalyst preparation- 5,10,15,20-tetraphenylporphinato aluminum chloride **4**



In a dry box, tetraphenylporphyrin (4.72 g, 7.67 mmol, 1 equiv) was dissolved in 200 mL of  $\text{CH}_2\text{Cl}_2$ , and  $\text{Et}_2\text{AlCl}$  (9.2 mL, 9.2 mmol, 1.2 equiv) was added slowly with stirring. After the addition was complete, the reaction mixture was left to stir for 4 hours.

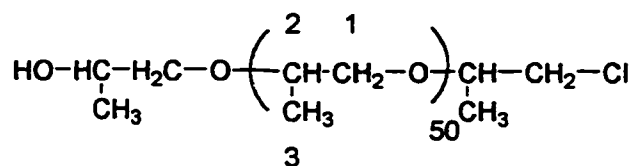
b) Catalytic Polymerization of Propylene Oxide



A solution of the prepared catalyst, tetraphenylporphinatoaluminum chloride **4**, with intense purple color was cooled to 0 °C in an ice water bath before propylene oxide (PO) (22.98 g, 0.396 mol, 52 equiv) was added via a long

needle from a sealed flask. The reaction was left to stir overnight under nitrogen flow at room temperature. Then the mixture was shaken well with conc. HCl (3 mL) and CH<sub>3</sub>OH (10 mL), and the methylene chloride was evaporated. After the weight of the dry residue was taken for molecular weight calculation, it was dissolved in diethyl ether and vacuum filtered through celite. The filtrate was transferred to the separatory funnel for acid wash with 20 mL of concentrated HCl. The ether layer was filtered through celite and washed with water, and celite filtered again. Next, the organic layer washed with a solution of 10 mL of 50% NaOH dissolved in 300 mL of water, and the ether layer filtered through celite. Two last times the organic layer was washed with 10% NaHCO<sub>3</sub> and H<sub>2</sub>O and filtered both times through celite. To the pink ether solution of PPO was added charcoal and anhydrous MgSO<sub>4</sub>. The mixture was allowed to stir overnight for complete catalyst removal. Filtration through celite followed by concentration in vacuo afforded a light yellow viscous liquid. In order to remove traces of water from PPO, it was distilled with 200 mL of toluene. The azeotropic mixture (toluene/water) was distilled off as a cloudy mixture. After clear toluene started to distill, the distillation was stopped. Excess of toluene was removed in vacuo. PPO (14.21 g) was collected (66%).

Analytical data for 7



M.W.: 3000

<sup>1</sup>H NMR: (250 MHz, acetone-d<sub>6</sub>,)



3.40 (d, 2H, H(1)), 3.31 (m, 1H, H(2)), 1.10 (d, 3H, H(3)).

$^{13}\text{C}$  NMR: (62.9 MHz, acetone- $\text{d}_6$ )

76.12 (C(1)), 73.80 (C(2)), 17.92 (C(3)).

GPC (Gel Permeation Chromatography): THF, calibrated for polystyrene

% Area = 100

M<sub>w</sub> (Daltons) 3010

Polydispersity 1.13

### **Preparation of PPO-Trimethylsilyl Ether (8)**

PPO (0.5120 g, 0.1829 mmol, 1 equiv.) was dissolved in 15 mL of pyridine. HMS (0.23 mL, 1.097 mmol, 6 equiv.) was added, and the solution was shaken. After addition of TMS (0.087 mL, 0.6859 mmol, 3.75 equiv.), the solution turned cloudy. Reaction proceeded almost immediately. Pyridine was vacuum distilled at 74 °C.

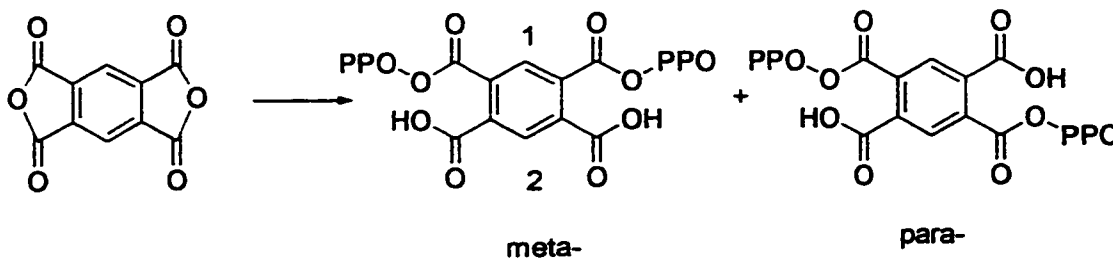
### Analytical data for 8:

$^1\text{H}$  NMR (250 MHz),  $\text{CDCl}_3$ :

3.43 (100H), 3.25 (48H), 1.00 (144H), 0.02 (7.98H)

M.W.: 3140 g/mol

### **Preparation Functional Macromonomer PMDA (PPO) Diester Diacid (9)**



Polypropylene oxide **7** (PPO) (6.34g, 0.0032 mol, 2 equiv) was dissolved in ethyl acetate (100 mL), and PMDA (0.35 g, 0.0016 mol, 1 equiv) was added. Reaction was allowed to reflux for 48 hours. The product was concentrated in vacuo. Yield was 96%.

Analytical data for **9**

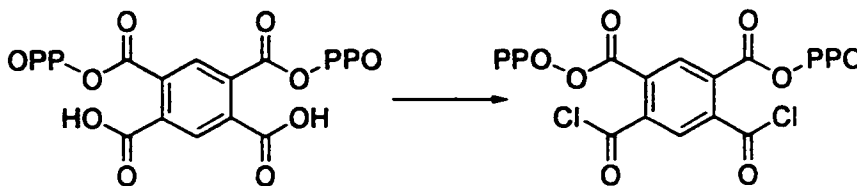
M.W.: 5000-6000

<sup>1</sup>H NMR: (250 MHz, acetone-d<sub>6</sub>),

12.1 (2H), 8.39 (1H, H(1)), 8.31 (1H, H(2)), 3.48-3.59 (176H methylene protons of PPO), 3.35-3.42 (88H methyne protons of PPO), 1.11 (264H methyl protons of PPO).

