Para-Linked Aromatic Poly(amic ethyl ester)s: Precursors to Rodlike Aromatic Polyimides. 1. Synthesis and Imidization Study

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ABSTRACT: The synthesis and characterization of several para-linked aromatic poly(amic ethyl ester)s are described. These substituted polyamides are precursors to rodlike aromatic polyimides. The poly(amic ethyl ester)s are based on 2,5-bis(ethoxycarbonyl)terephthalic acid and several substituted 1,4-diaminobenzene and noncoplanar 4,4′-diaminobiphenylene derivatives. Depending on the degree and type of substitution, the precursors are soluble to high concentrations in solvents such as DMF or NMP without the addition of inorganic salts. In addition to the characterization of the precursor polyamides, a detailed chemical and thermal study of the imidization process is presented, based on dynamic and isothermal TGA measurements and FT-IR spectroscopy investigations.

Introduction

Rodlike aromatic polycondensates, such as thermotropic polyesters, lyotropic polyamides, polybenzoxazoles, polybenzthiazoles, and polyimides, are useful as structural materials with exceptional mechanical and thermal properties. The synthesis and processing of these materials are generally more difficult than for conventional flexible chain polymers due to strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution or melting. There are two basic approaches for overcoming these difficulties.

First, a variety of *structural modifications* to the polymer backbone, such as bulky lateral substituents, flexible alkyl side chains, noncoplanar biphenylene moieties, and kinked and double-kinked comonomers, may be employed to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer chain. The majority of structure–property investigations on rodlike polymers have been on thermotropic aromatic polyesters[1] and lyotropic polyamides[2] and to a smaller extent on aromatic heterocyclic polymers, such as polybenzoxazoles,[3] polybenzthiazoles,[4] and polyimides.[5] Depending on the type and amount of structural modifications, the melting temperatures can be lowered and the solubilities improved, resulting in processable materials. However, these modifications generally affect the materials properties, such as solvent resistance, upper continuous use temperature, temperature stability, and ultimate mechanical properties, of the resultant polymers in a negative way.

Therefore, the second approach, the use of *processable precursor polymers* which subsequently can be converted to intractable rodlike polymers, is an attractive route to obtaining polymeric materials with high-performance properties. For example, poly(*p*-phenyleneterephthalamide), which is normally processed from concentrated sulfuric acid, can be processed as a polyanion precursor in solvents such as DMSO, which opens a wider range of potential applications.[6] Aromatic polyimides are generally prepared via a two-step process involving the synthesis of a processable poly(amic acid) precursor and an intramolecular ring closure to the polyimide. The imidization step is usually carried out in a solid state, thermally induced cyclization reaction. An important improvement over the use of poly(amic acid)s as precursors is the derivatization of the acid side groups in the form of alkyl esters.[7] This derivatization improves the hydrolytic stability and solubility of the precursor polymers and results in more favorable imidization characteristics.

However, investigations into unsubstituted rodlike aromatic polyimides[8] have been rather narrow, because the solubility of the precursor poly(amic acid)s is still relatively low. The chemistry of the poly(amic ester) route is much more suitable for the synthesis of rigid polyimides. It should be pointed out that the intramolecular cyclization from the random coil structures of both the poly(amic acid) and poly(amic ester) precursors which contain meta linkages, to polyimides with rodlike backbones is difficult to realize in the solid state due to the amount of conformational change required during this transformation. Therefore, this paper describes the synthesis, solution behavior, and thermal imidization of novel substituted para-linked aromatic poly(amic ethyl ester)s, which are precursors to rodlike polyimides. The extended conformation of these para-linked aromatic poly(amic ester) precursors should facilitate the conversion to rigid, rodlike polyimides. The poly(amic ester)s were synthesized from 2,5-bis(ethoxycarbonyl)terephthaloyl chloride with various substituted *p*-phenylenediamines and noncoplanar 4,4′-diaminobiphenylene derivatives. The substituted and noncoplanar diamines were selected to further improve the solubility of the poly(amic ester) precursors without significantly reducing their chain rigidity. In addition to the solution properties of the precursor poly(amic ethyl ester)s, a detailed chemical and thermal study of the imidization process is presented.

Results and Discussion

Monomer Synthesis. The most important monomer for this study is 2,5-bis(ethoxycarbonyl)terephthaloyl chloride (**2**). Its synthesis is outlined in Scheme I. The synthetic route was performed in analogy to general schemes outlined by Houlihan et al.,[7d] Volksen et al.,[7c] and Bell et al.[9] Pyromellitic dianhydride (PMDA) is refluxed in excess ethanol to form a mixture of isomers of bis(ethoxycarbonyl)phthalic acid **1a** and **1b**. Isomer **1a**, with the acid groups in para positions to each other is less soluble than the meta isomer **1b**. It can be isolated by a series of extractions in hot ethyl acetate. The purity of the product can be confirmed, for example, through ^{1}H NMR.[10] The meta isomer **1b** has two inequivalent

