

## SYNTHESIS AND PROPERTIES OF POLYIMIDES DERIVED FROM POLY(AMIC ALKYL ESTERS)

Willi Volksen

IBM Research Division, Almaden Research Center  
650 Harry Road, San Jose, CA 95120-6099 USA

**ABSTRACT:** The derivatization of pendant acid groups associated with the amic acid linkage of traditional polyimide precursors in the form of alkyl ester groups offers a unique solution to the hydrolytic instability exhibited by these precursors and offers additional benefits in the form of increased synthetic flexibility, more desirable imidization behavior, and improved mechanical properties. These improvements are a direct result of eliminating the "monomer-polymer" equilibrium associated with poly(amic acids) in solution. Synthetic aspects, precursor solution behavior, as well as ramifications with respect to the preparation of polyimide block copolymers and blends are discussed.

### INTRODUCTION

The utility of high temperature polymers as functional dielectric insulators for microelectronic applications has been recognized for many years as reflected by numerous publications in the scientific literature [1,2]. In this respect, polyimides have emerged as the main class of materials exhibiting many of the desirable properties necessary to realize the successful fabrication of semiconductor devices and high performance packages [3]. In contrast to the excellent properties exhibited by these polyimides, the processable polyimide precursor, i.e. poly(amic acid), possesses several undesirable characteristics, severely limiting the potential utility of this preparative approach. Such undesirable characteristics can be traced to a rather dominant side reaction of the poly(amic acid) [4,5]. As illustrated in Figure 1, of the proposed side reactions, such as imidization (pathway 1), isoimide and diamide formation (pathway 2) and hydrolysis (pathway 3), the most significant side reaction appears to be the amic acid/anhydride-amine equilibrium.

It is the presence of this equilibrium which introduces the hydrolytic instability generally associated with poly(amic acids). Of course, the water necessary for hydrolysis does not necessarily have to come from external sources, but can be generated in situ by side reactions such as isoimide and imide formation. Furthermore, imide formation can lead to physical crosslinking due to the general insolubility

associated with very rigid segments, while isoimide formation followed by diamide formation could eventually lead to chemical crosslinking. Although the former scenario is much more likely, i.e. physical crosslinking, the phenomenon of gellation of relative rigid poly(amic acids) after extended periods of storage at ambient temperatures is a reality. The issue of gellation can be readily prevented by storing the polyimide precursor solutions at low temperatures, which also happens to significantly decrease the equilibrium constant of the amic-acid back reaction and consequently minimizes hydrolytic molecular weight degradation.

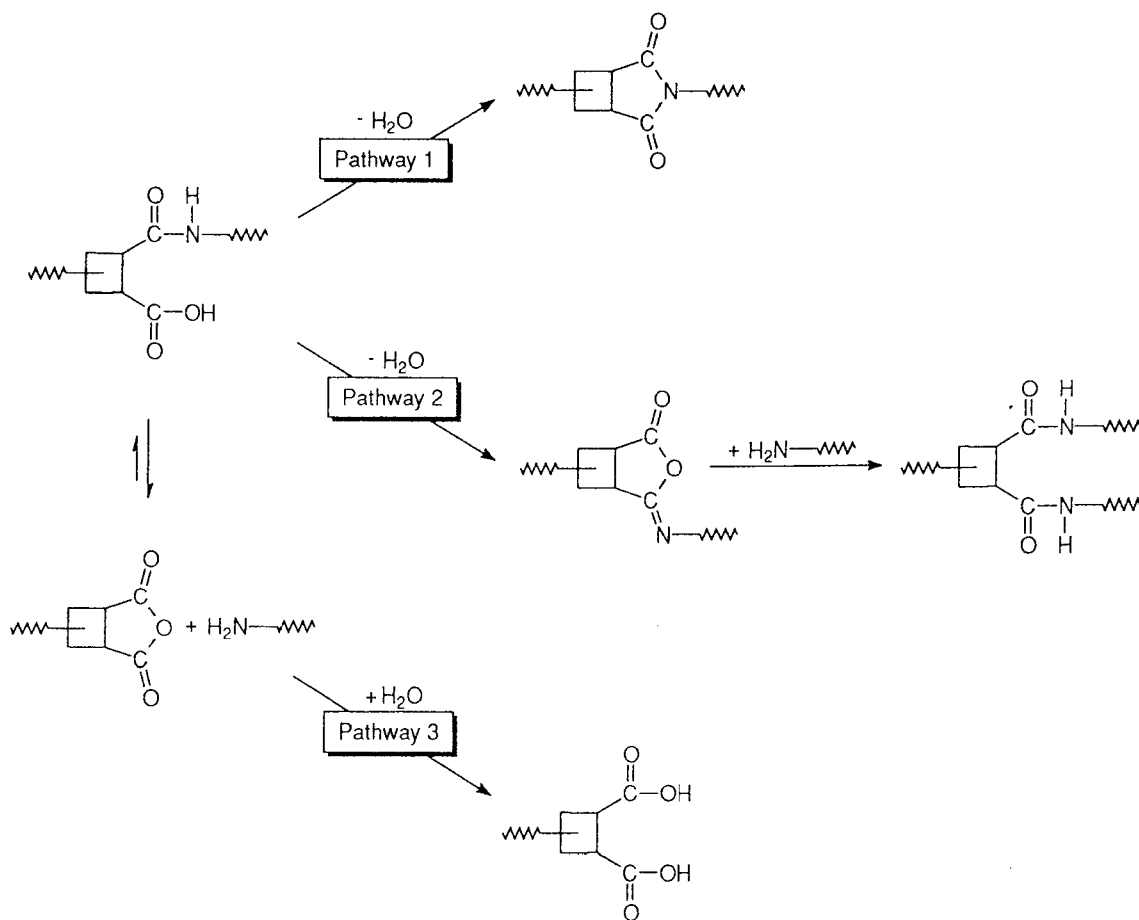


Figure 1. Potential Side-Reactions of Poly(amic acids).

