# Experimental and Theoretical Study of an Improved Activated Polycondensation Method for Aromatic Polyimides

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ABSTRACT: A novel and facile method for the synthesis of high molecular weight polyimides by low temperature solution polycondensation has been developed. This activated polycondensation method is based on the use in situ of both chloro(trimethyl)silane (CTMS) and a base such as pyridine (Py) as polycondensation promoters. The polymers here described have been prepared by direct polycondensation of 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride with a series of aromatic diamines of different reactivity, to demonstrate the feasibility of this synthetic method in polycondensation reactions. The effect in polyimidation reactions of the individual or combined use of CTMS and Py has been studied. The coupled use of CTMS and Py afforded polyimides having inherent viscosities up to 1.05 $dLg^{-1}$. Moreover, the formation of poly(amic acid silyl ester) took place in a shorter time than the classical reactions of dianhydrides and aromatic diamines. A quantum modeling study (DFT and semiempirical) has shown the influence of silylation on the reactivity of diamines. Also, it has permitted to study the pathways of the reaction, showing the necessity of a base to ensure that the formation of polyamic acid takes place.

## Introduction

The more usual route to the preparation of aromatic polyimides employs low-temperature polycondensation methods (most frequently carried out over a temperature range from −30 to +50 °C in an organic solvent). Polycondensation chemistry has been improved over the years, through the use of activated monomers. The activation of the monomers can be achieved either by activation of the electrophile, mainly using organophosphorous reagents,[1−3] or activation of the nucleophilic diamines. Common methods of activation of the diamines include their silylation[4] or the use of diisocyanates,[5] but very few examples besides these ones refer to the use of other diamine activators.[6]

The first synthesis of aromatic polyimides using silylated diamines was disclosed by Boldebuck and Klebe[7] in the patent literature in 1967. Afterward, in 1983, Korshak and his group reported the synthesis of aliphatic-aromatic polyimides from silylated diamines and aromatic tetracarboxylic dianhydrides.[8] More recently, aromatic polyimides have been also prepared from silylated diamines as showed by Imai and co-workers.[9] The silylation method has successfully been extended to the preparation of other condensation polymers, such as polyamides,[10−12] poly(ether sulfone)s,[13] poly(ether ketone)s,[14] polyesters,[15] or polysulfides.[16]

However, the use of silylated amines is also characterized by a number of disadvantages, such as the need to synthesize and purify activated monomers, which are not possible to obtain in a number of cases due to their sensibility to moisture, and the higher cost respect to the diamines. A key to this problem came with the use of in situ silylated diamines by adding chloro-(trimethyl)silane (CTMS) or other silylating agents to the diamine solutions. The in situ silylation of the diamines was first used as a polycondensation method in the synthesis of wholly aromatic polyamides by Kaneda et al.[17] Although this method avoids the drawback of possible hydrolysis when using silylated diamines as condensation monomers, very few examples relate its use in polyimides synthesis. Becker was the first to apply this method for the synthesis of para-linked aromatic poly(amic ethylester)s from 2,5-bis(ethoxycarbonyl)-terephthaloyl chloride and various diamines.[18] Furthermore, Oishi et al. described the synthesis of alicyclic polyimides by in situ silylation of alicyclic diamines with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide as a silylation agent. They claimed that this reagent is better than CTMS because of the elimination of trifluoroacetamide instead of hydrogen chloride.[19,20] However, no aromatic diamines were essayed in this case.

The in situ silylation shows two additional advantages compared to the use of previously synthesized silylated diamines: the CTMS present in the reaction solution ensures that small amounts of water do not destroy the moisture-sensitive dianhydrides, and moreover, the handling of silylated diamines is avoided and the procedure is much easier.

In previous papers,[21,22] we reported the synthesis of aromatic polyamides by formation of silylated diamines in situ and the role of a tertiary base such as pyridine (Py) as activating agent when added to the silylated diamines.[23] This recently explored activation method has proven to be efficient in the case of sterically hindered amines and amines with strong electron-withdrawing groups, which low reactivity could be improved through silylation.

Therefore, here we report the CTMS/Py-activated polycondensation of five aromatic diamines, with different steric and electronic features and hence with different reactivity, with 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), to form the corresponding polyimides (Scheme 1). They were characterized, and the molecular weight achieved in every case could be related with the diamines reactivity and the effect of polycondensation promoters.

## Experimental Section

**Materials.** Chloro(trimethyl)silane (CTMS), pyridine (Py) and anhydrous N-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich and used as received. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) (**2**), 4,4′-oxidianiline (**1a**), 4,4′-