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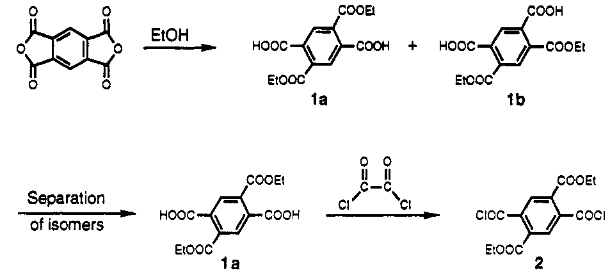
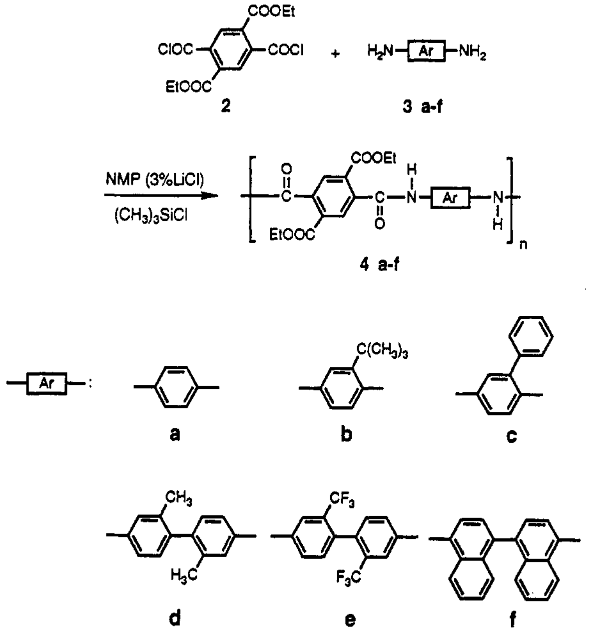
Scheme I
Synthesis of 2,5-Bis(ethoxycarbonyl)terephthaloyl Chloride (2)



Scheme II
Synthesis and Chemical Structures of Para-Linked Aromatic Poly(amic ethyl ester)s 4a–f



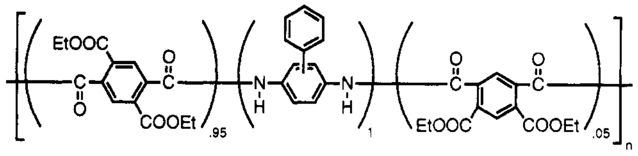
aromatic protons, resulting in two singlets at $\delta = 7.88$ and 8.07 ppm. The para isomer **1a** has two equivalent aromatic protons and shows only one singlet in the aromatic range at $\delta = 7.97$ ppm. The diacid **1a** can be converted to the acid chloride **2** by reacting with an excess of oxalyl chloride in ethyl acetate. The final product is recrystallized from dry hexane or petroleum ether.

The aromatic diamines **3a,b,d** are commercially available. Phenyl-substituted *p*-phenylenediamine (**3c**),[11] the noncoplanar 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (**3e**),[12] and 1,1′-binaphthyl-4,4′-diamine (**3f**),[5f,13] were synthesized according to multistep procedures described in the literature. Before use in the polymerization, all diamines were sublimed or distilled under high vacuum.

Polycondensation. Poly(amic alkyl ester)s are generally synthesized from diacid chlorides and free diamines in low-temperature solution polycondensations with polar aprotic solvents. These are typical conditions for the synthesis of aromatic polyamides. It was recently demonstrated that the synthesis of aromatic polyamides could be improved by the use of the more reactive silylated diamines.[2e,14] In particular, higher molecular weights are obtainable if monomers with bulky substituents are used. In this work, we used in situ formation of silylated diamines via the addition of chlorotrimethylsilane (TMSCl) to the polycondensation of 2,5-bis(ethoxycarbonyl)terephthaloyl chloride with free diamines (Scheme II).

The addition of TMSCl as an activator for the diamine has many advantages over the unactivated reaction. The presence of TMSCl forms the silylated diamine in situ and accelerates the polycondensation reaction, thereby reducing the possibility of potential side reactions. The presence of large substituents in a position ortho to the amine, such as in diamines **3b** and **3c**, which have *tert*-butyl and phenyl groups ortho to the amine, in addition to ester substituents in 2,5 positions on the terephthalic acid chloride derivative, lowers the reactivity significantly. But TMSCl activates the diamine sufficiently to allow the polymerization to proceed. In fact, polymer **4b** was formed only as oligomers in experiments without the addition of TMSCl. Also, since TMSCl is reactive with water, its presence ensures that small amounts of water will not destroy the moisture-sensitive acid chloride. Inherent viscosities of the polymers synthesized in the presence of TMSCl were generally higher than those of the polymers made without activator.

Table I
Influence of the Addition of Chlorotrimethylsilane and Reaction Time on the Inherent Viscosity of Poly(amic ethyl ester) 4c Containing 5% Meta-Linked Diacid Units



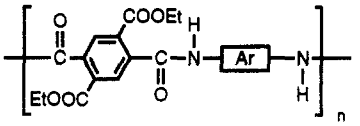
amt of TMSCl[a] (mol %)[b]	reaction time (h)	inherent viscosity[d] (dL/g)
0	1[c]	0.8
0	4	1.0
10	1[c]	1.6
10	4	1.6
50	1[c]	1.4
50	2	1.8
50	3	2.0
50	4	2.0
75	1[c]	1.5
75	4	1.5
100	1[c]	1.7
100	4	1.7

[a] TMSCl: chlorotrimethylsilane. [b] Mol % is relative to the number of amine groups present in the polymerization. [c] Samples taken from reaction mixture after 1 h. All other batches are individual runs. [d] 0.5 g/dL in NMP/LiCl (3% w/v) at 30 °C.