M.W.=58.08\*44\*2=5111

**Preparation of PMDA (PPO) Diester-Dichloride (**10**)**



The functional macromonomer **9** (6.64 g, 1.6 mmol, 1 equiv) was dissolved in ethyl acetate (light yellow solution), heated up to 55-58° C and slowly treated (dropwise) with oxalyl chloride (4.06 g, 32 mmol, 20 eq.). Reaction proceeded for 24 hours at the same temperature and turned brown-red in color. Several subsequent solvent additions and distillations were performed for oxalyl chloride removal. The flask was left for 12 hours under the

strong N<sub>2</sub> flow for complete isolation of oxalyl chloride. Finally, the product was concentrated in vacuo to afford brown-red viscous liquid with 100% yield.

**Analytical data for 10**

**M.W.:** 5000-6000

**<sup>1</sup>H NMR:** (250 MHz, acetone-d<sub>6</sub>)

8.57 (1H, aromatic), 8.54 (1H, aromatic), 3.48-3.45 (188H methylene protons of PPO), 3.35-3.42 (94H methyne protons of PPO), 1.08-1.11 (282H methyl protons of PPO).

M.W. = 58.08\*47\*2=5460

**Titration** (Metrohm 736 GP Titrino)

Method: Acid MW

Titrant: tetrabutylammonium hydride, 0,0444 m/L in methanol

M.W.: 5710

**6.3 Experimental Procedures for Poly(amic Alkyl Ester) Graft Copolymer**

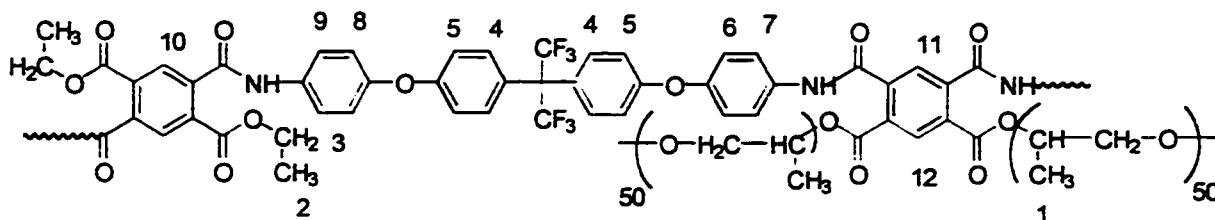
**Synthesis**

**A General Procedure for Graft Copolymer Preparation (14-16)**

A vial with a cap and a stirrer was charged with functional macromonomer PMDA (PPO) diester dichloride and transferred into the dry box where 2mL of NMP were added. Then PMDA (OEt) diester dichloride and 2mL more of NMP were added and stirred. Next, the diamine was added and 4 mL of NMP. The vial was vigorously shaken for immediate mixing. Last, the vial was charged with pyridine, taken out of the dry box and placed on a mechanical stirrer for

overnight or longer. The polymer solution was precipitated into a blender with a solvent mixture of 75% H<sub>2</sub>O and 25% CH<sub>3</sub>OH, stirred for 30 min, vacuum filtered and washed with H<sub>2</sub>O/CH<sub>3</sub>OH in the blender a second time. Precipitate was rinsed on a filter or in the blender with pure methanol, filtered, and dried. Dry polymers were placed into the vacuum stove at 50° C for overnight with a slight air flow to dry out residual H<sub>2</sub>O and CH<sub>3</sub>OH.

**Preparation of 5%-PMDA (PPO)/para-PMDA (OEt)/4-BDAF Graft Copolymer (14-I)**



In a dry box, in a 15 mL vial PMDA (PPO)diester dichloride (**10**) (0.175 g, 0.029 mmol) was dissolved in NMP; para-PMDA (OEt) diester dichloride (**11**) (1.3275 g, 3.824 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.9976 g, 3.853 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.87 mL, 0.85 g, 10.8 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a creamy-white solid (2.76 g, 79%).

**Analytical data for 14-I**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.04 (s, 2H, H(10)), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 1.5 H, H(1)).

% of PPO incorporated: 3.4% ( <sup>1</sup>H NMR)

Intrinsic viscosity 0.3242 dL/g

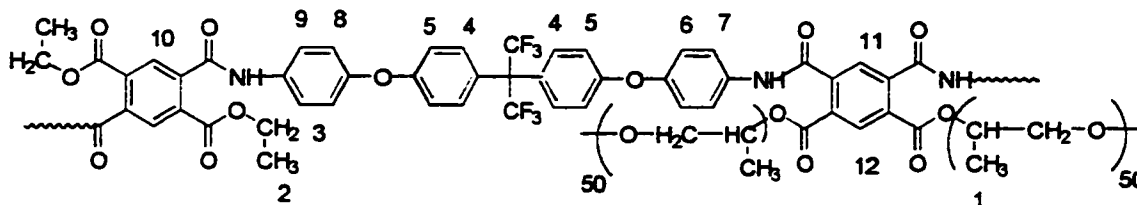
GPC: THF, calibrated for polystyrene

Mw (Daltons) =28,480

% Area =97.44

Polydispersity = 1.8

**Preparation of 10%-PMDA (PPO)/(para-PMDA (OEt)/4-BDAF Graft Copolymer (14-II)**



In a dry box, in a 15 mL vial PMDA-PPO dichloride (**10**) (0.3500 g, 0.0612 mmol) was dissolved in NMP; para-PMDA (OET) (**11**) (1.2505 g, 3.602 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.8995 g, 3.6636 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.83 mL, 0.81 g, 10.25 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated

according to the general procedure for polymer preparation and held in the vacuum stove to get dry. This afforded a pink-white solid (3.01 g, 86%).

**Analytical data for 14-II**

**<sup>1</sup>H NMR: (250 MHz, DMSO-d<sub>6</sub>)**

8.04 (s, 2H, H(10)), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 3.3 H, H(1)).