An equally important aspect of poly(amic acid) chemistry is the severe limitation this synthetic approach places on the preparation of block copolymers and polyimide blends. Since such polyimide modifications have to occur in the precursor state, i.e. poly(amic acid), the existence of the "monomer-polymer" equilibrium greatly

complicates the preparation of well-defined segmented block copolymers as well as poly(amic acid) blends. In both cases, the poly(amic acid) back-reaction causes significant scrambling of the monomer sequences, ultimately leading to random block copoly(amic acids). However, elimination of the acidic proton of the pendant carboxylic acid moiety, either in the form of its trialkylammonium salt or derivatized as an ester or amide, prevents the "monomer-polymer" equilibrium and stable polyimide precursors can be prepared [4,6,7]. For this reason poly(amic alkyl esters) allow the design of otherwise inaccessible polyimide systems, such as segmented block copolyimides and polyimide blends, and provided the impetus to investigate these materials further. Although, this description of experimental details and results has been restricted to PMDA/ODA based polyimides, the general concept and polymer behavior can be extrapolated to polyimides based on other dianhydrides and diamines.

## EXPERIMENTAL

### Starting Materials

Pyromellitic dianhydride (PMDA) and p,p'-oxydianiline (ODA) were commercially available materials, which were purified by one sublimation through 30 mesh, neutral alumina to remove colored impurities, followed by a second, neat sublimation to insure absolute dryness. N-methylpyrrolidone (NMP) was vacuum distilled from P<sub>2</sub>O<sub>5</sub> and stored under nitrogen. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone. All other reagents were used as commercially received, preferably in their anhydrous condition if available.

### Dialkyl Dihydrogen Pyromellitates

*Direct Esterification (Procedure A):* PMDA was suspended in a large excess of dry ethanol, freshly distilled from Mg. Typical proportions were ca. 25 gm of dianhydride to 125 mL of alcohol. The reaction mixture was then gradually heated to reflux yielding a homogeneous solution within 30 minutes. Reflux was continued for an additional 3 hours. The excess alcohol was then removed under vacuum on a rotovap at approximately 60 °C resulting in a crystalline mass of product coated to the outside of the reaction flask. At this stage it is desirable to retain a small amount of alcohol in the material to just keep the diester diacid slightly moist. This greatly facilitates removal of the material from the reaction flask. Final drying is achieved under vacuum at 50 °C for 16 hours. In the case of PMDA a quantitative yield of equal amounts of meta- and para-isomer in the mixture is produced.

*Esterification via the triethylammonium salt (Procedure B):* PMDA is suspended in either dichloromethane or ethyl acetate and treated with 2.1 equivalents of the desired alcohol. The reaction mixture is then cooled externally with an ice/water bath and 2.1 equivalents of dry triethylamine are added dropwise. Stirring is continued for 12 hours while allowing the reaction mixture to gradually return to ambient temperature. A homogeneous, yellow solution is obtained upon completion of the reaction. The excess solvent is removed under vacuum on a rotovap and the syrupy residue taken up in water. This solution is slowly added to a dilute, aqueous solution of hydrochloric acid which is cooled internally with ice and kept just slightly on the acidic side. A gummy, white precipitate forms. The mixture is allowed to stand for 30 minutes to facilitate decantation of the acidic water and washing with deionized water. This process is repeated several times. Eventually, the gummy precipitate crumbles and yields a crystalline material which can now be readily filtered. Drying of the material in vacuum at 50 °C for 16 hours provides the desired diester diacid in approximately 80 - 90 % yield with a corresponding isomer ratio slightly higher with respect to the para-isomer.

#### Dialkyl Dihydrogen Pyromellitate Diacyl Chloride

The prerequisite diester diacid is suspended in ethyl acetate and treated with several portions of oxalyl chloride. Several drops of dimethylformamide (DMF) are added over the course of the reaction to accelerate acyl chloride formation. The reaction generally requires overnight stirring to produce a clear solution after which it is heated to approximately 60 °C until gas evolution virtually ceases. The ethyl acetate is removed under vacuum at 50 °C on a rotovap yielding a clear, viscous mass which slowly crystallizes on cooling. In general, purification of the diester diacyl chloride can be achieved by recrystallization from hexane for the meta- or mixed isomers and cyclohexane for the para-isomer. To prevent hydrolysis of the desired diacyl chloride, a small amount of oxalyl chloride is added to the recrystallization solvent prior to dissolving the crude diester diacyl chloride. Recrystallization of the crude product is highly recommended to aid in the removal of DMF salts formed during the acyl chloride formation.

#### Poly(amic alkyl ester) Preparation

A three-necked flask equipped with a mechanical stirrer, liquid addition funnel and nitrogen bubbler was charged with freshly sublimed ODA (2.076 g, 10.37 mmole), dry NMP (ca. 40 mL) and dry pyridine (1.62 g, 20.45 mmole). The mixture was stirred at

ambient temperature until the diamine was completely dissolved. At this stage, the polymerization flask was cooled externally with a methanol/ice mixture until the internal temperature reached approximately 0-5 °C. Now, the diester diacyl chloride (3.456 g, 10.22 mmole) dissolved in dry THF (~ 10 mL) was added gradually so as to maintain an internal temperature of 5-10 °C. Once the diacyl chloride addition was complete, the already viscous polymerization mixture was allowed to return to ambient temperature. Stirring was continued for an additional 3 hours. The polymer was then precipitated by pouring the polymerization mixture into distilled water utilizing a Waring blender to facilitate polymer dispersion. The precipitated polymer was thoroughly washed with distilled water followed by methanol and finally ethyl acetate to promote drying. After vacuum drying at 50 °C for 24 hours, 4.83 g (99%) of the desired poly(amic alkyl ester) was obtained.

#### Measurements

Thermal analysis measurements were obtained on a Perkin-Elmer, Model TGA-7, utilizing a heating rate of 10 °C/min under nitrogen. Sample weights of at least 20 mg were employed.

Measurements of tensile properties were performed on an Instron 1122 at ambient conditions. A gauge length of 2.0 inches and a strain rate of 0.2 mm/min were used.

Dynamic mechanical thermal analyses were obtained from a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) in the tensile mode at a frequency of 10 Hz. All measurements were performed at a heating rate of 10 °C/min in air.