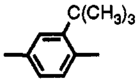
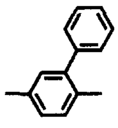
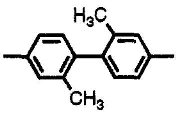
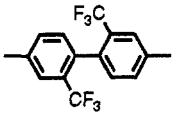
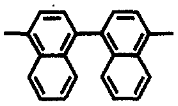
To optimize the polymerization conditions with respect to reaction time and TMSCl concentration, several reactions were carried out with varying amounts of chlorotrimethylsilane and different reaction times. The results are summarized in Table I. Polymer **4c** with the phenylated *p*-phenylenediamine was selected for this study. In these experiments, a mixture of 95% of the para-diacid chloride, 2,5-bis(ethoxycarbonyl)terephthaloyl chloride (**2**), and 5% of the meta-diacid chloride (to ensure solubility) derived from the free acid **1b** was used. The reaction was performed under inert and dry conditions in anhydrous NMP. Dried LiCl was added to further enhance the polymer solubility. All different reactions were carried out with the same batch of acid chloride and diamine under the same general conditions. The polymers were precipitated in water, washed with ethanol, and extracted with acetone. The polymers were dried under vacuum at 60 °C.

Different amounts of TMSCl relative to the number of amine functional groups (0, 10, 50, 75, and 100 mol %) were added. The time for which the polymerization was held at 30 °C was varied from 1 to 4 h. A comparison of the inherent viscosities of the polymers (Table I) made under the different conditions showed that, for this set of monomers, the optimum reaction conditions are at a concentration of 50 mol % TMSCl and a reaction time of 3 h minimum.

Table II
Solution Behavior of Para-Linked Poly(amic ethyl ester)s 4a–f



4 a - f

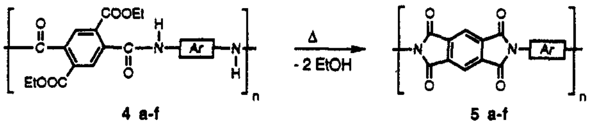
polym	Ar	η_{inh}[a] (dL/g)	NMP/LiCl[c]	NMP	DMAc/LiCl[c]	DMAc	DMF	DMSO
			solubility[b]					
4a		1.31	+ (8%)	–	–	–	–	–
4b		0.71	+ (50%)	+	+	+	+ (28%)	+
4c		0.86	+ (27%)	+	+	+	+ (12%)	+
4d		1.12	+	+	+	+	+	+
4e		1.34	+	+	+	+	+ (26%)	+
4f		1.22	+	+	+	–	–	+[d]

[a] Solubilities given for 5% solution (w/v) at room temperature: (+) stable solution; (–) not completely soluble. Number in parentheses is most concentrated solution prepared. [c] Concentration of LiCl is 3% (w/v). [d] Completely soluble at 80 °C.

These general polycondensation conditions were followed in the synthesis of the all para-linked aromatic (poly(amic ethyl ester)s **4a–f**. Some exceptions with respect to the reaction temperature were made. The unsubstituted poly(amic ethyl ester) **4a** was made at slightly higher temperatures and lower concentrations to prevent precipitation, as the solubility is much lower for this polymer. Polymer **4b** was synthesized at significantly higher temperatures as the bulky *tert*-butyl group ortho to the amine lowers the reactivity of the diamine through steric hindrance. Poly(amic ethyl ester)s with inherent viscosities in the range 0.7–1.4 dL/g were obtained.

Solution Properties of the Poly(amic ethyl ester)s. Table II summarizes the solubility of the poly(amic ethyl ester)s **4a–f** in different organic solvents and their inherent viscosities. The viscosity measurements were taken on 0.5% w/v solutions in NMP/LiCl (3% w/v) at 30 °C. Inherent viscosities taken on the polymer solutions with LiCl added generally read 10–20% lower than if they had been taken without LiCl. It can be seen that the inherent viscosities for the polymers with lateral substituents ortho to the amide groups are lower than for those which are unsubstituted in this position. Although this may be attributed to lower degrees of polymerization in these polymers, it is more likely that these lateral substituents ortho to the amide linkages decrease the chain rigidity in solution. The solvents in which solubility was examined were NMP/LiCl (3% w/v), DMAc/LiCl (3% w/v), NMP, DMAc, DMF, and DMSO. All the polymers were soluble to at least 5% in NMP/LiCl. Polymers **4b–e**, the polymers with lateral substituents and the polymers with noncoplanar biphenylene units, were soluble in all six solvents that were tested, while the unsubstituted polymer **4a** was not soluble even to 1% in any other solvent besides the NMP/LiCl. Polymer 4f with the binaphthyl moiety was only moderately soluble in the solvents with the inorganic salts as well as in NMP and DMSO, while showing extremely low solubility in DMAc and DMF. It is interesting that the three polymers with noncoplanar biphenyl or binaphthyl units **4d–f** show significantly better solubilities than the unsubstituted polymer **4a**, while the inherent viscosities are about the same. Higher concentration solutions were prepared for certain polymer/solvent systems. For example, a solution of polymer **4b** in NMP was prepared at 50% w/w. Polymer **4c** was soluble to 27% w/w in NMP. Polymer **4e** was dissolved up to 26% w/w in DMF. No indication of lyotropic liquid-crystalline behavior was observed for the investigated concentrations. This indicates that the chain stiffness of the polyamide backbone is effected by the type of substitution in the ortho positions of the terephthalic acid unit[2e,15] and by the substitution in ortho position of the diamine unit. For the thermal imidization studies, films of the polymers were cast from 3–5% solutions in DMF (NMP/LiCl for **4a**, NMP for **4f**) and coagulated in isopropanol. Fibers could be spun from more concentrated solutions.