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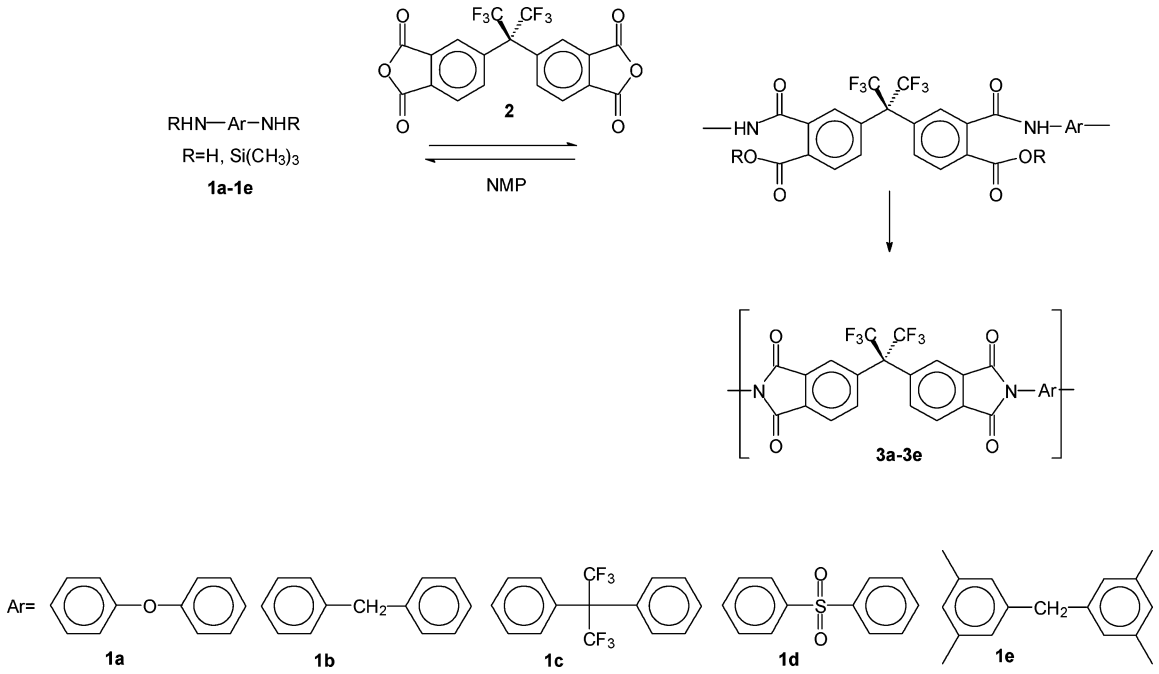
**Scheme 1. Synthesis of Polyimides**




methylenedianiline (**1b**), 4,4′-(hexafluoroisopropylidene)dianiline (**1c**), and 4,4′-methylene-bis(2,6-dimethylaniline) (**1e**) were all purchased from Aldrich, and they were sublimed just before use. 4,4′-Sulfonyldianiline (Merck) (**1d**) was recrystallized from water and dried at 120 °C under vacuum prior to be used.

**Polymers Syntheses.** Four experimental setups were arranged for each diamine/6FDA pair. Each flask, equipped with a mechanical stirrer under nitrogen atmosphere was charged with 3.5 mL of NMP and 5.0 mmol of diamine. Each mixture was stirred at room temperature until all solid had dissolved. Then the solutions were cooled to 0 °C and the required amount of CTMS (10.0 mmol) was slowly added to the second experiment, the necessary amount of CTMS and Py (10.0 mmol of each) was added to the third flask and the needed amount of Py (10.0 mmol) added to the fourth flask. The temperature of the four flasks was raised to room temperature, and the solutions were stirred for 15 min to ensure the formation of the silylated diamine in the appropriate cases. After this time, the solutions were once more cooled to 0 °C, and 6FDA (5.0 mmol) was rapidly added followed by 5 mL of NMP. The reaction mixtures were stirred for 15 min at 0 °C and then the temperature was raised up to room temperature and left overnight. Acetic anhydride (30 mmol) and Py (20 mmol) were then added to promote imidation and the reaction mixtures were stirred at room temperature for 6 h followed by heating for a further hour at 60 °C. Afterward, the flasks were cooled down to room temperature and the resulting polymer solutions were precipitated into 500 mL of water, washed several times with water and extracted in a Soxhlet extractor with ethanol to remove traces of solvent and oligomers. All the polymers were dried overnight under vacuum at 120 °C. Yields over 91% were obtained. Complete imidation (above 95%) was checked by ATR FT-IR.

**Measurements.** Inherent viscosities were measured at 25 °C with an Ubbelohde suspended level viscometer using NMP as solvent for all the polymers. The polymer concentration was 0.5 g/dL in every case.

FT-IR spectra of polyimides were recorded on a Perkin-Elmer RX-1 device, on films of a few micronmeters in width, using an attenuated total reflection accessory (ATR).

**Computational Methods.** Computer simulation was carried out by first drawing the molecules in the desktop of Cerius2[24] and optimizing the structures at the AM1 level of theory.[25] Subsequently, electronic energies and structures were calculated by density functional theory (DFT), without any geometrical constraint, by using the Becke's three parameter hybrid functional[26] and the Lee et al.[27,28] correlation functional with the 6-31G(d) basis set (B3LYP/6-31G(d)). Frequency calculations were performed on all the minimized structures to determine that satisfactory minima were obtained and also to calculate $\Delta H^0$ and $\Delta G^0$ values at 298 K. Semiempirical model calculations, AM1 and PM3, were performed with MOPAC version 6.0.[29] The Gaussian 03 and Gaussian 03W programs packages were used for the DFT calculations throughout this work.[30]

## Results and Discussion

Following previous investigations carried out by us on polycondensation reactions, a complete study on the synthesis of five aromatic polyimides has been carried out by an improved activated polycondensation method. To fully investigate the effect of the activating agents on the ability to obtain high molecular weight polyimides, four sets of reactions were employed: (1) a reaction where no activating agent was used, (2) a reaction where CTMS was used, (3) a reaction where Py was used in addition to CTMS, and (4) a reaction where Py was used.