**% of PPO incorporated: 7.0% ( <sup>1</sup>H NMR)**

**Intrinsic viscosity 0.3146 dL/g**

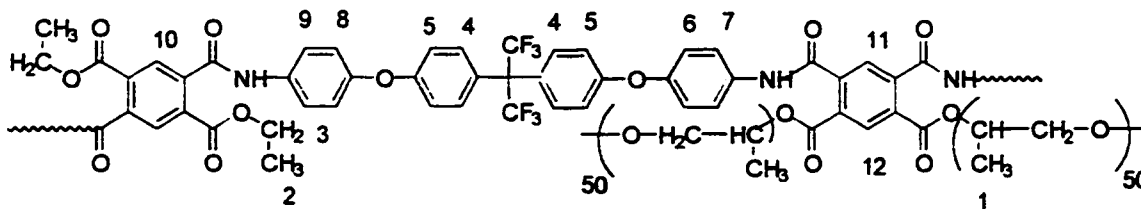
**GPC: THF, calibrated for polystyrene**

% Area = 93.76

Mw (Daltons) = 28,545

Polydispersity = 1.80

**Preparation of 15%-PMDA (PPO)/para-PMDA (OEt)/4-BDAF Graft Copolymer (14-III)**



In a dry box, in a 15 mL vial, PMDA (PPO)(**10**) (0.5250 g, 0.0919 mmol) was dissolved in NMP; para-PMDA (OEt) (**11**) (1.1740 g, 3.381 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.8022 g, 3.4737 mmol) and more NMP

were added next; the mixture was shaken vigorously. Pyridine (0.78 mL, 0.76 g, 9.72 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a creamy-white solid (2.54 g, 73%).

**Analytical data for 14-III**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.04 (s, 2H, H(10)), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 4.7 H, H(1)).

**% of PPO incorporated:** 9% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.2794 dL/g

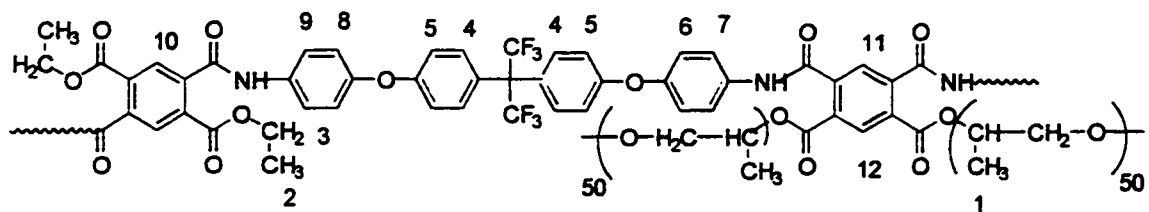
**GPC:** THF, calibrated for polystyrene

%Area =98.72

Mw (Daltons) =22906

Polydispersity = 1.86

**Preparation of 20%-PMDA/(PPO)/para-PMDA (OEt)/4-BDAF Graft Copolymer (14-IV)**



In a dry box, in a 15 mL vial, PMDA (PPO)(**10**) (0.7000 g, 0.1225 mmol) was dissolved in NMP; para-PMDA (OEt) (**11**) (1.0974 g, 3.161 mmol) was added

and stirred. Diamine, 4-BDAF (**13**), (1.7026 g, 3.2838 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.74 mL, 0.72 g, 9.19 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a dirty-white solid (2.65 g, 76%).

**Analytical data for 14-IV**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.04 (s, 2H, H(10)), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 6.24 H, H(1)).

**% of PPO incorporated:** 13% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.3194 dL/g

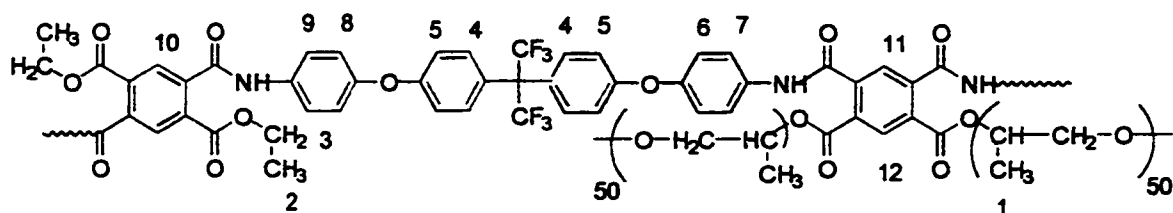
**GPC:** THF, calibrated for polystyrene

% Area =98.13

Mw (Daltons) =25,954

Polydispersity = 1.77

**Preparation of 35%- PMDA (PPO)/para-PMDA (OEt)/4-BDAF Graft Copolymer (14-V)**





In a dry box, in a 15 mL vial, PMDA-PPO-DC (1.2250 g, 0.214 mmol) was dissolved in NMP; para-PMDA-DEDC (0.8679 g, 2.5 mmol) was added and stirred. Diamine, 4-BDAF, (1.4071 g, 2.714 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.615 mL, 0.60 g, 7.59 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a dirty-yellow solid (1.86 g, 53%).

**Analytical data for 14-V**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.04 (s, 2H, H(10) para-), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 12.49H, H(1)).

**% of PPO incorporated:** 26% ( <sup>1</sup>H NMR)

**Intrinsic viscosity:** 0.2730 dL/g

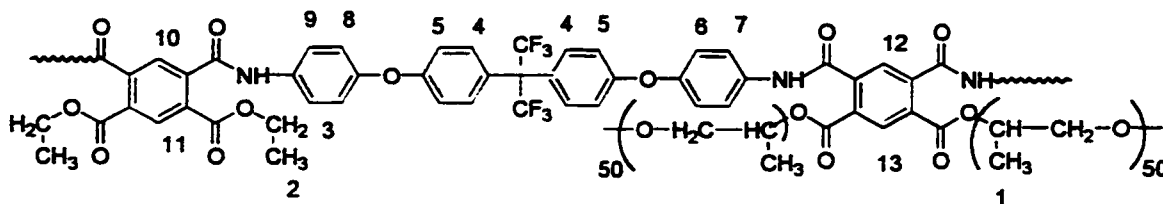
**GPC:** THF, calibrated for polystyrene

% Area = 100.00

Mw (Daltons) = 19214

Polydispersity = 1.7029

**Preparation of 5%-PMDA(PPO)/meta-PMDA(OEt)/4-BDAF Graft Copolymer (15-I)**



In a dry box, in a 15 mL vial, PMDA (PPO) (**10**) (0.175 g, 0.029 mmol) was dissolved in NMP; meta-PMDA (OEt) (**3**) (1.3275 g, 3.824 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.9976 g, 3.853 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.87 mL, 0.85 g, 10.8 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a white-gray powder (2.34 g, 67%).