Scheme III
Thermal Imidization of Poly(amic ethyl ester)s 4a–f to Rodlike Aromatic Polyimides 5a–f



Thermal Imidization. The poly(amic ethyl ester) precursors **4a–f** are thermally converted to the imides **5a–f** as illustrated in Scheme III. The thermal imidization process of the poly(amic ethyl ester)s was studied using both TGA and FT-IR spectroscopy.

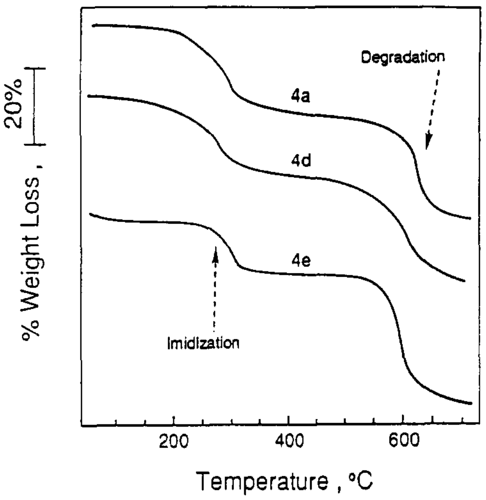


Figure 1. Thermogravimetric analysis (TGA) curves of poly(amic ethyl ester)s **4a**, **4d**, and **4e** (atmosphere, nitrogen; heating rate, 20 °C/min).

Table III
Thermogravimetric Analysis of Poly(amid ethyl ester)s 4a–f (Atmosphere, Nitrogen; Heating rate, 20 °C/min)

polym	imidization onset[a] (°C)	wt loss during imidazation (%)		5% degradation (°C)
		exp	calc[b]	
4a	185	25.2	24.1	585
4b	235	21.1	21.0	510
4c	210	20.9	20.1	560
4d	185	23.5	18.9	570
4e	190	17.7	15.5	570
4f	245	20.9	16.5	570

[a] By Extrapolation of curve back to 0% weight loss. [b] Calculated for loss of 2 ethanol molecules/repeat unit.

Thermogravimetric Analysis. The thermal properties of the polymers were first obtained by TGA. The scans were run from 50 to 750 °C under nitrogen at a heating rate of 20 °C/min. Selected scans for poly(amic ethyl ester)s **4a**, **4d**, and **4e** are shown in Figure 1. All the polymers showed two-step weight losses corresponding to the imidization process and thermal degradation. In the range 200–350 °C, the polymers showed a weight loss between 18 and 25% corresponding to the loss of ethanol during imidization. Table III compares some of the data from the TGA curves with calculated weight losses for imidization. There is a good correlation between the calculated and experimental weight losses, indicating that all the ethanol is driven off and a high degree of imidization is obtainable. Generally a slightly higher amount of weight loss was experimentally observed. This can be explained by the loss of absorbed moisture, but end-group effects and potential chain breakage during imidization might be responsible for this observation. The second step on the TGA curves starts at temperatures above 550 °C (5% weight loss around 570 °C) and corresponds to the thermal degradation of the polyimides. Polymer **4b** with the *tert*-butyl substituent and polymer **4d** with methyl groups on the biphenylene unit show some weight loss beginning at lower temperatures (above 300 °C), which can be attributed to the decreased thermal stability of the aliphatic substituents. The shape of the weight loss curve above 400 °C for polymer **4b** indicates, however, that the *tert*-butyl group may be removed as isobutene in a separate thermal process before degradation of the polyimide backbone. This has the potential to be another route for obtaining the unsubstituted polyimide **5a**.