## **RESULTS AND DISCUSSION**

#### Monomer Preparation

The initial step in the preparation of poly(amic alkyl esters) involves the derivatization of the dianhydride in the form of a diester diacid. This diester diacid can then be activated via its acyl chloride to enable the material to enter a polymer forming reaction, generally leading to well-defined polymers. Such diester diacids are readily formed by the reaction of dianhydrides with normal alcohols (direct esterification) as reported by Bell and coworkers [8] or in the case of acidic alcohols, such as trifluoroethanol, via the triethylammonium salt [9] (see Figure 2). Tertiary alkyl esters cannot be prepared by either approach and require the use of the corresponding potassium alkoxides [10].

The latter approach is also applicable to normal alcohols and thus offers a distinct advantage over the direct esterification scheme in cases of high boiling or relatively expensive alcohols. Since only stoichiometric amounts of the alcohol are required, excess alcohol is neither wasted nor presents removal problems. In either case, by carefully drying the reagents, clean isomeric mixtures of the desired diester diacid without significant contamination of mono- or triester are readily obtained in quantitative yield.

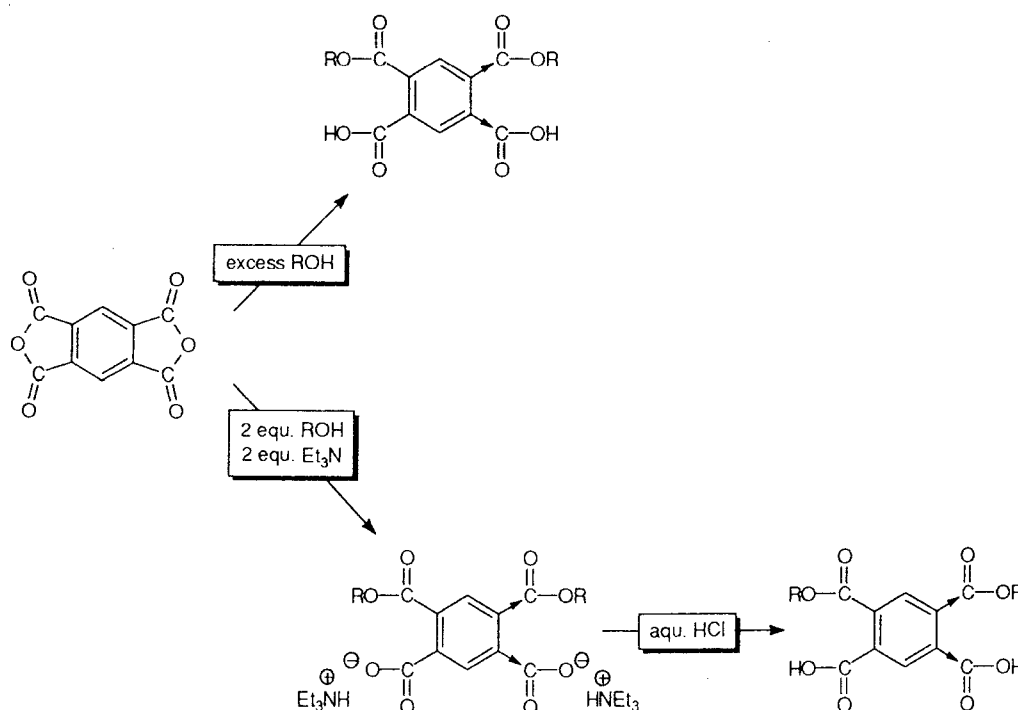


Figure 2. Esterification Routes of Aromatic Dianhydrides.

An additional advantage provided by the direct derivatization of the monomer is presented by the possibility to separate structural isomers prior to polymerization. This, of course, allows the preparation of isomerically pure poly(amic alkyl esters). Separation of the structural isomers is readily achieved in cases of highly symmetrical molecules, such as PMDA based systems, where only two structural isomers are possible. In the case of PMDA derived diesters, the isomer in which the carboxylic acid groups are para-catenated, 2,5-dicarboalkoxyterephthalic acid, represents the less soluble isomer and generally crystallizes from a concentrated solution of the isomer mixture in the alcohol utilized in the direct esterification route [8]. The corresponding

isomer in which the carboxylic acid groups are meta-catenated, 4,6-dicarboalkoxyterephthalic acid, has been prepared by selective extraction of the original isomer mixture [10]. As shown in Table 1, ethyl acetate extraction of the original isomer mixture at a diester diacid concentration of 0.40 g/mL yields almost quantitative separation of the meta-isomer, soluble fraction, from the para-isomer, insoluble fraction. Recrystallization of the respective isomers from butyl acetate increases the isomeric purity to 99%.

Table 1. Ethyl Acetate Extraction Data for Diethyl Dihydrogen Pyromellitate Isomer Mixture.

Diester Diacid Conc. (g/mL)	Soluble Fraction		Insoluble Fraction Yield (wt%)
	Yield (wt%)	<i>meta/para</i> Ratio	
0.15	56.4	89/11	43.6
0.20	53.5	90/10	46.5
0.25	51.6	87.13	48.4
0.30	52.6	91.9	47.4
0.40	50.0	95.5	50.0
0.50	32.8 <sup>a</sup>	-	67.2

<sup>a</sup> Crystallization of the para-isomer occurred

### Polymer Preparation and Properties

As illustrated in Figure 3 and described in detail in the experimental section, poly(amic alkyl esters) were readily prepared via low temperature polycondensation in NMP. Initially, pyridine was employed as an acid scavenger, so as to facilitate the preparation of high molecular weight polymer. Presumably, large amounts of HCl could protonate the diamine monomer and hinder the formation of high molecular weights by temporarily off-setting the initial monomer stoichiometry. This in turn would provide ample time to permit the diacyl chloride moiety to be hydrolyzed by residual water in the solvent or moisture absorbed into the reaction mixture and thus produce dead chain-ends. However, with the discovery that poly(amic alkyl esters) exhibited a pronounced

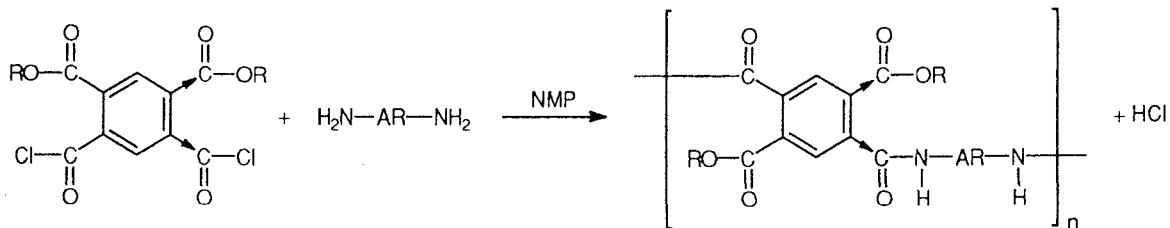


Figure 3. Low Temperature Polycondensation to Prepare Poly(amic alkyl esters).