The synthesis of aromatic polyimides under the above-described reaction conditions, was carried out by reacting the dianhydride 6FDA and the corresponding diamines (**1a**−**1e**) as shown in Scheme 1. First, the diamine was dissolved in NMP followed by addition, when appropriate, of the stoichiometric amount per reactive group of CTMS, Py or both. Finally, the stoichiometric amount of 6FDA was poured into the reaction mixture. To minimize experimental error, flasks of the same size and shape were used for reactions using the same solvent, the same monomers concentration, the same concentration of reaction promoters and under the same stirring, time and temperature conditions. Although the relation between inherent viscosity and molecular weight can only be rigorously taken when the viscosimetric equation is known, we considered that this relation could be reasonably adapted in our case to compare the results for the same type of polymer. With the purpose of generalizing the results for the synthesis of polyimides, five diamines with different chemical and electronic characteristics were used: **1a** with electron-donating groups, **1b** with similar reactivity to that of aniline, **1c** and **1d** with electron-withdrawing

**Table 1. Inherent Viscosity (dL/g) of Polyimides as a Function of the Activating Agents**

| polyimides | $\eta$ (dL/g) | $\eta$ (dL/g) CTMS | $\eta$ (dL/g) CTMS + Py | $\eta$ (dL/g) Py |
|---|---|---|---|---|
| **3a** | 0.68 | 0.47 | 0.96 | 0.44 |
| **3b** | 0.81 | 0.37 | 1.05 | 0.54 |
| **3c** | 0.51 | 0.31 | 0.77 | 0.34 |
| **3d** | 0.27 | 0.21 | 0.29 | 0.16 |
| **3e** | 0.79 | 0.14 | 1.01 | 0.50 |

groups, and in addition **1e**, a diamine presenting steric hindrance due to the methyl substituents ortho to the amino group. The results of the polymerization reactions are summarized in Table 1.

In this work, the experimental and theoretical study has been carried out dealing with the formation of the poly(amic acid) or its silyl ester achieved by reaction of the dianhydride with the corresponding diamine, because this step is the key one in the process of formation of polymers with a certain degree of polymerization. The ulterior cyclodehydration process was experimentally optimized in order to wholly imidize the intermediate to the corresponding polyimide.

**Polymerization under Standard Conditions.** Polycondensations in the absence of any catalyst (Scheme 2, R: H) were relatively rapid, affording colorless poly(amic acid) intermediates. Imidization was completed in a few hours by chemical treatment, giving colorless and viscous polyimide solutions. The obtained polyimides presented inherent viscosities ranging between 0.27 and 0.81 dL/g (Table 1). The lowest viscosity value corresponded to diamine **1d**, with relatively lower reactivity due to electronic effects as it will be commented later.

**Polymerization with CTMS.** Polycondensation of diamines **1a**−**1e** with 6FDA was conducted under silylation conditions described previously by us for polyamides.[21,23] These reactions were slightly slower than the other examples included in this study and afforded polyimides with inherent viscosities ranging between 0.14 and 0.47 dL/g. Contrarily to what had been observed in our previous works with polyamides, the addition of CTMS produced a decrease in the viscosity values with respect to those of polyimides obtained by the conventional polymerization method. These results seem to be a priori in disagreement with the fact that silylation of diamines increases their reactivity as our previous works had shown.[21,23] Quantum mechanical DFT studies (see below) show that silylation increases the electronic density on the nitrogen atom and the energy of the HOMO orbital ($E_{HOMO}$), making it easier for a nucleophilic attack upon the dianhydride to form the amide group. In this way, unreactive diamines, e.g., **1c** and **1d** should be, after silylation, almost as reactive as aniline is. Also, the reactivity of silylated diamines is strongly favored owing to the better ability of the trimethylsilyl group to act as a leaving group.

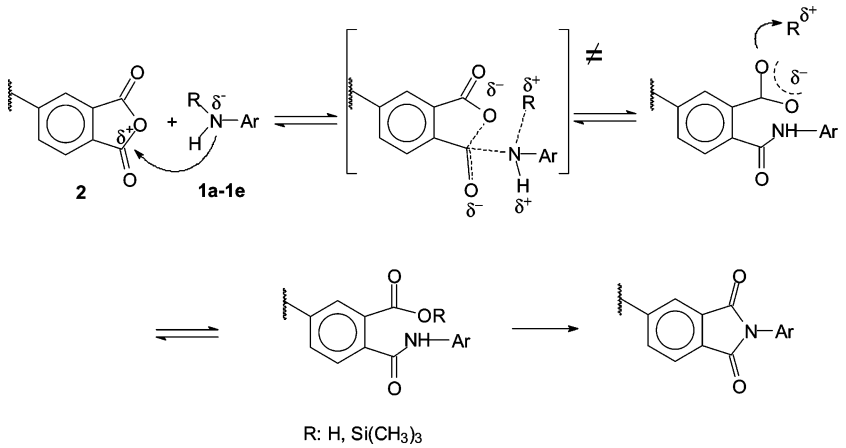
Therefore, the strange behavior found here may be due to the diverse reaction pathway followed by polyamides and polyimides. The reaction pathway yielding the latter ones involves two stages (Scheme 2, R = $Si(CH_3)_3$). First a soluble O-silyl polyamic ester is obtained by nucleophilic attack of the silylated amine to the dianhydride, followed in a second step by subsequent imidization to the desired polyimide. The first step is crucial to attain high molecular weight chains.

Although this step may be facilitated by the use of the more reactive silylated amines, the presence in the reaction media of the hydrochloric acid evolved during the silylation step can lead to depropagation of the polymerization. Protonation of the amino groups by low-molecular-weight products of an acidic nature is known to result in chain termination during low-temperature polycondensation. The protons present in the solution medium, coming from the silylation reaction, interact with the electron rich parts of the transition state moiety, hindering the ability of the TMS group to be released, and hence the reaction is not able to progress to the final O-silyl polyamic ester compound. It should be noted out at this point, that the process of formation of the poly(amic acid silyl ester) is thermodynamically reversible, and small variations in the equilibrium constant could bring about an increase of the reverse reaction rate, and consequently a decrease of the molecular weight of the final polymer.