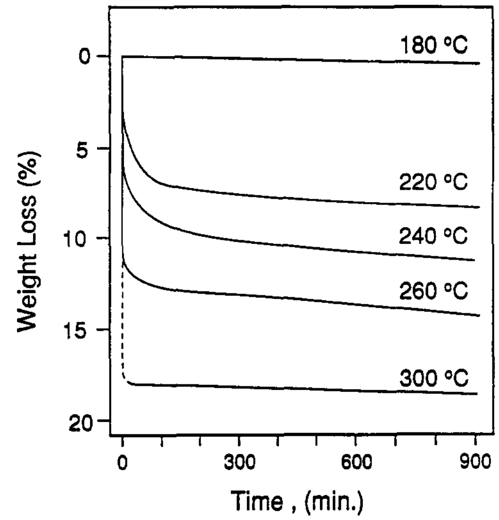


Figure 2. Isothermal gravimetric analysis (ITGA) curves for poly(amic ethyl ester) **4e** under nitrogen at 180, 220, 240, 260, and 300 °C.

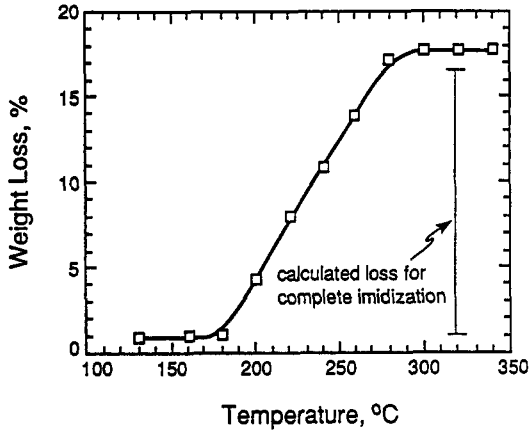


Figure 3. Isothermal TGA data for poly(amic ethyl ester) **4e**. Total weight loss in percent after 900 min ploted as a function of temperature.

To get more information about the kinetic behavior of the imidization, isothermal TGAs were run on the poly(amic ethyl ester)s at temperatures between 130 and 350 °C for 15 h. Figure 2 shows some of the recorded scans for polymer **4e** with trifluoromethyl groups on the noncoplanar biphenylene units. Figure 3 illustrates the observed behavior by showing the total weight loss after 15 h plotted as a function of temperature.

Below 180 °C there is essentially no imidization. At temperatures above 200 °C the shape of each curve looks similar. Most of the weight loss occurs in a relatively short time frame, which shortens with increasing imidization temperature. After this time of rapid imidization, there is not much more weight loss over the remaining time. The degree of imidization correlates with the temperature at which the measurement was done and is incomplete at temperatures below 300 °C. This may have to do with the fact that there is restricted chain mobility, and after all the facile molecular rearrangements have occurred, further imidization becomes difficult. In addition, the glass transition temperatures of the poly(amic ethyl ester) precursors are most likely in this same temperature range and will increase with increasing imidization. It is interesting to note that glass transition temperatures for a variety of similarly substituted para-linked aromatic polyamides were found to be in the range of 220–280 °C.[2e,16] As the temperature is raised above T_g, molecular mobility increases and imidization proceeds. However, as the degree of imidization increases, the glass transition temperature rises and at some point surpasses the isothermal test temperature, at which point further rearrangements

Table IV
Infrared Absorption Spectroscopy Peak Assignments for Selected Key Vibrations of Aromatic Poly(amic ethyl ester)s and Polyimides

	poly(amic ester) vibrations		polyimide vibrations	
peak[a] assignment no.	wavenumber (cm^{-1})	type of vibr	wavenumber (cm^{-1})	type of vibr
1	3301	N–H str (amide)		
2	2988	C–H str (ester)		
3			1777	C=O str (imide I)
4	1716	C=O str (ester)		
5			1716	C=O str (imide II)
6	1661	C=O str (amide I)		
7	1529	N–C–O str (amide II)		

[a] See Figures 4 and 5.

become impossible and further imidization can occur only with some amount of chain cleavage. Indications for chain-cleaving reactions and the formation of new end groups was found by the appearance of anhydride vibrations in the FT-IR spectra, which will be discussed later. This fact illustrates the importance of preorientation in the precursor state. The overall weight loss does not change at higher temperatures between 300 and 350 °C, only the time needed to reach this weight loss is decreased. The maximum weight loss reached at temperatures above 300 °C is about 1% higher than the amount calculated for the loss of two ethanols per repeat unit. The additional weight loss may again be explained by end-group effects of chain-cleaving reactions during imidization. The calculation of the expected weight loss assumes infinite molecular weight and does not take into account the thermal instability of the end groups.

FT-IR Spectroscopy. A temperature-controllable hot stage was made to fit the FT-IR so that scans could be taken at various temperatures and with various heating rates. While heating films of the poly(amic ethyl ester)s with a temperature program (160–350 °C, 5 °C/min), IR scans were taken every 10 °C. In this way, the imidization could be studied by following specific chemical changes.[10,17] Table IV lists some selected IR vibrations for the poly(amic ethyl ester)s as well as for the polyimides in which some change in intensity occurs during the imidization process.