sensitivity toward base [11], low temperature polycondensations without the benefit of an acid scavenger were also tried. Quite surprisingly, similar viscosity polymerization reactions were observed, yielding well-defined poly(amic alkyl esters). As shown in Figure 4, for low temperature solution polycondensations carried out under similar

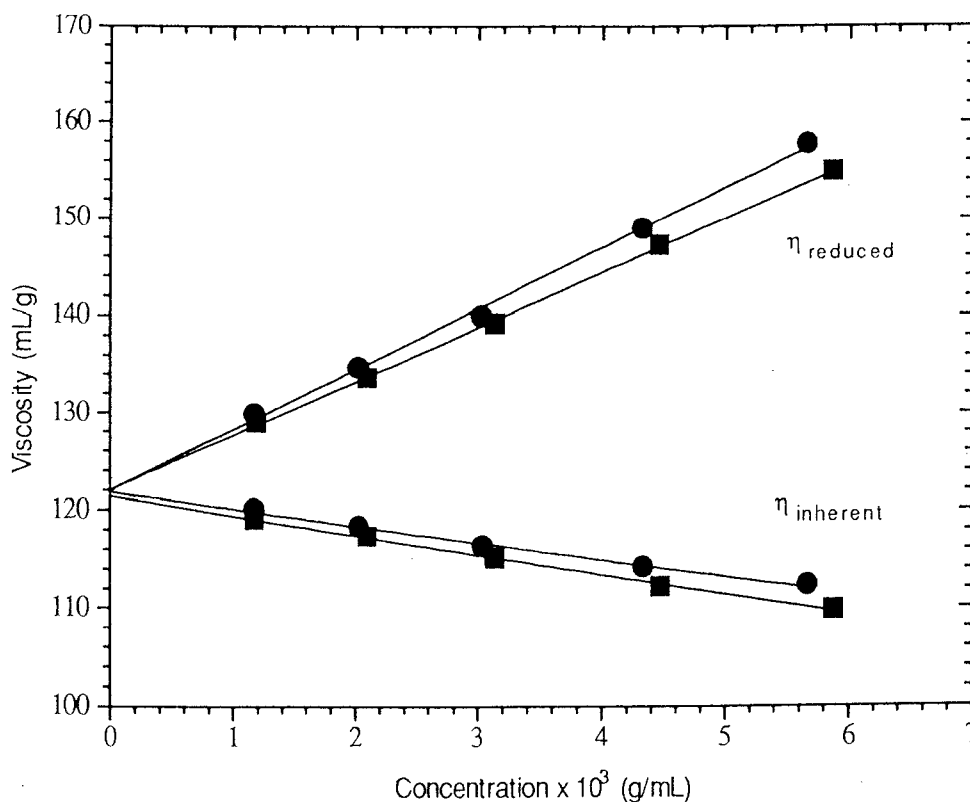


Figure 4. Solution viscosity of para-PMDA poly(amic ethyl ester) in NMP at 27 °C. Effect of acid-scavenger a) ● - with pyridine, b) ■ - without pyridine.

conditions and differing only by the presence or absence of added acid-acceptor, i.e. pyridine, observed molecular weights were virtually identical as evidenced by intrinsic



viscosity determinations. This seems to suggest that the NMP solvent displays enough basic character to effectively act as an acid-scavenger. Thus, although the solvent medium is certainly much weaker in basic character as compared to aromatic amines, the tremendous excess of this material is sufficient to effectively shift the equilibrium of protonated amine groups toward the deprotonated form. The deprotonated amine can now readily react with acyl chloride groups to form the desired amide linkage.

Unlike the corresponding poly(amic acids), poly(amic alkyl esters) can be precipitated after polymerization, and after thorough washing with deionized water and methanol yield materials with low ionic contaminants, i.e. chloride ion. Since these polymers can be isolated in solid form, they exhibit excellent shelf-life and can be reformulated to virtually any concentration desired.

Conversion of the poly(amic alkyl esters) to the corresponding polyimide is generally achieved by thermal curing at elevated temperatures. Whereas poly(amic acids) exhibit maximum imidization rate between 150 - 200 °C, poly(amic alkyl esters) imidize at higher temperatures as shown in Table 2 and consistent with earlier reports [7].

Table 2. Imidization Characteristics of Poly(amic alkyl esters)

Poly(amic alkyl ester)	Temp. of Max. Imidization (°C)	Imidization Temperature Regime (°C)
t-Butyl	193	170-210
Ethylglycolyl	217	190-350
Propargyl	224	200-300
Ethyl	255	240-350
Isopropyl	269	240-290

Interestingly, the imidization temperature of the various poly(amic alkyl esters) inversely tracks the acidity of the parent alcohol, except for the t-butyl ester. This particular polyimide precursor imidizes in a similar temperature regime as the corresponding poly(amic acid), in part due to the fact that the precursor readily splits out isobutene and imidizes as the amic acid [12]. Although not illustrated here, the para-alkyl esters imidize at temperatures slightly lower than the corresponding meta-alkyl esters, presumably due to the preferred conformation of the para-isomer toward thermal imidization [13].

Generally, the higher imidization temperatures of poly(amic alkyl esters) are desirable since solvent evaporation, i.e. polar, aprotic solvents, require temperatures in excess of 200 °C to be completely volatilized. By shifting the evolution of imidization by-products to higher temperatures, internal stress build-up due to shrinkage from both solvent evaporation and imidization by-product volatilization occurring simultaneously is minimized. Higher imidization temperatures may also contribute to formation of closer to equilibrium morphologies, especially in the case of block copolyimides.

