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NOTE

An Improved Method for Preparing Very High Molecular Weight Polyimides

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Silylated diamines, as more nucleophilic reactants than diamines, were first reported as very suitable monomers for the synthesis of aromatic polyamides by Oishi et al.[1,2] Shortly after, polyimides from dianhydrides and silylated diamines were reported by the same authors.[3,4] Since then, the "silylation method" has successfully been extended to a variety of polyimides and to the preparation of other condensation polymers, such as poly(ether sulfone)s,[5] poly(ether ketone)s,[6] polyesters,[7] or polysulfides.[8] The initial disadvantages of this method, regarding water sensitivity and rigorous control of the reaction conditions, can be overcome with the use of *in situ* silylated diamines. This is performed by adding trimethylchlorosilane (TMSCl) or other silylating agents to the diamine solutions before adding the electrophilic monomer. The *in situ* silylation of the diamines presents some advantages; i.e., the TMSCl ensures that small amounts of water do not destroy the moisture-sensitive dianhydrides and, moreover, the experimental procedure is much easier as handling of silylated diamines is avoided.

Not many examples have been reported in the literature, apart from silylation, regarding the *in situ* activation of amino groups. Although there are references dealing with the use of condensing agents[9] or the use of silylated monomers plus a catalyst, for example $(NH_4)_2SO_4$, acids, etc.,[10] in the synthesis of wholly aromatic polymers, very few examples refer to the role of an organic base as an activating agent.[11,12]

In previous papers,[13,14] we reported the synthesis of aromatic polyamides and polyimides by *in situ* silylation of diamines, and it was studied the role of a tertiary base such as pyridine as an activating agent when added to the silylated diamines.[15,16] This recently explored activation method has proven to be very efficient, yielding high molecular weight polymers even for diamines with steric hindrance. However, only medium−low molecular weight polymers were obtained from diamines with electron-withdrawing groups. Thus, polyimides with inherent viscosity of only 0.4 dL/g could be obtained when 4,4′-diaminodiphenyl sulfone (DDSO) was used.

These results prompted us to investigate the effect of several activation agents in order to find out a general method to achieve high molecular weights irrespective of the electronic features of the aromatic diamines. Thus, several bases, with pK_a ranging from 5.14 to 11.9, such as pyridine, *N*,*N*-dimethylaminopyridine (DMAP), triethylamine (Et_3N), 1,3-diazabicyclo[5.4.0]undecane (DBU), and isoquinoline (IQ) were investigated as individual activating agents or as a pair (base/cobase) in the synthesis of polyimides. Moreover, other reaction conditions (base/cobase relative amount, reaction temperature, solvent, etc.) were also explored and here included.

The results reported herein were obtained from a complete investigation of the best reaction conditions in the synthesis of polyimides from unreactive diamines: 6FDA-DDSO and 6FDA-6FpDA (Scheme 1). The latter is a polyimide with outstanding gas separation properties which has found applications not only as polymer membrane but also as an efficient waveguide and as a coating on proton detectors and other advanced applications when its molecular weight is very high.[17]

The synthesis of aromatic polyimides was carried out by reacting the dianhydride 6FDA with diamines through a base-assisted *in situ* silylation of the diamine. The polymerization was performed by dissolving the diamine, the necessary amount of TMSCl (1 mol/mol of amine), the corresponding base (1 mol/mol of amine), and eventually cobase (0.05−0.5 mol/mol of pyridine). Finally, the required stoichiometric amount of 6FDA was poured into the reaction mixture. Inherent viscosity values were taken as a measure of the molecular weight. 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 polymer.

As previously reported, the presence of TMSCl and pyridine as a base always caused an increase in the viscosity with respect to those of polymers prepared without base, which indicates a clear base-assisted reaction when using *in situ* silylation conditions.[16]

The results obtained for the reaction between 6FpDA and 6FDA are summarized in Table 1. With the exception of DBU (the strongest base among those studied), the presence of a base together with TMSCl always produced an increase in the viscosity with respect to those polymers prepared in its absence. However, when the pK_a of the base was higher than a critical value, the polymers showed lower inherent viscosity than those prepared using the classical two-step way (no TMSCl and no base).