Figures 4 and 5 show some of the FT-IR scans as examples for polymers **4d** and **4e**, the polymers with noncoplanar biphenylene moieties. In these figures, spectrum a shows the poly(amic ethyl ester) precursor at 180 °C, spectrum b shows the partially imidized sample at 270 °C, and spectrum c is of the polyimide taken at 320 °C. The IR spectra of the poly(amic ethyl ester) films show characteristic amide absorptions at approximately 3301 cm^{-1} for the N–H stretch, 1661 cm^{-1} for the amide carbonyl stretch (amide I), and 1529 cm^{-1} for the N–C–O stretch (amide II). As the imidization proceeds, these absorptions decrease in intensity and the characteristic imide absorptions begin to appear, particularly the imide I carbonyl stretch at about 1777 cm^{-1}. A small absorption also begins to develop at about 1855 cm^{-1} (carbonyl stretch of the anhydride structures) formed from acid end groups or chain-cleavage reactions. This anhydride absorption seems to increase early upon heating, reach a maximum around 280–300 °C, and then decrease again slightly. The anhydride formation is believed to be a result of chain cleavage. Its decrease toward the final stages of imidization may be the result of interchain reactions or even slow decomposition. The aliphatic IR absorption from the ester side groups of the precursor polymers (3322 cm^{-1}) disappears as expected with ongoing imidization. The imide II carbonyl stretch and the ethyl ester carbonyl stretch overlap at about 1716 cm^{-1}, so this absorption appears at all stages of the conversion.

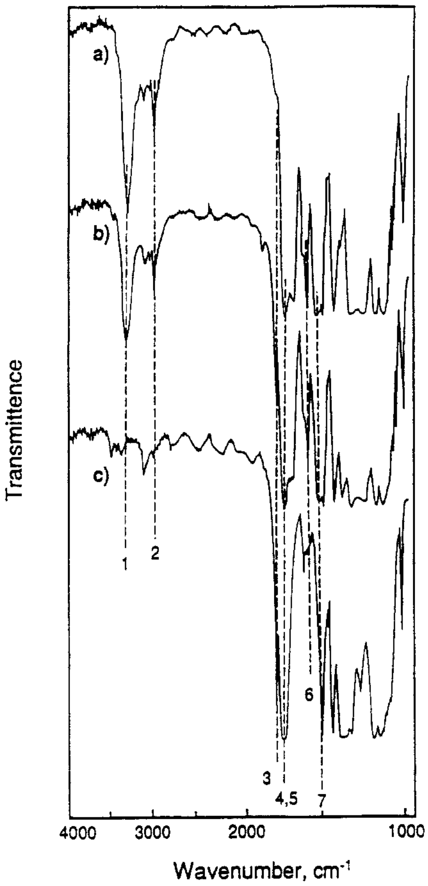


Figure 4. FT-IR spectra during thermal imidization of solution cast film of poly(amic ethyl ester) **4e** (atmosphere, nitrogen; temperature program 180 to 320 °C at 5 °C/min): (a) spectrum of poly(amic ethyl ester) **4e** at 180 °C; (b) spectrum of partially imidized polymer at 270 °C; (c) spectrum of fully imidized sample **5e** at 320 °C (numbers refer to peak assignments from Table IV).

The use of the FT-IR in conjunction with variable temperature scans allows the following of chemical reactions or intramolecular transitions at specific IR active parts of polymers. As a qualitative example, Figures 6 and 7 plot peak height versus temperature for selected key vibrations during the imidization of poly(amic alkyl ester)s **4e** and **4d**. In the imidization reaction, these plots are similar to TGA thermograms. It is interesting that the imide vibrations begin to appear before the amide vibrations really begin to disappear.

Conclusions

In comparison to poly(amic acid)s, para-linked aromatic poly(amic ethyl ester)s have several advantages as precursors to rigid, rodlike aromatic polyimides. The synthesis of aromatic poly(amic ethyl ester)s, which is usually performed under typical aromatic polyamide synthesis conditions, can be improved by the addition of chloro-

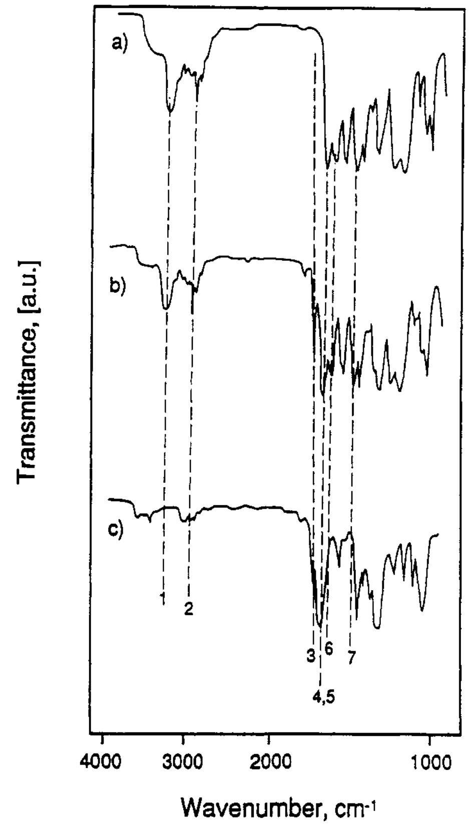


Figure 5. FT-IR spectra during thermal imidization of solution cast film of poly(amic ethyl ester) **4d** (atmosphere: nitrogen, temperature program: 180 to 320 °C at 5 °C/min): (a) spectrum of poly(amic ethyl ester) **4d** at 180 °C; (b) spectrum of partially imidized polymer at 270 °C; (c) spectrum of fully imidized sample **5d** at 320 °C (numbers refer to peak assignments from Table IV).