One of the most profound effects of preparing polyimides via its poly(amic alkyl ester) precursor manifests itself in the mechanical properties of the corresponding materials. As shown in Figure 5, elongation-at-break, a very useful property in conjunction with the modulus in determining the relative toughness of a material, are

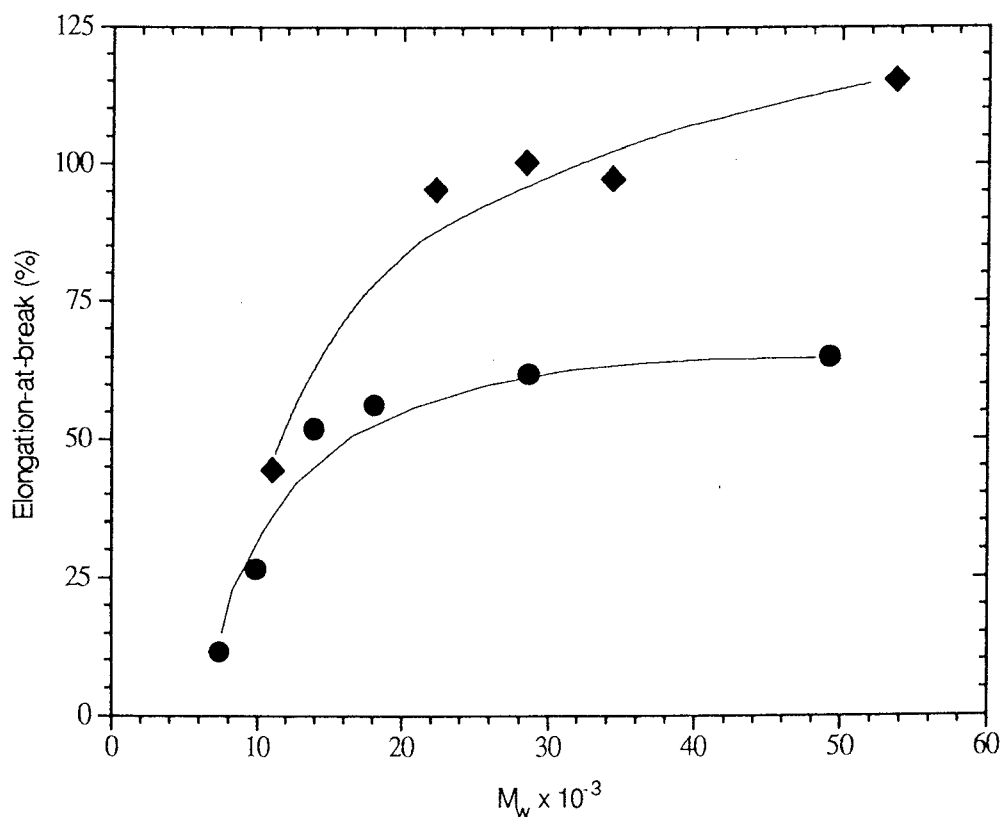


Figure 5. Elongation-at-break versus PMDA/ODA precursor molecular weight for polyimides derived from (●) poly(amic acid) and (◆) poly(amic ethyl ester).

much higher for polyimides derived from the poly(amic alkyl ester) precursor. Thus, the elongation-at-break values are nearly doubled and more in line with PMDA/ODA

polyimide films prepared via chemical imidization of the precursor poly(amic acid) [14]. This suggests that in the case of poly(amic alkyl esters) hydrolytic molecular weight degradation during thermal curing is minimized, consistent with the chemical imidization data. More importantly, these findings could prove of great value for polyimide systems which are brittle in nature. Preparing such polyimides via its poly(amic alkyl ester) precursor could provide the necessary improvements in mechanical properties to make them of greater interest.

#### Base-Catalyzed Imidization of *ortho*-Amide Alkyl Esters

The conversion of poly(amic alkyl esters) to polyimides in the presence of base has only been reported recently [11], although the chemical imidization of these polyimide precursors with acetic anhydride/pyridine has been claimed in the chemical literature [15]. The chemical imidization of poly(amic alkyl esters) is based on the observation that such precursors precipitated upon prolonged standing at ambient temperatures when formulated at low concentrations for size exclusion chromatography [16]. Distillation of the NMP from phosphorus pentoxide to remove low levels of methylamine, a known impurity, eliminated this unusual behavior. In addition, when studying the chemical conversion of poly(amic acids) with N-methyl-p-tolyl triazine to the desired methyl ester, significant levels of the corresponding polyimide were always observed. Of course, p-toluidine is a by-product of the reaction and is present in copious amounts toward the end of the methylation reaction, which requires stoichiometric amounts of reagent. This tendency of producing significant levels of imidization of the poly(amic alkyl ester) could always be traced to the presence of base.

Based on model compound studies [11], indications are that the base-catalyzed imidization process may involve a two-step mechanism as illustrated in Figure 6. The first step corresponds to the partial or complete proton abstraction from the amide group with the formation of an iminolate anion. Since this iminolate anion has two possible tautomers, the reaction can proceed in a split reaction path to either an isoimide or imide-type intermediate. Although model reactions employing isoimide model compounds point toward an extremely fast isomerization to the imide in the presence of base, all indications are that the isoimide itself is not a likely intermediate in the base-catalyzed imidization of amic alkyl esters.