**Analytical data for 15-I**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 1H, H(10) meta-), 7.87 (s, 1H, H(11) meta-), 7.76 (d, 4H, H(9)),  
7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H,  
H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 1.3H, H(1)).

**% of PPO incorporated:** 2.9% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.2799 dL/g

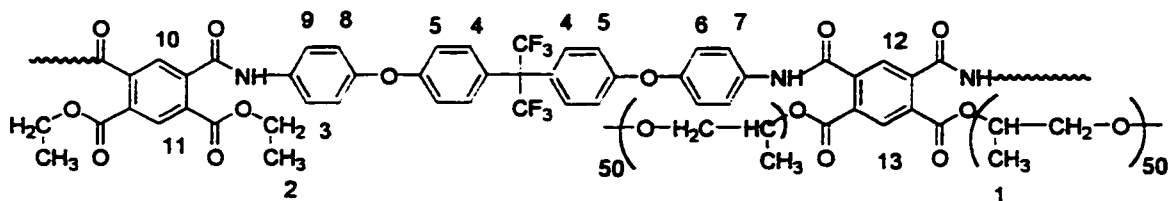
**GPC:** THF, calibrated for polystyrene

% Area =99.54

Mw (Daltons) = 12,419

Polydispersity = 1.7287

**Preparation of 10%-PMDA(PPO)/meta-PMDA (OEt)/4-BDAF Graft Copolymer (15-II)**



In a dry box, in a 15 mL vial, PMDA-PPO (0.3500 g, 0.058 mmol) was dissolved in NMP; meta-PMDA (OEt) (1.2497 g, 3.600 mmol) was added and stirred. Diamine, 4-BDAF, (1.8988 g, 3.66 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.83 mL, 0.81 g, 10.25 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a creamy-white powder (3.00 g, 86%).

**Analytical data for 15-II**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 1H, H(10) meta-), 7.87 (s, 1H, H(11)meta-), 7.76 (d, 4H, H(9)),  
7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H,  
H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 4.1H, H(1)).

**% of PPO incorporated:** 9.1% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.4187 dL/g

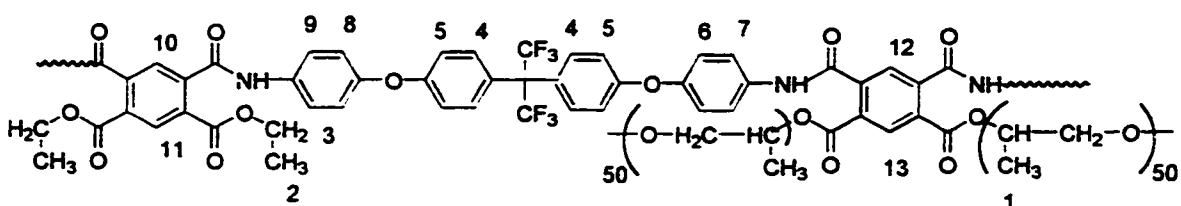
GPC: THF, calibrated for polystyrene

% Area =93.92

Mw (Daltons) =11,886

Polydispersity = 1.6553

**Preparation of 15%-PMDA (PPO)/meta-PMDA (OEt)/4-BDAF Graft Copolymer (15-III)**



In a dry box, in a 15 mL vial, PMDA PPO) (**10**) (0.5250 g, 0.0875 mmol) was dissolved in NMP; meta-PMDA (OEt) (**3**) (1.2451 g, 3.586 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.9049 g, 3.67 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.83 mL, 0.81 g, 10.3 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove to dry. This afforded a dirty-white solid (3.02 g, 86%).

**Analytical data for 15-III**

<sup>1</sup>H NMR: (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 1H, H(10) meta-), 7.87 (s, 1H, H(11) meta-), 7.76 (d, 4H, H(9)), 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H, H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 6H, H(1)).

% of PPO incorporated: 13.6% (<sup>1</sup>H NMR)

Intrinsic viscosity 0.2540 dL/g

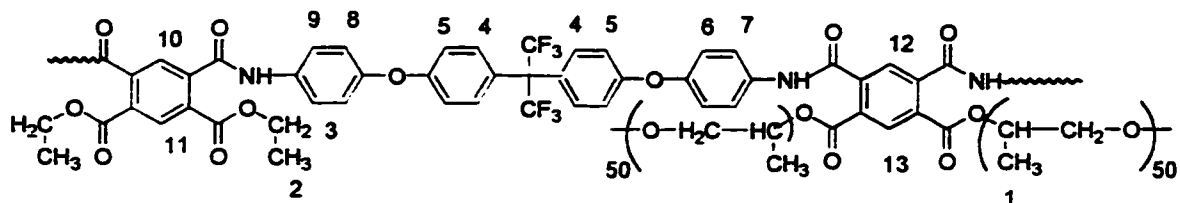
GPC: THF, calibrated for polystyrene

% Area =96.45

Mw (Daltons) =15,085

Polydispersity = 1.8322

**Preparation of 20%-PMDA (PPO)/meta-PMDA (OEt)/4-BDAF Graft Copolymer (15-IV)**



In a dry box, in a 15 mL vial PMDA (PPO) (**10**) (0.7000 g, 0.1167 mmol) was dissolved in NMP; meta-PMDA (OEt) diester dichloride (**3**) (1.0986 g, 3.16 mmol) was added and stirred. Diamine, 4-BDAF (**13**), (1.7013 g, 3.28 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.74 mL, 0.73 g, 9.18 mmol) was added last. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove at 50°C to dry. This afforded a creamy-white solid (2.73 g, 78%).