In conclusion, as shown in Figure 1, there is a clear relationship between the basic character of the base and the viscosity achieved. Thus, high values of viscosity (0.65 and 0.77 dL/g) were obtained for the polymers prepared by *in situ* silylation assisted by bases of low basicity (isoquinoline and pyridine) while low values of viscosity (0.21, 0.32, and 0.49 dL/g) were obtained with stronger bases.

Another approach was envisioned by using a small amount of another base, a cobase, with higher pK_a, i.e., DMAP, along with pyridine. The function of the base on the *in situ* silylation polyimidation, which has been already reported,[16] consists in favoring the silylation of the diamine (where a high base pK_a is unfavorable) and in addition on increasing the transfer of electronic density of the silylated amine to the dianhydride moiety, which is a critical step of the reaction, mainly for diamines with electron-withdrawing groups. This transfer opens the anhydride cycle simultaneously with the trimethylsilyl group elimination. As the cobase (higher pK_a) interacts more strongly with the silicon atom, when compared with pyridine, the trimethylsilyl removal is made easier, and hence the reaction is favored. The combined use of small amounts of DMAP as cobase, with

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Scheme 1. Synthesis of 6FDA-6FpDA and 6FDA-DDSO Polyimides

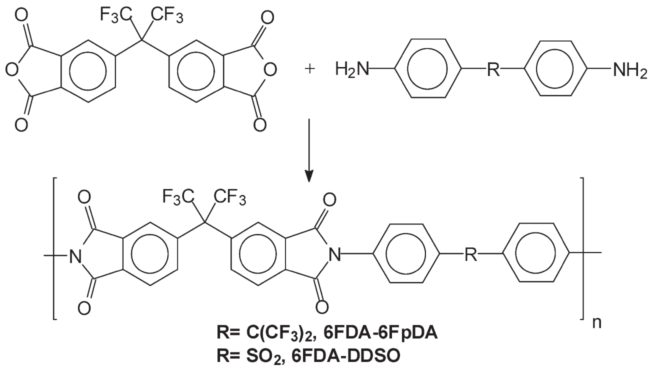

Table 1. Inherent Viscosity (η) of 6FDA-6FpDA as a Function of the Activating Agent, Base, and Solvent

solvent	silylating agent	base	base pK_a	η (dL/g)[a]
NMP				0.51
NMP	TMSCl			0.31
NMP		Py		0.34
NMP	TMSCl	Py	5.28	0.77
NMP	TMSCl	IQ	5.14	0.65
NMP	TMSCl	DMAP	9.70	0.32
NMP	TMSCl	Et_3N	11.0	0.49
NMP	TMSCl	DBU	11.9	0.21
DMAc				0.58
DMAc	TMSCl	Py		0.84

[a] Measured in NMP at 25 ± 0.1 °C, with 0.5% polymer concentration.

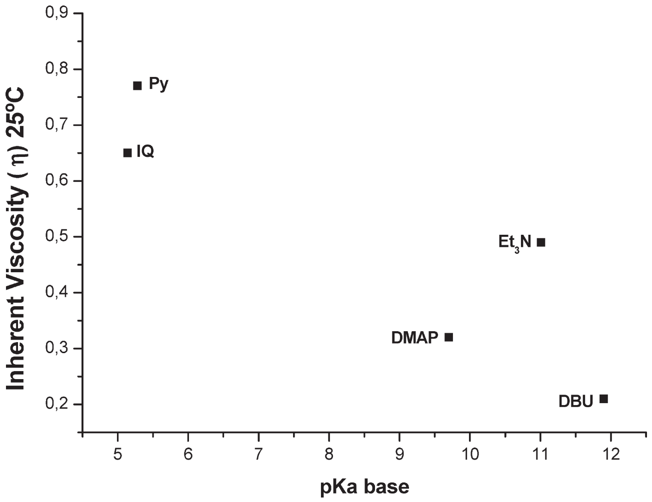

Figure 1. Plot of the inherent viscosity (η) vs the base pK_a for the reaction of 6FDA-6FpDA using different bases as activating agents.

pyridine as base, produced an increase in the viscosity values (Table 2). In this way, a noticeable enhancement on the viscosity (from 0.77 to 0.94 dL/g) was attained in the synthesis of polyimide 6FDA-6FpDA, when 10 mol % of DMAP relative to moles of pyridine was employed (Table 2). The results revealed that the amount of cobase was crucial for the development of the reaction, and above a certain amount of cobase, depropagation reactions took place, leading to a drop of the molecular weight.