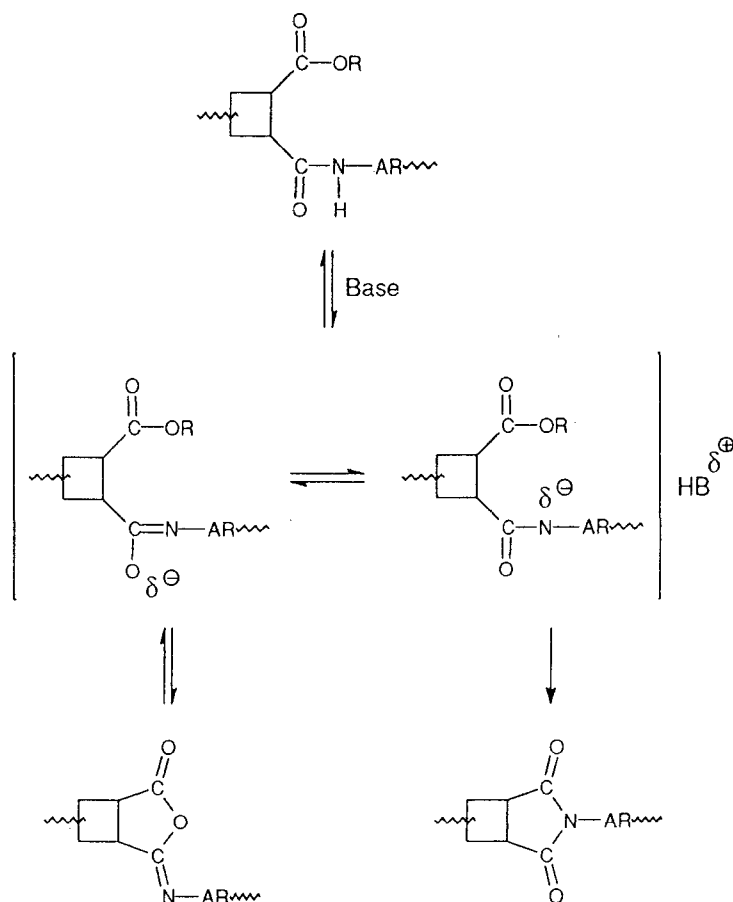


Figure 6. Proposed Mechanism of the Base-Catalyzed Imidization Reaction.

Investigations of base-catalyzed imidization of polymeric systems, in particular PMDA/ODA based poly(amic alkyl esters), have been complicated due to the insolubility of the corresponding polyimide at imidization levels exceeding 40 %. At this stage, it appears that the base-catalyzed polymer imidization reaction is significantly slower at ambient temperatures as compared to the phthalamide model compounds. Most of the initial work was based on IR studies of supported polymer films with the amine catalyst either added to the poly(amic alkyl ester) solution prior to spin-coating or via flooding the polymer film after spin-coating. In either case, relatively low levels of imidization were observed, possibly due to loss of the relatively volatile amines during curing studies at elevated temperatures. Alternatively, a skin-core effect could also explain these results. Since IR measurements determine the bulk imidization level, degrees of imidization at the surface could be quite high. However, if evaporation of the

base was minimized by reapplying the neat amine prior to the post-bake step, respectable levels of imidization could be achieved as illustrated in Table 3.

Table 3. Imidization Levels of PMDA/ODA Based Poly(amic ethyl ester) in the Presence of Diethylamine.

Poly(amic alkyl ester)	Degree of Imidization (%)	
	80 °C	120 °C
PMDA/ODA	80	90
BPDA/ODA	66	80

#### Polyimide Blends and Imide Containing Multiphase Block Copolymers

A very practical and economical way to improve polymer properties is via modification of polymer properties through the use of polymer blends. However, in the case of polyimides, which are generally insoluble in their final, imidized form, blending has to occur in the precursor state. Traditionally, two chemically different poly(amic acids) are combined in solution and then thermally imidized. Unfortunately, such homopoly(amic acids) do not form well-defined molecularly mixed blends. Instead, the "monomer-polymer" equilibrium causes fragmentation of the respective homopoly(amic acids) followed by recombination of different fragments, leading to segmented, blocky copoly(amic acids) and ultimately extensive monomer randomization [17]. As a result, such solution mixtures change with time and ultimately result in polyimide properties which are comparable to a random copolyimide of similar chemical composition as synthesized from the individual monomers [18].

However, if one of the blend components does not display such fragmentation-recombination behavior, i.e. poly(amic alkyl esters), then a stable polymer-polymer blend is possible. By controlling the polymer composition, molecular weight of the components, curing temperature profile and film thickness, transparent polyimide films can be prepared. It turns out that the transparency of such films does not result from true molecular mixing of the components, but rather as a result of microphase-separated domains less than 0.5  $\mu\text{m}$  in size [19]. This multiphase behavior is exhibited by the high temperature dynamic mechanical behavior of a blend derived from *meta*-PMDA/PDA poly(amic ethyl ester) and 6F/BDAF based poly(amic acid). Figure 6 shows

the dynamic storage modulus,  $E'$ , and loss modulus,  $E''$ , of polyimides derived from this blend as a function of temperature and composition. The rigid PMDA/PDA homopolyimide displays only a small decrease in  $E'$  over the entire temperature range up to 500 °C. In contrast, the 6F/BDAF polyimide exhibits a distinct  $T_g$  at approximately 260 °C as indicated by the sharp drop in  $E''$ . All of the mixtures studied, reflect a distinct softening as indicated by a drop in  $E'$  at a temperature associated with the glass transition of the 6F/BDAF component. This constant  $T_g$  suggests almost total exclusion of the two components irrespective of the relative composition.