Analytical data for 15 IV

<sup>1</sup>H NMR: (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 1H, H(10) meta-), 7.87 (s, 1H, H(11) meta-), 7.76 (d, 4H, H(9)),  
 7.33 (d, 4H, H(8)), 7.14 (d, 4H, H(4)), 7.05 (d, 4H, H(5)), 4.21-4.29 (q, 4H,  
 H(3)), 1.15-1.21 (t, 6H, H(2)), 1.00 (d, 6H, H(1)).

% of PPO incorporated: 16.7% ( <sup>1</sup>H NMR)

Intrinsic viscosity 0.2279 dL/g

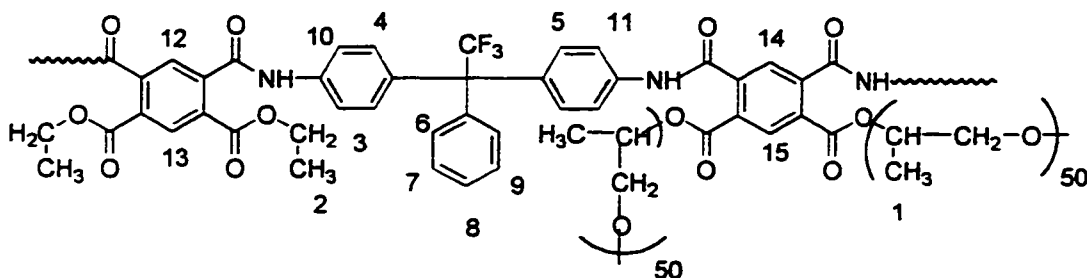
GPC: THF, calibrated for polystyrene

% Area =97.58

Mw (Daltons) =14,130

Polydispersity = 2.2144

**Preparation of 5%-PMDA (PPO)/meta-PMDA (OEt)/3-FDA Graft Copolymer (16-I)**



In a dry box, in a 15 mL vial, PMDA-PPO (**10**) (0.175 g, 0.0292 mmol) was dissolved in NMP; meta-PMDA (OEt) (**3**) (1.6689 g, 4.8 mmol) was added and stirred. Diamine, 3-FDA (**12**), (1.6559 g, 4.84 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (1.1 mL, 1.1 g, 13.552 mmol) was added last. Amounts of the reagents were calculated for 3.5 g of the polymer. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for

polymer preparation and held in the vacuum stove at 50°C to dry. This afforded a dirty-white solid (2.73 g, 78%).

**Analytical data for 16-I**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 0.85H, H(13) meta-), 8.09 (s, 0.15H, H(14) meta-), 7.89 (s, 0.15H, H(15) meta-), 7.83 (s, 0.85H, H(12) meta-), 7.70 (d, 4H, H(11,12)), 7.39 (m, 3H, H(7,8,9)), 7.04 (m, 6H, H(4,5,6)) 4.23-4.26 (q, 4H, H(3)), 1.13-1.19 (t, 6H, H(2)), 1.01 (d, 1.6H, H(1)).

**% of PPO incorporated:** 4.5% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.1760 dL/g

**GPC:** THF, calibrated for polystyrene

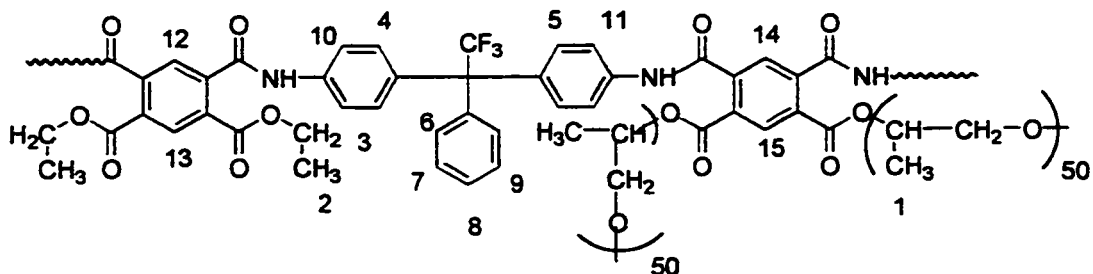
% Area =96.13

Mw (Daltons) =6.362

Polydispersity = 1.6689

**Preparation of 10%-PMDA-(PPO)/meta-PMDA (OEt)/3-FDA Graft Copolymer**

**(16-II)**



In a dry box, in a 15 mL vial PMDA-PPO (**10**) (0.25 g, 0.042 mmol) was dissolved in NMP; meta-PMDA-DEDC (**3**)(1.1255 g, 3.24 mmol) was added and

stirred. Diamine, 3-FDA (**12**), (1.1244 g, 3.284 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.74 mL, 0.73 g, 9.2 mmol) was added last. Amounts of the reagents were calculated for preparation of 2.5 g of the polymer. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove at 50°C to dry. This afforded a dirty-white solid (1.81 g, 72%).

**Analytical data for 16-II**

**<sup>1</sup>H NMR:** (250 MHz, DMSO-d<sub>6</sub>)

8.27 (s, 0.56H, H(13) meta-), 8.09 (s, 0.14H, H(14) meta-), 7.89 (s, 0.16H, H(15) meta-), 7.83 (s, 0.61H, H(12) meta-), 7.70 (d, 3H, H(11,12)), 7.39 (m, 2.5H, H(7,8,9)), 7.04 (m, 4.5H, H(4,5,6)) 4.23-4.26 (q, 4H, H(3)), 1.13-1.19 (t, 6H, H(2)), 1.01 (d, 2.83H, H(1)).