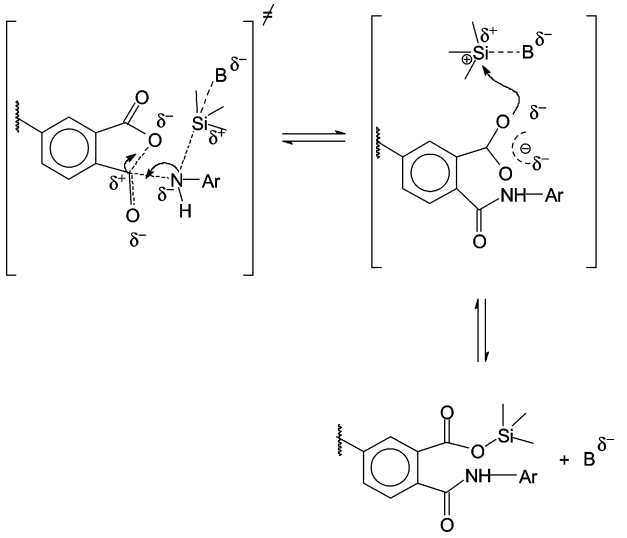
This problem can be avoided by the use of previously synthesized and purified silylated diamines. It is interesting to note that the decrease of the molecular weight seems constant for most of the diamines: **1a**, **1b**, **1c**, and **1e**, independent of their chemical reactivity or structure.

**Polymerization with CTMS and Py.** Polycondensation was conducted as above, under the in situ silylation conditions described previously, in the presence of pyridine as catalyst (Scheme 3). The first part of the reaction prior to the imidization step proceeded faster than in the two previous cases (nonactivated or CTMS-activated reactions) and the apparent viscosity of the reaction solution increased rapidly from the very early stage of the polymerization reaction. These reactions afforded polyimides with inherent viscosities ranging between 0.29 and 1.05 dL/g, indicating that the highest molecular weights have been obtained for all the polyimides under these conditions. These results suggest that the use of CTMS leads to reactive *N*-silylated diamines, as previously observed, and that the presence of Py permits to trap efficiently the HCl present in the reaction media, result of the in situ silylation of diamines,

**Scheme 2. Synthesis of Polyimides under Standard Conditions (R = H) and with CTMS (R = $Si(CH_3)_3$)**



**Scheme 3. Synthesis of Polyimides with CTMS and Py**



and also is able to interact with the trimethylsilyl moiety enhancing the reaction rate, because the electronic interaction on the group increases the length of the Si−N bonds and brings about a higher electronic density on the nitrogen atom, favoring the electronic transfer to the oxygen atoms of the anhydride group and hence helping the opening of this moiety, crucial step in the reaction (transition state in Scheme 3).

Since it is not entirely clear if the role of Py is merely as an HCl acceptor or if it also causes activation of the reactive group, we decided to further investigate the polyimidation reaction using only Py as activator.

**Polymerization with Py.** The reactions in the presence of pyridine were conducted as described above. Under these conditions, polyimides with inherent viscosities ranging between 0.16 and 0.54 dL/g were obtained. These values are lower than those obtained when the reaction proceeded without additives, and similar to the obtained values when only CTMS was used. This result seems to indicate that either a basic or acid media conduces to depropagation reactions and therefore yields low molecular weight polymers.[31]

The low molecular weights obtained are anomalous because it is accepted that a base increases the reaction rate between an anhydride and an amine. However, the results obtained in this paper clearly show that the polymerization degree is much lower than that obtained when an aprotic polar solvent is used without any base.

A preliminary theoretical study seems to indicate that the nitrogen of pyridine, because of its high electronic density, is able to interact with the electron-poor aromatic anhydride moiety increasing its electronic density and consequently lessening its reactivity. Additional theoretical results and a more thorough discussion on this topic will be presented in a future paper.[32]

**Theoretical Study.** A theoretical study of the polyimidation reaction was also carried out. First, the electronic and geometric parameters of 6FDA and the aromatic diamines were calculated both by semiempirical, AM1, and DFT, B3LYP/6-31G(d), methods. Also, and for simplicity sake, phthalic anhydride (PTA), aniline, 4-nitroaniline and 2,6-dimethylaniline were used as models and also for the calculation of the diverse reaction pathways of the imidation reaction, which have been used to justify the reactivity of these monomers.

**Silylation of Aromatic Amines.** The mechanism of amine silylation has not yet been clearly determined, but it is experimentally observed that the presence of a base is necessary

**Table 2. Δ*H* and Δ*G* Values for the Silylation Reaction between Amines and CTMS**

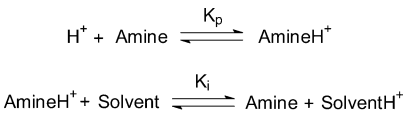
| reaction | Δ*H* (kcal/mol) | Δ*G* (kcal/mol) |
|---|---|---|
| aniline | 15.6 | 17.1 |
| 4-nitroaniline | 15.2 | 16.8 |
| 2,6-dimethylaniline | 20.7 | 22.4 |

**Table 3. HOMO Energy and HOMO−LUMO Energy Gap of Non Silylated and Silylated (in Parenthesis) Diamines**

| compound | $E_{HOMO}$ (eV) | $\Delta E_{gap}$ (eV) |
|---|---|---|
| aniline | −5.39(−5.20) | 2.78(2.59)[a] |
| 4-nitroaniline | −6.25(−6.03) | 3.64(3.42)[a] |
| 2,6-dimethylaniline | −5.24(−5.34) | 2.63(2.73)[a] |
| **1a** | −4.86(−4.69) | 1.75(1.58) |
| **1b** | −5.07(−4.89) | 1.96(1.78) |
| **1c** | −5.51(−5.30) | 2.40(2.19) |
| **1d** | −5.67(−5.46) | 2.56 (2.35) |
| **1e** | −4.92(−5.06) | 1.81(1.95) |

[a] $\Delta E_{gap} = E^{PTA}_{LUMO} - E^{amine\ model}_{HOMO}$, $E^{PTA}_{LUMO} = -2.61$ eV. $\Delta E_{gap} = E^{6FDA}_{LUMO} - E^{diamine}_{HOMO}$, $E^{6FDA}_{LUMO} = -3.11$ eV.