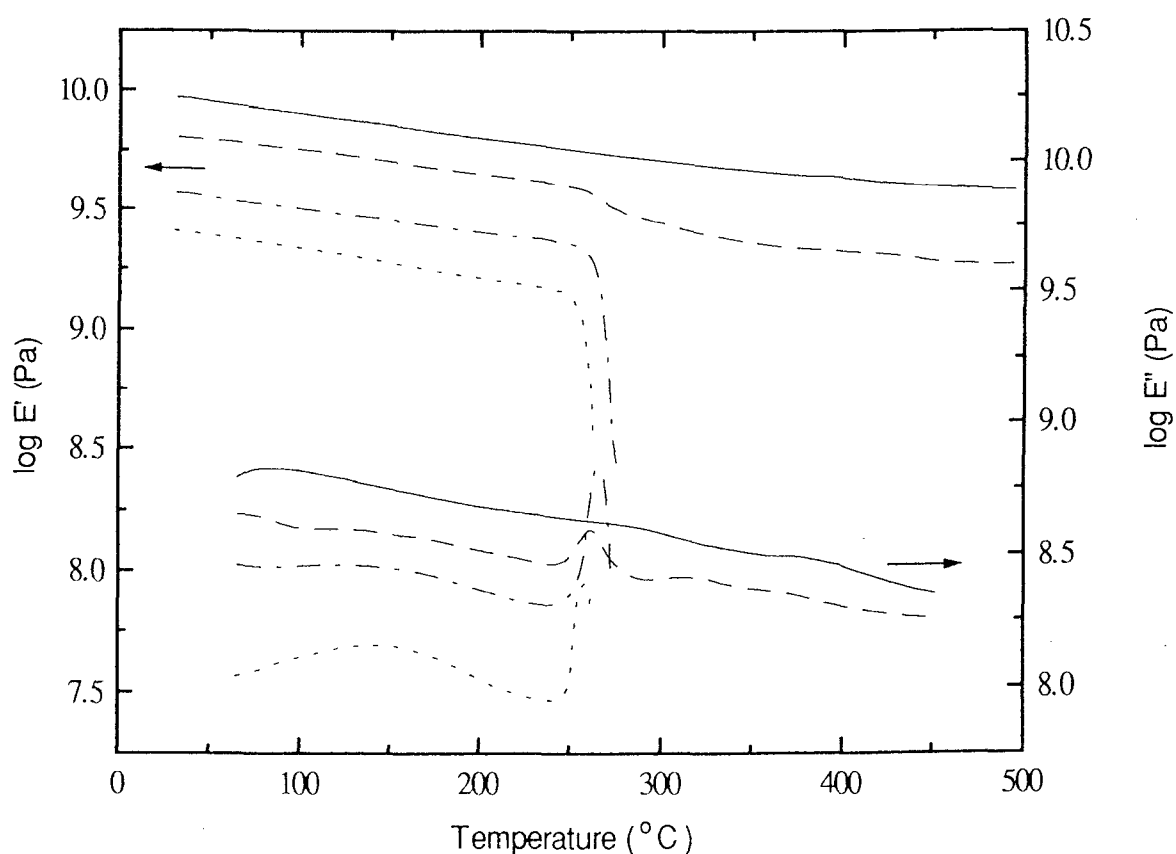


Figure 7. High temperature dynamic mechanical behavior for PMDA/PDA-6f/BDAF polyimide blends of varying compositions as measured at 10 Hz. (—) PMDA/PDA homopolymer, (---) PMDA/PDA-6F/BDAF = 70/30, (-·-) PMDA/PDA-6F/BDAF = 30/70 and (···) 6F/BDAF homopolymer.

Another area in which polyimide precursor chemistry can be advantageously applied is in the preparation of polyimide block copolymers. The use of block copolymers facilitates the design of materials with varying molecular architecture, block lengths, and

composition, giving rise to a wide range of properties and morphologies. With the proper choice of morphology it is then possible to design block copolymers which exhibit the desirable properties of each homopolymer constituent. Case in point, melding the highly desirable self-adhesion of an engineering thermoplastic, e.g. poly(phenylquinoxaline) or poly(aryl ether-sulfone), with the ordered morphology and mechanical properties of a rigid polyimide, allows for improving the interlayer adhesion of traditional polyimides, while maintaining the excellent high temperature, dimensional stability [20,21]. The preparation of such segmented, block copolymers is readily achieved by utilization of the poly(amic alkyl ester) precursor route to polyimides. This route not only allows more synthetic flexibility over the traditional poly(amic acid) route due to its greater solubility in a variety of mixed solvents, but also prevents randomization reactions as already discussed in the case of polyimide blends.

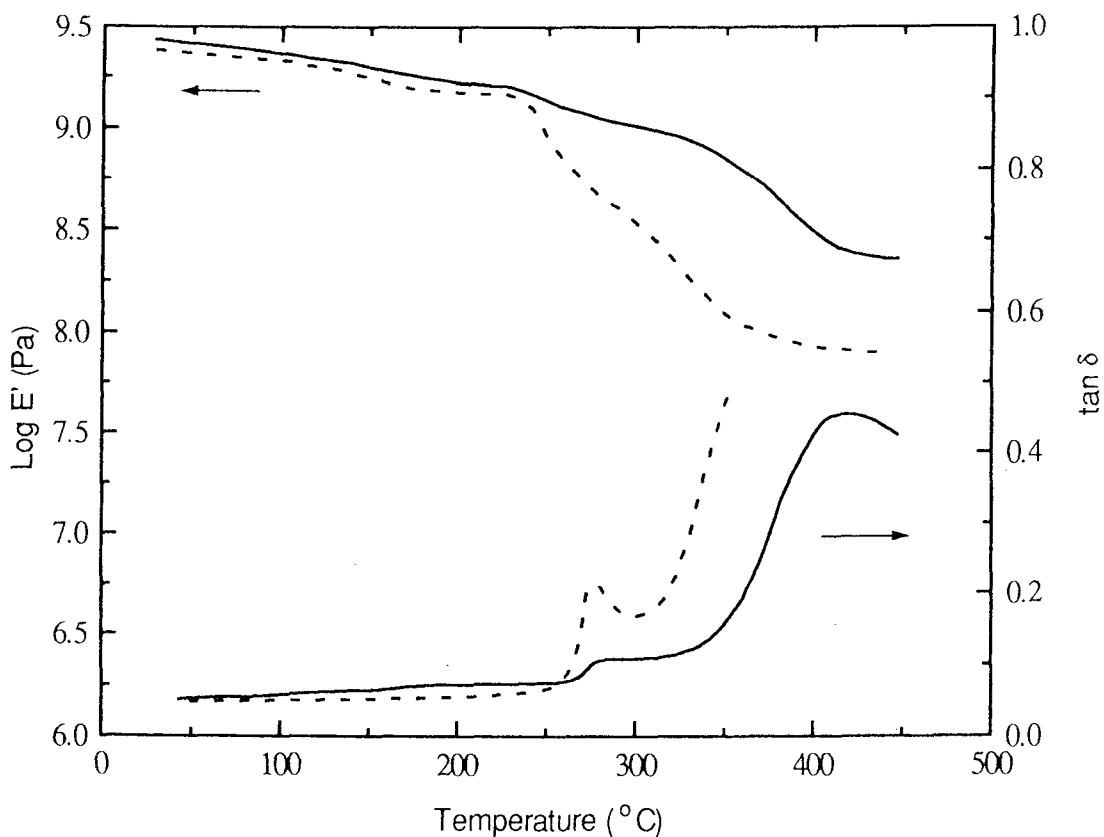


Figure 8. Dynamic mechanical behavior for poly(imide-co-aryl ether phenylquinoxaline) block copolymers as a function of temperature and composition. (—) 16 wt% PQE and (---) 55 wt% PQE. PQE molecular weight = 15,500.

