Synthesis of Aromatic Polyisophthalamides by *in Situ* Silylation of Aromatic Diamines[†]

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Introduction

Wholly aromatic polyamides are thermally stable polymers, with high molecular rigidity and high transition temperatures. Therefore, these polymers cannot be prepared in the molten state and are synthesized by solution condensation methods in polar organic solvents, usually from diamines and very reactive species such as diacyl chlorides.

Aromatic diamines are less basic and less nucleophilic than aliphatic diamines, and therefore, their reactivities are very low in some cases, mainly when there are electron-withdrawing groups connected to the phenyl rings.

In 1983, Bowser and co-workers showed that aliphatic amides could be prepared in excellent yields from silylated amines and acid chlorides.[1]

In the field of polymer chemistry, the use of silylated amines became important with the synthesis of aromatic polyamic acids and polyimides by Korshak[2] and the synthesis of aromatic polyamides and polyimides by Imai and co-workers.[3−6]

In spite of the advantages of this reaction,[3] the main drawback of using silylated diamines as condensation monomers is their great ability to hydrolize, which hinders the isolation and purification of these monomers. Therefore, we have considered the formation of silylated diamines *in situ* by adding trimethylchlorosilane (TMSCl) to the diamine solutions that, after the addition of a diacid chloride, give the polyamides.

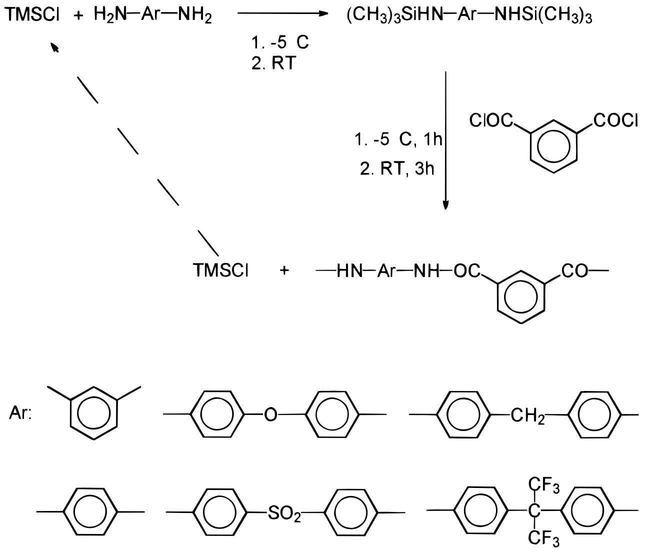
This method has been used previously by Becker and Schmidt,[7] who synthesized poly(amic alkyl esters) as intermediates of rodlike polyimides, by reacting 2,5-bis(ethoxycarbonyl)terephthaloyl chloride with diamines in the presence of TMSCl.

Kaneda et al. had earlier reported[8] the synthesis of polyterephthalamides in the presence of inorganic salts and TMSCl. These authors observed an increase of the viscosity when adding TMSCl, but they did not consider the formation of silylated diamines as reponsible for that positive effect.

Experimental Section

Materials. Trimethylchlorosilane (TMSCl) was twice distilled at normal pressure under nitrogen. Isophthaloyl chloride (IPC) was recrystallized from hexane and finally distilled at reduced pressure. *p*-Phenylene diamine (PPD) and *m*-phenylene diamine (MPD) were purified by vacuum distillation; 4,4′-oxydianiline (DDE), 4,4′-methylenedianiline (DDM), and 4,4′-sulfonyldianiline (DDS) were sublimed twice before use. 4,4′-Hexafluoroisopropylidenedianiline (D6F) was kindly supplied by Hoechst Celanese and was used as received. *N,N*-dimethylacetamide (DMAc) was vacuum distilled twice, the first time over phosphorus pentoxide and the second time over calcium hydride. Subsequently, it was stored in a dark glass bottle over molecular sieves (4 Å).

Scheme 1. Synthesis of Polyisophthalamides from Silylated Diamines Prepared *in Situ*.



Polymer Syntheses. A flask equipped with a mechanical stirrer and in a nitrogen atmosphere was flame dried and charged with 15 mL of DMAc and 0.01 mol of diamine. The mixture was stirred at room temperature until all solids had dissolved. Then the solution was cooled to −5 °C and the required amount of TMSCl was slowly injected. The temperature was raised to room temperature, and the solution was stirred for 15 min to assure the formation of the silylated diamine. After this time, the solution was once more cooled to −5 °C, and 0.01 mol of IPC was rapidly added using a funnel which was subsequently rinsed with 5 mL of DMAc. The reaction mixture was then stirred for 1 h at that temperature, after which it was heated to room temperature and left for a further 3 h. The resulting polymer solution was precipitated into 500 mL of water, washed with hot water and hot methanol, and extracted in a Sohxlet extractor with acetone to remove solvent and oligomers. The polymer from D6F required extraction in methanol, since it manifested swelling in acetone. All of the polymers were dried overnight under vacuum at 120 °C. Yields over 95% were obtained.

Measurements. The inherent viscosities were measured at 25 °C with an Ubbelohde suspended level viscometer using DMAc as solvent for all the polymers. The polymer concentration was 0.5 g/dL

Results and Discussion

The synthesis of aromatic polyamides was carried out by reacting isophthaloyl chloride and silylated diamines prepared *in situ*, as shown in Scheme 1. The polymerization was performed by dissolving the diamine in DMAc and adding different amounts of TMSCl into the solution. Finally, the required stoichiometric amount of IPC was poured into the reaction mixture.