**% of PPO incorporated:** 7.4% ( <sup>1</sup>H NMR)

**Intrinsic viscosity** 0.0967 dL/g

**GPC:** THF, calibrated for polystyrene

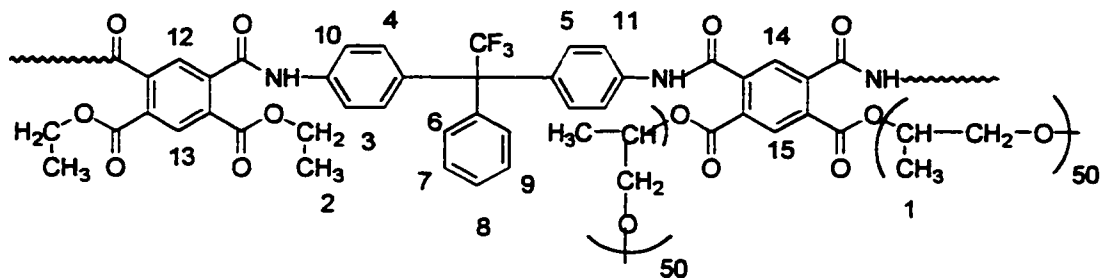
% Area =97.91

Mw (Daltons) =4,824

Polydispersity = 1.4985



**Preparation of 15%-PMDA (PPO)/meta-PMDA (OEt)/3-FDA Graft Copolymer  
(16-III)**



In a dry box, in a 15 mL vial PMDA-PPO-DC (**10**) (0.375 g, 0.0625 mmol) was dissolved in NMP; meta-PMDA-DEDC (**3**) (1.10591 g, 3.051 mmol) was added and stirred. Diamine, 3-FDA (**12**), (1.0659 g, 3.113 mmol) and more NMP were added next; the mixture was shaken vigorously. Pyridine (0.70 mL, 0.68 g, 8.72 mmol) was added last. Amounts of the reagents were calculated for preparation of 2.5 g of the polymer. The mixture was placed on a mechanical stirrer for 12 hours. The polymer solution was precipitated according to the general procedure for polymer preparation and held in the vacuum stove at 50° C to dry. This afforded a dirty-white solid (1.17 g, 50%).

**Analytical data for 16-III**

**<sup>1</sup>H NMR (DMSO-d<sub>6</sub>)**

8.27 (s, 0.85H, H(13) meta-), 8.09 (s, 0.15H, H(14)meta-), 7.89 (s, 0.15H, H(15)meta-), 7.83 (s, 0.85H, H(12)meta-), 7.70 (d, 4H, H(11,12)), 7.39 (m, 3H, H(7,8,9)), 7.04 (m, 6H, H(4,5,6)) 4.23-4.26 (q, 4H, H(3)), 1.13-1.19 (t, 6H, H(2)), 1.01 (d, 2.5H, H(1)).

**% of PPO incorporated: 7.25% ( <sup>1</sup>H NMR)**



8.27 (s, 0.85H, H(13) meta-), 8.09 (s, 0.15H, H(14)meta-), 7.89 (s, 0.15H, H(15)meta-), 7.83 (s, 0.85H, H(12)meta-), 7.70 (d, 4H, H(11,12)), 7.39 (m, 3H, H(7,8,9)), 7.04 (m, 6H, H(4,5,6)) 4.23-4.26 (q, 4H, H(3)), 1.13-1.19 (t, 6H, H(2)), 1.01 (d, 8.1H, H(1)).

% of PPO incorporated: 23% ( <sup>1</sup>H NMR)

Intrinsic viscosity = 0.1056 dL/g

GPC: THF, calibrated for polystyrene

% Area =90.62

Mw (Daltons) =3560

Polydispersity = 1.4571

#### **6.4. Experimental Procedures for Polyimide/PPO Composite Preparation**

##### **Preparation of p-PMDA/4-BDAF Polyimide/PPO Composite 17 (Thick Films)**

Each of the previously prepared polyamic alkyl esters **14** in the form of dry powder (0.3 g) was dissolved in NMP (1 mL) and placed on a mechanical stirrer for overnight. Polymer solutions were cast on the glass slides with the thickness 25. Then slides were placed on the hot plate, equipped with a temperature controller and an argon line. Thermal imidization occurred during 'ramp and soak' temperature program (soak toll was 5° C/min, and the temperature was held for an hour at 80° C, 150° C, 250° C, and 300° C under Ar). Composite **17-I** (p-PMDA-4-BDAF/5% PPO) was obtained as a transparent but cracked film; **17-II** (p-PMDA-4-BDAF/10%PPO) and **17-III** (p-PMDA-4-BDAF/15%PPO-) were opaque and cracked; **17-IV** and **17-V** were transparent

and not cracked. The two last films were firm enough to be sliced off the glass as one piece. After cooling down, one half of each film was scraped from the glass slide for isothermal TGA characterization.

**Analytical data for 17-I**

**TGA: Isothermal, air, 4 hours, 300° C**

**Weight loss = 4%**

**Analytical data for 17-II**

**TGA: Isothermal, air, 4 hours, 300° C**

**Weight loss = 11.1%**

**Analytical data for 17-III**

**TGA: Isothermal, air, 4 hours, 300° C**

**Weight loss = 10.2%**

**Analytical data for 17-IV**

**TGA: Isothermal, air, 4 hours, 300° C**

**Weight loss = 13.8%**

**DSC: Heating rate 10° C/min; Temperature range 30-400° C**

**T<sub>g</sub> = 303.28° C**

**DMTA:**

**T<sub>g1</sub> = -80° C at low temperature**

**T<sub>g2</sub> = 275° C at high temperature**

**Analytical data for 17-V**

**TGA: Isothermal, air, 4 hours, 300° C**

**Weight loss = 27%**

**TGA: Dynamic, air, heating rate 10° C/min, temperature range 30-450° C**

Weight loss = 25.5%

DSC: Heating rate 10° C/min; Temperature range 30-400° C

Tg = 275° C

**Preparation of m-PMDA/4-BDAF Polyimide/PPO Composites 18 (Thick Films)**

Each of the previously prepared polyamic alkyl esters **15** in the form of dry powder (0.3 g) was dissolved in NMP (0.7 mL) and placed on a mechanical stirrer for overnight. Polymer solutions were cast on the glass slides with the thickness 15. Then slides were placed on the hot plate, equipped with a temperature controller and an argon line. Thermal imidization occurred during 'ramp and soak' temperature program (soak toll was 5° C/min, and the temperature was held for an hour at 80° C, 150° C, 250° C, and 300° C under Ar). Composite **18-I** (m-PMDA-4-BDAF/5% PPO) and **18-II** (10%PPO...) were obtained as transparent but cracked films; **18-III** (15%PPO...) were opaque and cracked; **18-IV** was transparent and not cracked. After cooling down, one half of each film was scraped from the glass slide for isothermal TGA characterization.