**Scheme 4. Equilibrium Reactions Involved in the Protonation of Amides in the Presence of Aprotic Solvents**



$K_p$: protonation constant.
$K_i$: proton interchange constant.

to obtain silylated diamines whether good yields and high reaction rates are to be achieved. The presence of a tertiary amine acting as a base is so important that the stronger is the base (lower p$K_a$), the faster will be the silylation rate. However, it is necessary to control the basicity of the employed tertiary amine since if its basicity is very high the diamine can be disilylated, becoming less reactive toward electrophilic systems because of steric effects. When the silylation is carried out with no added base, the bases present in the reaction medium are strictly the own aromatic diamine and the reaction solvent, and hence, the reaction rate will depend on the p$K_a$ of these compounds. Thus, in the beginning of the silylation reaction, the amine that is not reacting with CTMS will act as a base, and hence, the theoretical yield of silylation will be 50%. Afterward, the equilibrium between the protonated diamine, that acted as base, and the basic solvent (Scheme 4), even having a much lower basicity, will permit the system to evolve to a higher silylation yield.

In a first stage, a study of silylation was carried out for aniline, 4-nitroaniline and 2,6-dimethylaniline. The study consisted on calculating the enthalpy and Gibbs free energy at 298 K by using the Force keyword in the program Gaussian. The energy implied in the silylation reaction was determined by means of the following equations:

$$\Delta H^{\text{silylation}} = (\Delta H^{\text{SiAm}} + \Delta H^{\text{HCl}}) - (\Delta H^{\text{Am}} + \Delta H^{\text{CTMS}})$$

and

$$\Delta G^{\text{silylation}} = (\Delta G^{\text{SiAm}} + \Delta G^{\text{HCl}}) - (\Delta G^{\text{Am}} + \Delta G^{\text{CTMS}})$$

and the results of these calculations are shown in Table 2.

Speaking on thermodynamic terms, it could be observed that the silylation of aniline and 4-nitroaniline is endoergic in about 17 kcal/mol, with Δ*G* differences for these two molecules lower than 0.3 kcal/mol, whereas the silylation of 2,6-dimethylaniline showed a free energy value 4.5 kcal/mol higher than for aniline

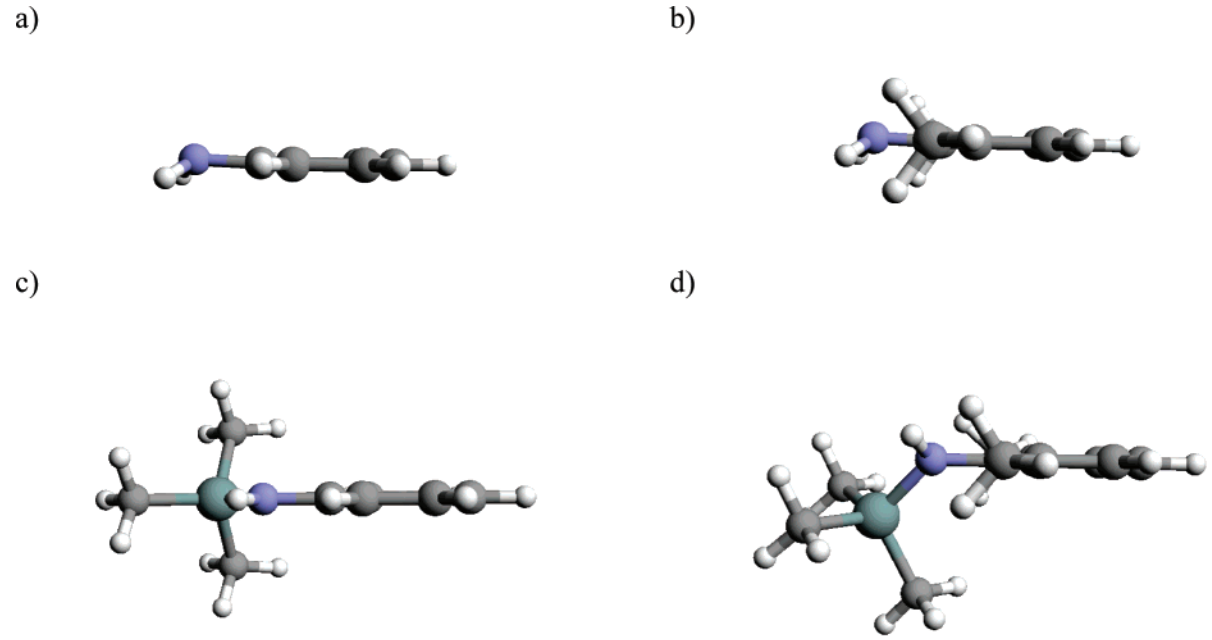



**Figure 1.** Geometries of unsilylated and silylated aniline (a, c) and 2,6-dimethylaniline (b, d).

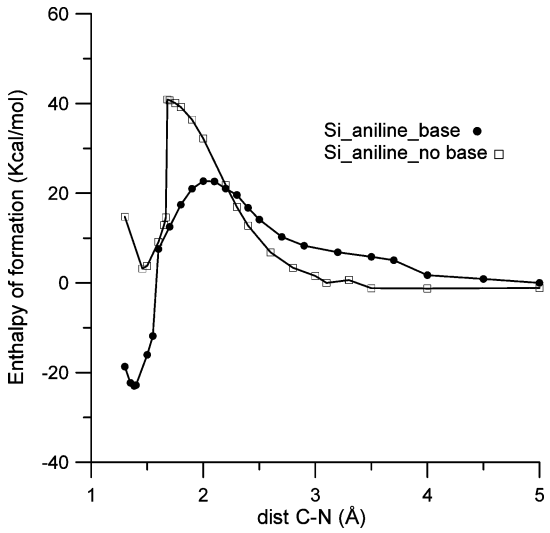



**Figure 2.** Representation of the enthalpy of formation vs the reaction distance, for the reactions of phthalic anhydride with *N*-trimethylsilylaniline in the presence and absence of base.

and 4-nitroaniline. Similar values and tendencies were obtained when enthalpies, $\Delta H$, were considered. Therefore, even though this thermodynamic treatment does not consider steric effects during the reaction process, because only initial and final stages are considered, silylation of amines with two *o*-methyl groups seems to be more unfavored.