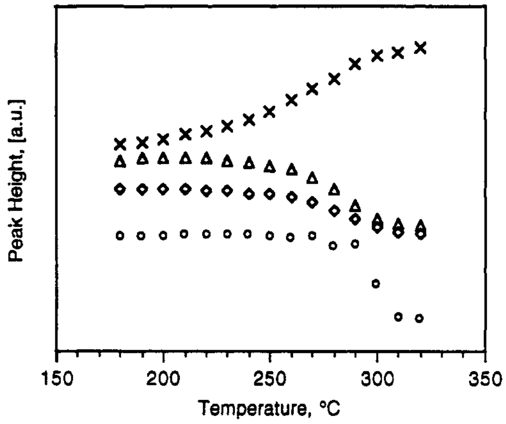


Figure 6. Peak height of selected vibrations versus temperature during thermal imidization of solution cast film of poly(amic ethyl ester) **4e** (atmosphere: nitrogen, heating rate 5 °C/min): (△) N–H stretch (3301 cm^{-1}); (◇) aliphatic C–H stretch, ester (2988 cm^{-1}); (×) imide I (1777 cm^{-1}); (○) amide I (1661 cm^{-1}).

trimethylsilane as activator. Depending on the degree and type of substitution, para-linked aromatic poly(amic ethyl ester)s are soluble to high concentrations in solvents such as DMF or NMP without inorganic salts as additives. The solutions could be processed into films and fibers. Chemical and thermal studies of the imidization process, based on dynamic and isothermal TGA measurements and on FT-IR spectroscopy investigations, show that the imidization process for these materials is controllable and goes to completion. Current work concentrates on a detailed investigation of potential lyotropic behavior, the conversion of oriented para-linked aromatic poly(amic ethyl ester)s to rodlike aromatic polyimides and on physical properties of rodlike aromatic polyimides.

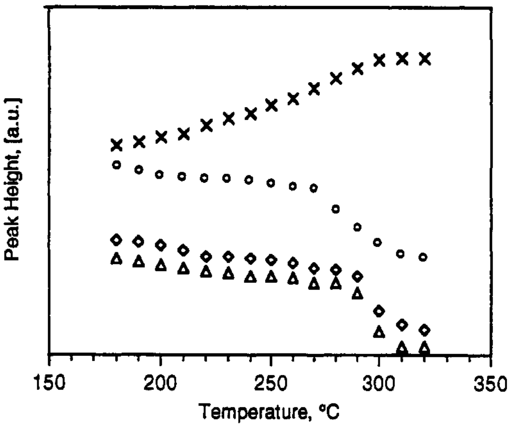


Figure 7. Peak height of selected vibrations versus temperature during thermal imidization of solution cast film of poly(amic ethyl ester) **4d** (atmosphere; nitrogen; heating rate, 5 °C/min): (△) N–H stretch (3301 cm^{-1}); (◇) aliphatic C–H stretch, ester (2988 cm^{-1}); (×) imide I (1777 cm^{-1}); (○) amide I (1661 cm^{-1}).

Experimental Section

Materials. *Solvents.* Anhydrous *N*-methylpyrrolidone (NMP) was obtained from Aldrich. THF was dried by refluxing over potassium under inert atmosphere. Petroleum ether was dried with sodium. Ethanol ($\sim$100%) from Fisher Scientific was dried with CaO$_2$. All other solvents were used as received. *Reagents*: Pyromellitic dianhydride (PMDA, 99.6%) was obtained from Chriskev. Oxalyl chloride (Eastman-Kodak) and chlorotrimethylsilane (TMSCl, Aldrich) were distilled under normal pressure and inert gas. The aromatic diamines **3a,b,d** are available (**3a**, Aldrich; **3b**, Air Products; **3d**, Bayer AG). The other diamines were synthesized according to literature procedures (**3c**, ref 11; **3e**, ref 12; **3f**, refs 5f and 13). Prior to polymerization, all diamines were sublimed or distilled under ultrahigh vacuum and stored in a glovebox.

Monomer Synthesis. The synthesis of the 2,5-diethylbis(ethoxycarbonyl)terephthaloyl chloride (**2**) follows a general synthetic scheme outlined by Houlihan et al.,[7d] Volksen et al.,[7c] and Bell et al.[9] in the literature.

2,5-Bis(ethoxycarbonyl)terephthalic Acid (**1a**). Pyromellitic dianhydride (500 g, 2.3 mol; 99.5+%) was refluxed in 1.5 L of ethanol (100%) until all solids dissolved and then for an additional 2 h. The ethanol was partially evaporated until a solid just began to precipitate (about 50% volume). The solution was cooled to room temperature. The precipitate was filtered and washed with ethanol, leaving a mixture of isomers, about 70% para isomer **1a** and 30% meta isomer **1b**. ^{1}H NMR was used to determine the relative amounts of **1a** and **1b** remaining in the filtrate. Compound **1a** has two equivalent aromatic protons (δ = 7.97 ppm) while the aromatic protons in **1b** are not equivalent and therefore show two different chemical shifts (δ = 7.88 and 8.07 ppm). The separation of the isomers was performed using a 7:3 (by weight) ratio of ethyl acetate:isomer mixture. This heterogenous extraction mixture was heated to 75 °C and filtered hot. This type of extraction was repeated 8–10 times until ^{1}H NMR failed to detect the presence of any meta isomer. The pure para product **1a** was dried under vacuum at 60 °C (mp 201–203 °C).