To investigate the effect of the different reaction conditions on the ability to obtain high molecular weight polymers (the higher the reaction rate, the lower the possibility of potential side reactions and the higher the molecular weight), a set of reactions was performed by varying the amount of TMSCl, the diamine, and the reaction temperature. Inherent viscosity values were taken as a measure of the molecular weight of the polyamides obtained. Although this relationship can be rigorously established only when the viscosimetric equation is known, we considered that it could be used to compare the results for the same type of polymers.

With the purpose of optimizing the reaction, six different diamines were used, DDE and PPD, with

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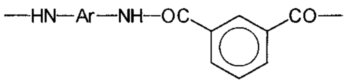
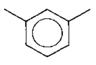
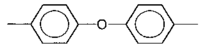
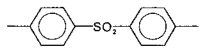
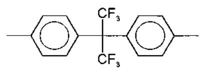
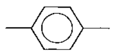
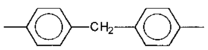
Table 1. Inherent Viscosity (dL/g) of Polyisophthalamides as a Function of the Amount of TMSCl Used in the Reaction



	% TMSCl (mol/mol amino group)					
Ar	0	20	40	60	80	100
	0.92	1.52	1.83	1.42	1.44	1.52
	2.20	2.32	2.84	2.68	2.41	2.38
	0.97	1.21	1.52	1.48	1.38	1.42
	0.74	1.12	1.63	1.29	1.15	1.06
	1.23		1.78			
	1.65		2.05			

electron-donating groups, D6F and DDS, with electron-withdrawing groups, and MPD and DDM, with a reactivities similar to that of aniline.[9]

Table 1 shows the inherent viscosities obtained with different amounts of TMSCl. As can be observed, the presence of TMSCl always causes an increase in the viscosity with respect to those of the polymers prepared in its absence.

As shown in the table, the maximum increase of viscosity always corresponds to the polymers obtained with 0.4 mol of TMSCl per mole of amino group (40%). This result suggests that a stoichiometric amount of TMSCl is not necessary. In fact, the stoichiometric reaction only gives a viscosity similar to that obtained when 20% TMSCl per mole of amino group was added. These results agree with those obtained by Becker and Schmidt on the synthesis of poly(amic alkyl esters).[7] These authors found that the maximum of viscosity was achieved at a concentration of 0.5 mol of TMSCl per mole of amino group. However, they studied that reaction using 0, 10, 50, 75, and 100% TMSCl. Thus, both experiences seem to justify that the maximum of inherent viscosity does not correspond to the addition of a stoichiometric amount. Moreover, a batch of five reactions of MPD and IPC with a mere 5% TMSCl gave polyamides with a substantial increase in the inherent viscosity (values ranging from 1.10 to 1.27 versus 0.92 for the unsilylated diamine). This seems to indicate that the TMSCl can participate in the amidation reaction of more than one amino group, as is shown in Scheme 1.

The effect of the reaction temperature on the viscosity was also studied between −25 and 0 °C in the reaction of MPD with IPC. A maximum was found at −12 °C, as shown in Figure 1, indicating a very high reactivity of *in situ* silylated aromatic diamines on polyamidation reactions at low temperatures.

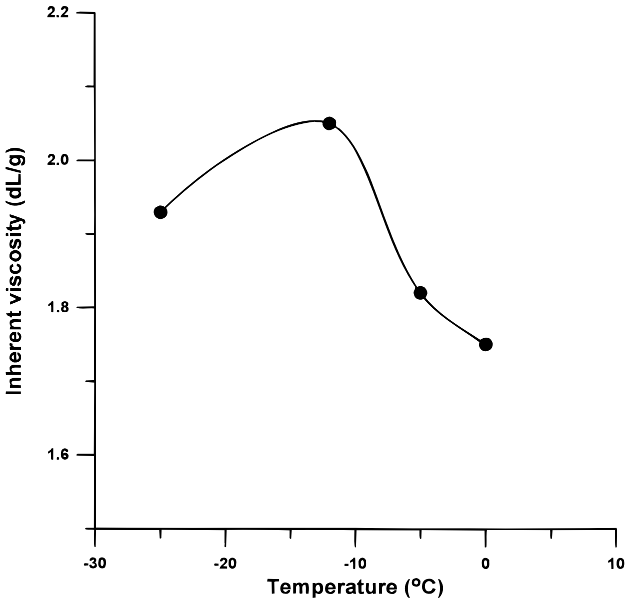


Figure 1. Plot of the inherent viscosity of the polyisophthalamide obtained from MPD and IPC versus the polymerization temperature.

Conclusions

The reaction between aromatic diacid chlorides and *in situ* silylated diamines is an easy and very convenient method for the synthesis of high molecular weight aromatic polyamides. Furthermore, the method shows two additional advantages regarding the use of previously synthesized silylated diamines: (1) Since TMSCl is very reactive with water, its present in the reaction solution ensures that small amounts of water will not destroy the moisture-sensitive acid chloride. (2) The handling of silylated diamines is highly simplified, allowing one to carry out the polyamidation reaction without special glassware and sophisticated operation, just as a classical low-temperature polyamidation.

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References and Notes

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