**General Electronic Features.** The data obtained for the $E_{HOMO}$ of the silylated and non-silylated diamines and amine models are shown in Table 3. The energy gap between the lowest unoccupied molecular orbital (LUMO) of 6FDA and the highest occupied molecular orbital (HOMO) of the unsilylated diamines ($\Delta E_{gap} = E^{6FDA}_{LUMO} - E^{diamine}_{HOMO}$) ranged from 1.75 eV (**1a**) to 2.56 eV (**1d**). Regarding the models, $\Delta E_{gap} = E^{PTA}_{LUMO} - E^{amine\ model}_{HOMO}$ showed higher values, which ranged from 2.63 to 3.64 eV due to the higher value of $E^{PTA}_{LUMO}$. The silylated amines showed mostly higher values of $E_{HOMO}$ and consequently lower values of $\Delta E_{gap}$, thus indicating a softer behavior in this reaction. In conclusion, if this energy gap is responsible for the chemical reactivity, silylation should decrease the activation energy of the reaction, thus increasing the overall reaction rate. Therefore, this result is consistent with the obtained experimental results where the in situ silylation of the diamine brings about an increase of reactivity and consequently of the molecular weight of the final polymer. However, an exception has to be noted out. Thus, for amines with ortho substitution, **1e** and 2,6-dimethylaniline, the silylated amines showed lower values of $E_{HOMO}$ than the unsilylated ones. This result can be explained by geometrical reasons as discussed below.

**Geometry Characteristics.** As it was commented in a previous paper,[22] several geometrical differences between silylated and unsilylated amines can be observed. To quantify these differences, an amine flip angle can be considered. This angle is defined as the sum of the bond angles at the amino group, $\Sigma$, and gives a measure of the planar or pyramidal nature of this group. Therefore, it can be related with the hybridization type of the nitrogen atom. In this context, this sum is 360° for a $sp^2$ planar geometry and 328.5° for an ideal $sp^3$ pyramidal geometry. These $\Sigma$ values obviously depend on the electronic features of the amines, and thus, amines with electron-donating groups have a behavior much closer to a $sp^3$ geometry while amines with electron-withdrawing groups have an intermediate behavior between $sp^3$ and $sp^2$ geometries, with $\Sigma$ values much closer to 360°. Silylated amines are planar because of the electronic properties of the silicon atom, which forms an extended conjugation of the aromatic ring, the nitrogen atom and the cited silicon atom.

However, the silylation of **1e** and 2,6-dimethylaniline brings about important conformational changes, and thus these ortho-substituted amines have $\Sigma$ values of 352.1 and 352.8°, respectively. Also, and more significant in this case (see Figure 1, where the geometries of aniline and 2,6-dimethylaniline, in unsilylated and silylated forms are represented), the steric hindrance pushes the trimethylsilyl group away from the amino group (the distance N−Si is higher on these systems than on the structures without methyl groups). This lengthening brings about as consequence a more electropositive silicon and hence a higher electronic density of the nitrogen. This combination of geometric parameters, due to the steric interaction between the bulky trimethylsilyl group and the *o*-methyl groups, is

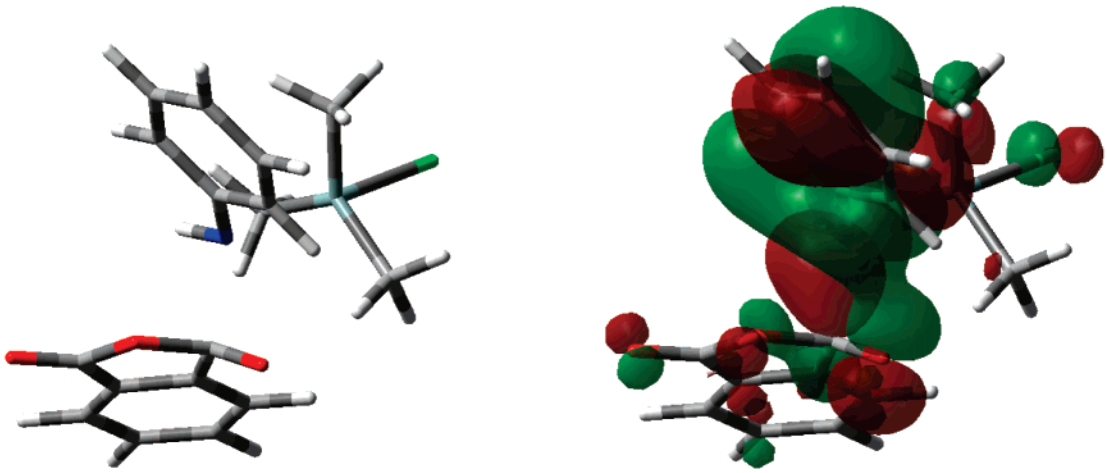


**Figure 3.** Transition state of the reaction between *N*-trimethylsilylaniline and phthalic anhydride. Geometrical picture (left) and geometrical picture including the HOMO (right).