In this fashion, a suitable amine-terminated oligomer, in this case an aryl ether phenylquinoxaline (PQE), is coreacted with a monomeric diamine and a diester diacyl chloride. Since the majority of amine functionalities are initially associated with the monomeric diamine, primarily amic ester segments are formed. As the reaction proceeds to completion, however, these segments are incorporated along with the PQE segments providing the desired poly(amic alkyl ester-co-aryl ether phenylquinoxaline). At this stage the material is precipitated and thoroughly washed to remove any homopolymer contamination. The well-defined copolymer is then formulated and thermally cured to yield the desired poly(imide-co-aryl ether phenylquinoxaline). Salient features of such a system are illustrated in Figure 8, showing the dynamic mechanical behavior of these copolymers as a function of temperature. Two transitions, as reflected by the drop in the storage modulus,  $E'$ , are apparent. The first transition at ca. 250 °C corresponds to the PQE glass transition, while the second transition is at approximately 360 °C is characteristic of the dynamic mechanical spectra of rigid polyimide homopolymers. Again, such behavior demonstrates the phase separated morphology of these copolymers along with retention of the ordered morphology characteristic of the parent polyimide. Obviously, the desirable high temperature properties associated with the polyimide structure have been retained. However, more significantly, self-adhesion of fully cured polyimide layers can be improved to the point where two sequential layers on top of each other are indistinguishable from one another, effectively laminating the layers and precluding any peel measurements.

## CONCLUSIONS

Although poly(amic alkyl esters) have been known for many years, their utility in a variety of potential applications has only recently come to fruition. The ability to utilize poly(amic alkyl esters), which are soluble polyimide precursors devoid of hydrolytic instability, provides for polyimides with enhanced mechanical properties, i.e. particularly elongation, as well as a pathway to isomerically pure polyimide precursors. Such isomeric poly(amic alkyl esters) generally exhibit improved solubility, especially in cases dealing with highly rigid polyimides. The hydrolytic stability and absence of precursor fragmentation reactions permits the preparation of well-defined polyimide blends as well as segmented block copolyimides. Additionally, the improved solubility of these precursors in conjunction with higher imidization temperatures facilitates not only the preparation of such modified polyimides, but also promote the development of near



equilibrium morphologies. Finally, base-catalyzed imidization of poly(amic alkyl esters) may provide a convenient pathway to fully imidized structures at temperatures far below traditional thermal imidization cures. Obviously, such curing would be highly attractive in the case of applications precluding the high temperature excursions necessary to fully imidize high  $T_g$  polyimides. It is also possible to envision photosensitive polyimide schemes using photogenerated bases.

## ACKNOWLEDGEMENTS

The author expresses his gratitude to P.M. Cotts, D. Hofer, R. Giesa, J.L. Hedrick, J.W. Labadie, M. Sanchez, T. Pascal, D.Y. Yoon, M. Ree, and S. Rojstaczer for their contributions to various aspects of this research project.

## REFERENCES

1. C.E. Sroog, *J. Polym. Sci., Macromol. Rev.*, **11**, 161 (1976).
2. A.M. Wilson, *Thin Solid Films*, **83**, 145 (1981).
3. R.R. Tummala, R.W. Keyes, W.D. Grobman and S. Kapur, "Thin-film Packaging", in *Microelectronics Packaging Handbook*, R.R. Tummala and J. Rymaszewski, eds., New York: Van Nostrand-Reinhold, Chapter 9 (1989).
4. R.J.W. Reynolds and J.D. Seddon, *J. Polym. Sci., Part C*, **23**, 45 (1968).
5. D. Fjare, *Macromolecules*, **26(19)**, 5143 (1993).
6. J.A. Kreuz, A.L. Endrey, F.P. Gay and C.E. Sroog, *J. Polym. Sci., A1*, **4**, 2607 (1966).
7. S. Nishizaki and T. Moriwaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **71**, 559 (1968).
8. V.L. Bell and R. A. Jewell, *J. Polym. Sci., A1*, **5**, 3043 (1967).
9. W. Volksen, R. Diller and D.Y. Yoon, Recent Advances in Polyimide Science and Technology, W.D. Weber and M. Gupta, Editors, Mid-Hudson Chapter of Soc. Plast. Eng., Poughkeepsie, New York, 1987, 102.
10. R. Diller, A.F. Arnold, Y.Y. Cheng, P.M. Cotts, M. Khojasteh, E.H. Macy, P.R. Shah and W. Volksen, **US Patent 4,849,501** (1989).
11. W. Volksen, T. Pascal, J. Labadie and M. Sanchez, *Proceed. ACS Division of Polym. Materials: Sci. and Eng.*, **66**, 235 (1992).
12. F.M. Houlihan, B.J. Bachman, C.W. Wilkins and C.A. Pryde, *Macromolecules*, **22**, 4477 (1989).

13. L.A. Laius, M.I. Tsapovetsky, Polyimides: Synthesis, Characterization, and Applications, K.L. Mittal, Ed., Plenum Press, New York, 1984, Volume 1, 295.
14. M.L. Wallach, *J. Polym. Sci., A2*, **6**, 953 (1968).
15. Ye.D. Molodtsova, G.I. Timofeyeva, S.A. Pavlova, Ya.S. Vygorskii, S.V. Vinogradova, V.V. Korshak, *Polym. Sci. USSR*, **A19(2)**, 399 (1977).
16. S.H. Kim and P.M. Cotts, *J. Polym. Sci., Polym. Physics Ed.*, **29**, 109 (1991).
17. P.M. Cotts, W. Volksen, S. Ferline, *J. Polym. Sci., Part B: Polym. Physics*, **30**, 373 (1992).
18. M. Ree, D.Y. Yoon, W. Volksen, *J. Polym. Sci., Part B: Polym. Physics*, **29**, 1203,(1991).
19. S. Rojstaczer, M. Ree, D.Y. Yoon and W. Volksen, *J. Polym. Sci., Part B: Polym. Physics*, **30**, 133 (1992).
20. J. L. Hedrick, J.W. Labadie, T.P. Russell, T. Palmer, *Polymer*, **32**, 950 (1991).
21. J.L. Hedrick, W. Volksen, D.K. Mohanty, *Polymer Bulletin*, **30**, 33 (1993).