Analytical data for 18-I

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 3.4%

Analytical data for 18-II

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 9.1%

Analytical data for 18-III

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 13.5%

Analytical data for 18-IV

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 17.5%

DMTA:

Tg<sub>1</sub> = -75° C at low temperature

Tg<sub>2</sub> = 275° C at high temperature

**Preparation of m-PMDA/3-FDA Polyimide/PPO Composites 19 (Thick Films)**

Each of the previously prepared polyamic alkyl esters **16** in the form of dry powder (0.3 g) was dissolved in NMP (0.7 mL) and placed on a mechanical stirrer for overnight. Polymer solutions were cast on the glass slides with the thickness 15. Then slides were placed on the hot plate equipped with a temperature controller and an argon line. Thermal imidization occurred during 'ramp and soak' temperature program (soak toll was 5° C/min, and the temperature was held for an hour at 80° C, 150° C, 250° C, and 300° C under Ar). Composite **19-I** (m-PMDA-3-FDA/5% PPO), **19-II** (10% PPO...) were obtained as opaque, cracked films; **19-III** (15% PPO...) were transparent but cracked; **19-IV** (20% PPO...) was opaque, but had only two cracks.

Analytical data for 19-I

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 5.25%

Analytical data for 19-II

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 9.75%

**Analytical data for 19-III**

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 8.7%

**Analytical data for 19-IV**

TGA: Isothermal, air, 4 hours, 300° C

Weight loss = 20.5%

DSC: Heating rate 10° C/min; Temperature range 30-400° C

Tg = was not obviously seen

**General Procedure for Spinning on Silicon Wafers: Preparation of Polyimide/PPO Composites (Thin Films) (17-19)**

Solutions (20%) of the polyamic alkyl esters **14** were prepared by dissolving 0.1 g of each polymer in the 0.4 g of the solvent mixture of 1:1 cellosolve acetate (2-ethoxyethyl acetate)/DMF and filtering through acrodiscs of 0.2 microns. For polyamic alkyl esters **15** and **16**, 25% solutions were prepared. Several drops of each solution were spun on silicon wafers using two different speeds: 7 minutes at 500 RPM and 5 minutes at 2000 RPM. After spinning, each wafer was placed immediately on the hot plate (80° C) for an hour. Then thin films were heated up to 300° C with temperature ramp 5° C/min in the argon atmosphere. Cured thin films were subjected to refractive index and thickness measurements.

## **6.5. Experimental Procedure for Preparation of Porous Polyimides**

### **General Procedure for Preparation of Porous Polyimides (Thick Films) 20-22**

Cured under Ar thick films on glass (second halves) 17-19 were placed on the hot plate (280° C) under air for 6 hours to burn out PPO. After cooling down, a small piece of each film was used to determine density of the particular polymer (Table 25) using density column (two measurements).

### **Preparation of the Density-Gradient Column**

A density-gradient column was prepared using method of continuous filling with liquid entering the gradient tube becoming progressively less dense. Apparatus was assembled as shown in the Figure 21 using beakers of the same diameter. Water-calcium nitrate with the density range from 1.00 to 1.60 g/cm<sup>3</sup> was chosen as the liquid system for this research. For the gradient tube of 1300 mL, it took 1180 mL of water (liquid A) and 700 mL of saturated solution of Ca(NO<sub>3</sub>)<sub>2</sub> (liquid B). The siphon tube between beaker B and the gradient tube was primed with dense liquid, and the siphon tube between beaker A and beaker B was filled with water. After turning on a high-speed magnetic stirrer in the beaker B, a stopcock between beaker B and gradient tube was open, and the flow was adjusted as very slow speed-5 mL/min., permitting the liquid to flow down the side of the tube. When filling was completed, standard glass



floats in the density range 1.07-1.41 g/cm<sup>3</sup> were placed in the gradient-density column for calibration.

The calibration graph is presented in the Figure 22.

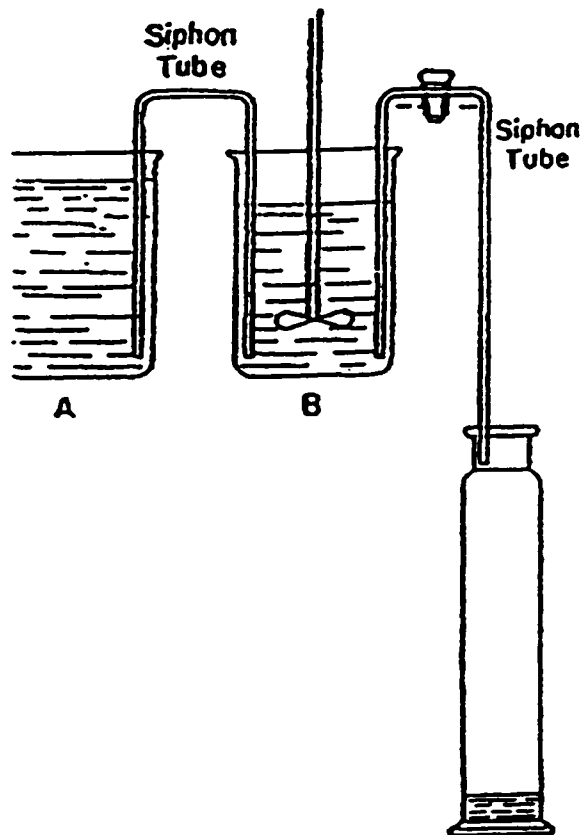
**Table 25.** Density Measurements for Porous Polyimides 20-22.