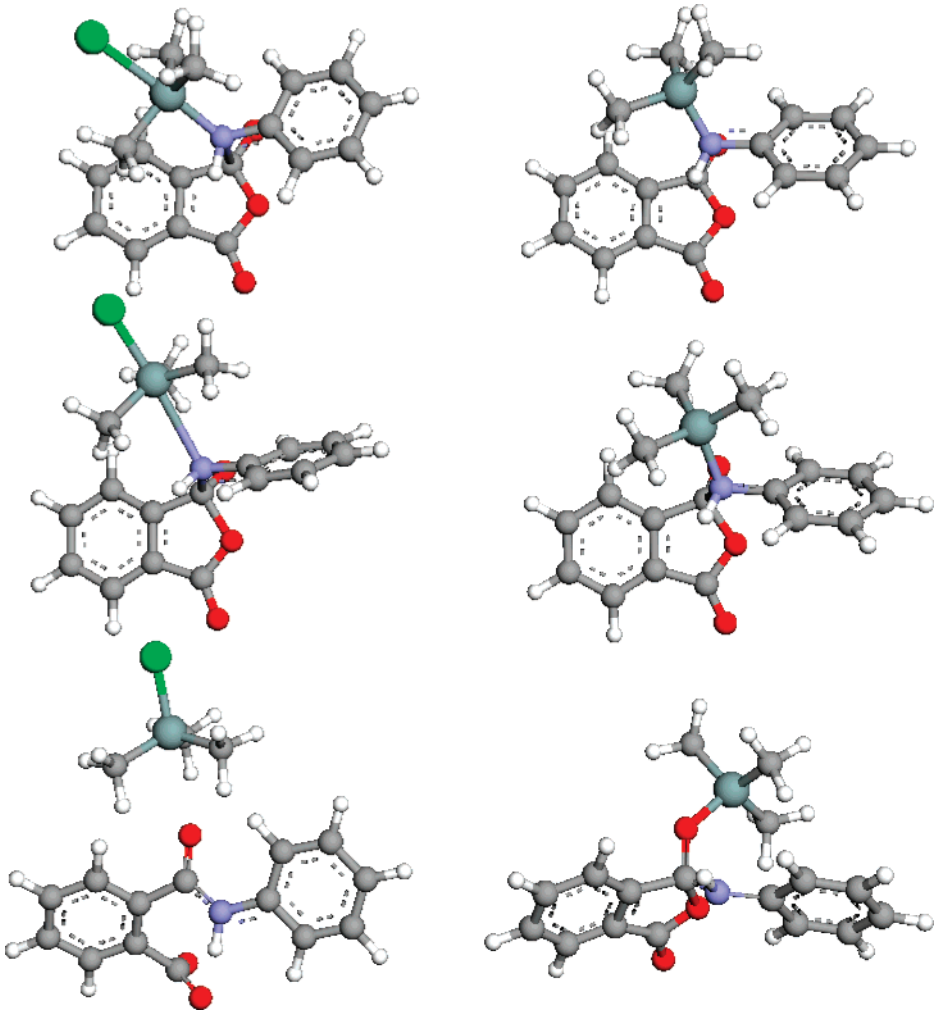


**Figure 4.** Geometrical representation of the initial, maximum enthalpy and final structure for the reaction between *N*-trimethylsilylaniline and phthalic anhydride with base (left) and without any base (right).

responsible for the observed changes in the electronic properties, mainly $E_{HOMO}$, which follow an tendency opposite to that of the other silylated diamines without ortho groups, as discussed above.

However, because of the increased N−Si distance, the feasibility of the silylated amine with *o*-methyl groups to release the trimethylsilyl group is higher, and thus the interaction with a base, a necessary and crucial step for the reaction to be successful as will be discussed below, is favored. In conclusion, the reaction rate should be high enough due to this combination of electronic and steric facts. This agrees congruently with the experimentally obtained results where very good viscosities were observed for the reaction with CTMS and Py.

**Pathways of the Imidation Reaction.** A study of the polyimidation reaction was also carried out to determine the energy profile corresponding to the reaction of silylated and unsilylated amines with anhydrides in the presence or absence of pyridine. To perform the study, phthalic anhydride (PTA)

and both silylated and unsilylated amines were used. The reaction pathways were obtained by placing the molecules at an initial distance where the interaction between them was very low and then systemically decreasing the distance between the nitrogen of the amine and the carbonyl carbon of the anhydride (XHN)−(C═O) (initial distance 5 Å) while allowing the whole system to attain a minimum energy state at every distance.

The first step consisted of simulating the reaction of PTA with Si−aniline in the presence or absence of a base. Chlorine ion was chosen as the base, for computational simplicity. The base was placed near the trimethylsilyl group ($d_{Cl-Si}$ = 3 Å) and the system was allowed to evolve freely. A representation of the enthalpy of formation vs the reaction distance is shown in Figure 2. It can be clearly seen that the presence of base plays a very significant role in the reaction mechanism. When it is present, the pathway evolves smoothly, passing through a maximum that corresponds to the transition state and giving way, after the maximum, to the elimination of a molecule of CTMS. The HOMO of the transition state, depicted in Figure 3, shows that when the trimethylsilyl group is being released, denoted by a higher N−Si distance, an electronic transfer from the nitrogen of the amine to the oxygen atoms of the anhydride (mainly to the hinge oxygen and to the oxygen of the carbonyl group where the amine is interacting) occurs. This electronic reorganization increases the O−(C═O) and C═O distances and is the responsible of the opening of the anhydride. This mechanism is also able to explain the much lower reactivity of diamines with strong electron-withdrawing groups. In this case, the injection of electronic density from the nitrogen instead of being transferred to the hinge oxygen, O, and to the oxygen of the carbonyl group, is also relocated on the electron-withdrawing moiety (sulfone or nitro and in a much less extension on the hexafluoroisopropylidene group), decreasing the probability of successfully opening the anhydride group. In this way, the observed experimental evidence is a lower reactivity and molecular weight.