2,5-Bis(ethoxycarbonyl)terephthaloyl Chloride (**2**). The diacid **1a** (68 g, 0.22 mol) was mixed with 500 mL of ethyl acetate under a light stream of inert gas. The mixture is placed under a light stream of inert gas which is bubbled through a dilute NaOH bath upon leaving the reaction. The flask was cooled in an ice bath, and excess (64 g, 0.51 mol) oxalyl chloride was added dropwise to the stirred reaction mixture. The temperature was raised until gases (HCl, CO$_2$, and CO) began to evolve from the reaction, about 50 °C. The reaction mixture was held at this temperature until all solids dissolved, plus an additional hour. The ethyl acetate and excess oxalyl chloride were distilled off, and the crude product was dried under vacuum at 60 °C. The product was recrystallized three times from dry petroleum ether and carefully dried until TGA showed no weight loss below 120 °C (mp 103–104 °C).

Table V
Polymerization Conditions for Synthesis of Poly(amic ethyl ester)s 4a–f

polym	initial[a] temp (°C)	final[b] temp (°C)	polym concn (% w/v)
4a	25	40	2
4b	0	70	5
4c	0	30	5
4d	0	30	5
4e	0	30	5
4f	0	30	5

[a] Temperature at which monomers are added, stirred for 1 h. [b] Temperature for final polycondensation, stirred for 3 h.

Polymerization. A typical synthesis for aromatic polyamides was used for the poly(amic ethyl ester) polymerizations. All glassware for the polycondensations was dried under vacuum with a heat gun and flushed with argon. The entire polymerization procedure is performed under inert atmosphere and with anhydrous solvents. The polymerization conditions are described in detail for polymer **4c**.

1,4-Diamino-2-phenylbenzene (**3c** 1.98 g, 10.8 mmol) and 3.0 g of dry LiCl were weighed into a three-neck flask. Anhydrous NMP (100 mL) was injected, and the mixture was mechanically stirred until all solids dissolved. The solution was cooled to 0 °C, and chlorotrimethylsilane (1.17 g, 10.8 mmol) was injected. Acid chloride **2** (3.73 g, 10.8 mmol) dissolved in 3 mL of dry THF was rapidly dropped into the diamine solution from an addition funnel, and the funnel was rinsed into the reaction with an additional 2 mL of dry THF. The reaction mixture was stirred for 1 h at 0 °C and then slowly heated to 30 °C for an additional 3 h. The resulting 5% polymer solution was precipitated in 1 L of water, washed twice with 100 mL of ethanol, and extracted with acetone in a Soxhlet extractor for 2 days to remove any remaining NMP, LiCl, monomers, soluble oligomers, and side products. The polymer was dried under vacuum over night at 60 °C. Preparative yields were found to be between 90 and 95%. The conditions used for the other polymers varied slightly, and they are summarized in Table V.

Characterization Methods. Solubilities tests were performed on the poly(amic ethyl ester)s **4a–f** in six different solvents, NMP/LiCl (3% w/v), DMAc/LiCl (3% w/v), NMP, DMAc, DMF, DMSO, using 5% solutions w/v at room temperature. More concentrated solutions were made at 50 °C. Dilute solution viscometry was done using a Lauda automatic viscometer on 0.5 g/dL solutions in NMP/LiCl (3% w/v) at 30 °C. Thermal analysis was done using a Mettler TA 50 (TGA) under nitrogen atmosphere with heating rates between 5 and 20 °C/min. Further thermal imidization studies were done using a Perkin-Elmer 1600 FT-IR. For the dynamic temperature FT-IR experiments, the spectrometer was equipped with a modified Mettler hot stage which was purged with nitrogen. ^{1}H NMR spectra were measured on a 300-MHz NMR in deuterated DMSO for the terephthalic acid derivatives or $CDCl_3$ for the acid chloride.

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Registry No. **1a**, 16927-06-3; (**1b**)(**2**)(**3c**) (copolymer), 143969-54-4; **2**, 6423-33-2; **4a** (SRU), 143969-62-4; **4a** (copolymer), 143969-55-5; **4b** (SRU), 144041-52-1; **4b** (copolymer), 143969-56-6; **4c** (SRU), 144041-51-0; **4c** (copolymer), 143969-57-7; **4d** (SRU), 143969-63-5; **4d** (copolymer), 143969-58-8; **4e** (SRU), 143969-64-6; **4e** (copolymer), 143969-59-9; **4f** (SRU), 143969-65-7; **4f** (copolymer), 143969-60-2; **5d**, 117456-41-4; **5e**, 129219-40-5; $ClSiMe_2$, 75-77-4; EtOH, 64-17-5; pyrromellitic dianhydride, 89-32-7.