No. of Polyimide	Composition	Density, g/cm <sup>3</sup>
20-I	5% (PMDA-PPO-DC)-(para-PMDA-DEDC)-4-BDAF	1.40
20-II	10%(PMDA-PPO-DC)-(para-PMDA-DEDC)-4-BDAF	1.36
20-III	15%(PMDA-PPO-DC)-(para-PMDA-DEDC)-4-BDAF	1.34
20-IV	20%(PMDA-PPO-DC)-(para-PMDA-DEDC)-4-BDAF	1.34
20-V	35%(PMDA-PPO-DC)-(para-PMDA-DEDC)-4-BDAF	1.38
21-I	5% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-4-BDAF	1.41
21-II	10% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-4-BDAF	1.27
21-III	15% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-4-BDAF	1.21
21-IV	20% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-4-BDAF	1.14
22-I	5% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-3-FDA	1.34
22-II	10% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-3-FDA	1.21
22-III	15% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-3-FDA	1.23
22-IV	20% (PMDA-PPO-DC)-(meta-PMDA-DEDC)-3-FDA	1.00

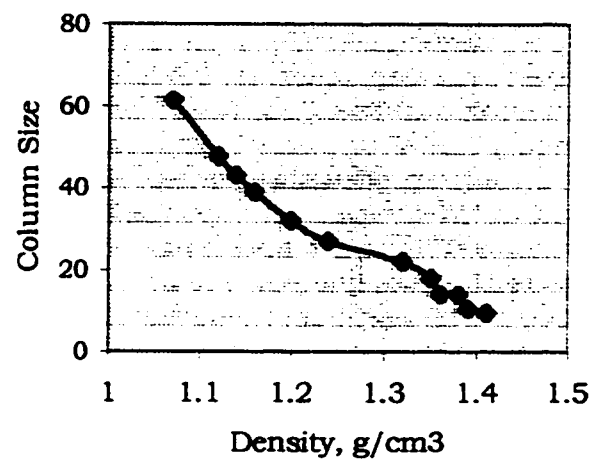
**General Procedure for Preparation of Porous Polyimides (Thin Films) 20-22**

Thin films 17-19, spun and cured on the silicon wafers, were placed on the hot plate under air for an hour at 240° C. The foamed thin films (20-22) were subjected to refractive index measurements using a Metricon model 2010 Prism Coupler.

**Figure 21.** Apparatus for the Gradient Tube Preparation.



**Figure 22.** Calibration of the Density Column



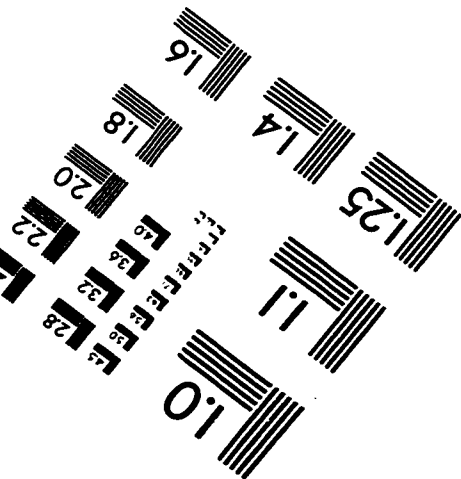
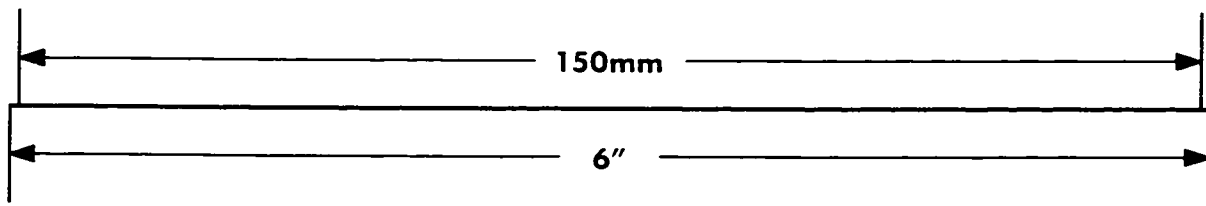
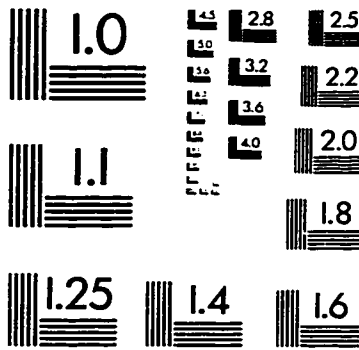
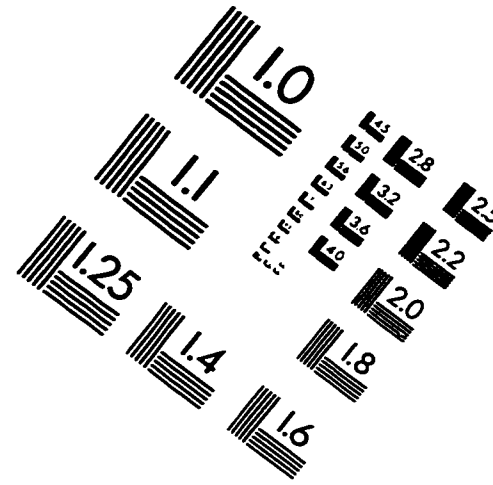
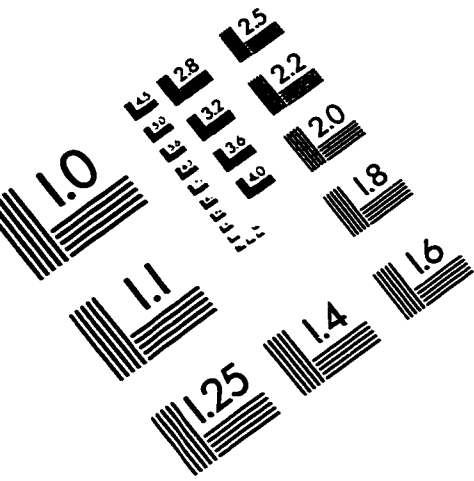
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# IMAGE EVALUATION TEST TARGET (QA-3)



**APPLIED IMAGE, Inc**  
 1653 East Main Street  
 Rochester, NY 14609 USA  
 Phone: 716/482-0300  
 Fax: 716/288-5989

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