The opening of the dianhydride ring occurs immediately after the elimination of the trimethylsilyl, giving way to the intermediate amide. Thus, it can be assumed that a crucial step for the progress of the reaction is the extraction of the trimethylsilyl group, which is favored by the base.

However, when there is no base in the system, it evolves in a very different form. The decrease of the reaction distance (XHN)−(C═O) causes a continuous increase of the heat of formation, even when the distance is significantly shorter than the corresponding to the transition state observed in the first case. When the distance is reduced to a value of 1.68 Å, the stress in the system is so high that the trimethylsilyl is eliminated, with a sudden decrease on the enthalpy.

In this case, the oxygen atom of the C═O where the reaction is taking place acts as the base and interacts with the trimethylsilyl (the distance O−Si is 1.81 Å when the reaction distance is 1.46 Å, which corresponds to the structure of lower enthalpy of formation after the elimination of trimethylsilyl). However, because of the lack of base, the opening of the anhydride does not take place, and no amide forms in this case. Moreover, as it can be seen in Figure 2, the reaction in this case is endoergic (the enthalpy at 1.46 Å is higher than the enthalpy at 5 Å).

Consequently, it seems that the presence of a base in the system is necessary to achieve a reasonable transition state with an enthalpy of formation not extremely high and to ensure the extraction of the trimethylsilyl group, the opening of the anhydride and the formation of the amide. According to this, the base acts not only as an acid acceptor but also as a catalyst, significantly reducing the activation energy and ensuring the reaction. A depicting showing the initial, maximum enthalpy and final structures is presented in Figure 4.

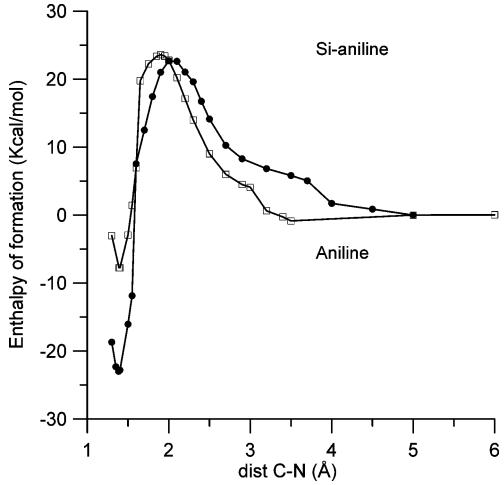



**Figure 5.** Representation of the enthalpy of formation vs the reaction distance for the reactions of phthalic anhydride with silylated and unsilylated aniline.

A comparison of the reaction of PTA with silylated and unsilylated aniline in the presence of a base has also been carried out, and the results are shown in Figure 5. As can be seen, the difference in the enthalpy of both transition states is not very important, the silylated one being slightly more favored.

However, a significant difference can be observed in the enthalpy of formation of the products if a (XHN)−(C═O) distance around 1.4 Å is considered. The products derived from the unsilylated aniline have a much higher enthalpy (∼15 kcal/mol), and consequently, the reaction can reverse more straightforwardly than in the silylated case, where a very high barrier has to be surmounted.

Finally, the reaction paths of Si−aniline and Si−nitroaniline were compared. In this case, both reaction paths were quite similar, but the enthalpy of the transition state was higher for Si−nitroaniline, thus confirming the results obtained from the energy of frontier orbitals.

## Conclusions

The in situ silylation of aromatic diamines with CTMS in the presence of an acid acceptor such as Py has proved to be a facile and convenient method to obtain high molecular weight polyimides. The silylation of amines increases their nucleophilicity making it easier for a nucleophilic attack of the silylated amine to the carbonyl group to form the intermediate poly(amic acid silyl ester). The use of a tertiary base, such as Py, together with CTMS, has an active role in the progress of the reaction, acting as an acid acceptor and favoring the elimination of the trimethylsilyl moiety, which seems to be a controlling step in the reaction. In addition, the polymerization reaction proceeds at high rate and the apparent viscosity of the reaction mixture increases rapidly from the very early stage of the reaction. From the study here described, it can be concluded that when the polymerization, in the context of poly(amic acid silyl ester) formation, is carried out using only Py or CTMS as activating reagents, the depropagation, or reverse, reactions are favored, and low molecular weight polyimides are obtained. In reactions with hindered diamines, the use of Py in addition to CTMS also led to a significant increase on the viscosity values and high molecular weight polyimides were obtained. In conclusion,

this new combination of in situ amine silylation with a tertiary base is able to give polyimides with molecular weights much higher than those obtained using conventional polycondensation methods, by means of a very easy and workable synthetic process.

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(31) It is well-known that the outstanding solubility of polyimide **3c** is due to the presence of two hexafluoroisopropylidene groups within its structure. This polyimide, widely employed in diverse advanced applications, is highly soluble in a range of solvents, NMP, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, *m*-cresol, and acetone and even in pyridine. Owing to this high solubility, two reactions of **1c** with 6FDA were accomplished using neat pyridine as solvent in order to clarify the role of pyridine in these reactions. The first one did not employ CTMS and the second did. The obtained results were very interesting because the use of the silylating agent rendered a polyimide with an inherent viscosity of 0.75 dL/g while the reaction without CMTS gave a very low molecular weight polymer with a viscosity of 0.18 dL/g.
(32) These experimental results along with a study of the effect of several bases, having different p$K_a$'s, in the synthesis of **6FDA−6FpDA** is being performed, and this study will be published shortly elsewhere.

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