Furthermore, the use of DMAc as a solvent instead of NMP, under the optimized conditions of base and amount of cobase, meant an additional improvement and yielded a further increase on the viscosity up to 10%. Also, experiments where the concentration of monomers was scaled up 4-fold produced polyimides with a viscosity up to 1.24 dL/g using DMAc as solvent. This result represents a great advance since the polyimide 6FDA-6FpDA with an inherent viscosity above 1 dL/g has never been reported to our knowledge.

Table 2. Inherent Viscosity (η) of 6FDA-6FpDA as a Function of the Cobase Amount and Solvent

solvent	silylating agent	base	DMAP (%)	η (dL/g)[a]
NMP	TMSCl	Py	5	0.86
NMP	TMSCl	Py	10	0.94
NMP	TMSCl	Py	25	0.57
NMP	TMSCl	Py	50	0.62
DMAc	TMSCl	Py	10	1.03
DMAc	TMSCl	Py	5	1.15[a]
DMAc	TMSCl	Py	10	1.24[a]

[a] These reactions were carried out with 20 mmol of 6FDA and 6FpDA.

Table 3. Inherent Viscosity (η) of 6FDA-DDSO as a Function of the Experimental Conditions

solvent	silylating agent	base	DMAP (%)	η (dL/g)
NMP				0.31
NMP	TMSCl			0.21
NMP		Py		0.16
NMP	TMSCl	Py	10	0.48
DMAc				0.35
DMAc	TMSCl	Py	10	0.54

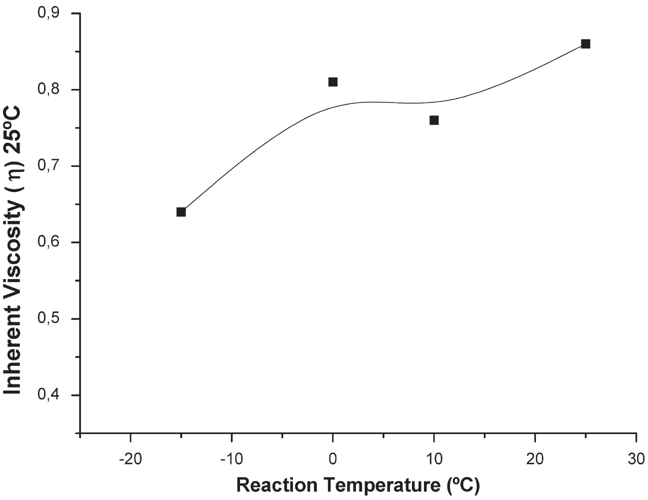

Figure 2. Plot of the inherent viscosity (η) vs reaction temperature for the synthesis of 6FDA-6FpDA using Py and 5% of DMAP.

The effect of the reaction temperature on the viscosity was also studied between −15 and 25 °C in the synthesis of polyimide 6FDA-6FpDA from 6FDA and 6FpDA. A gradual increase on the viscosity was found with the temperature as shown in Figure 2.

Finally, the best conditions outlined for 6FDA-6FpDA were extended to the synthesis of polyimide 6FDA-DDSO. The results are shown in Table 3 and compared with the results previously reported.[16]

As can be seen, when no DMAP was used, medium−low molecular weight polymers were attained. However, when a combination of pyridine and DMAP was used, high molecular weight polyimides were obtained. The use of DMAc as solvent instead of NMP improved the result (from 0.48 to 0.54 dL/g).

Thus, the *in situ* silylation of aromatic diamines with TMSCl in the presence of a base such as pyridine has proved to be a facile and convenient method to obtain high molecular weight polyimides. When the polymerization is carried out using neat pyridine as an activating reagent or TMSCl with no base, reverse reactions are favored, and low molecular weight polyimides are obtained.

The use of stronger bases, such as DMAP, Et_3N, or DBU, together with TMSCl as activating agents, yields low molecular weight polyimides.

However, the use of small amounts (0.1 mol per mole of pyridine) of a strong base (cobase) (e.g., DMAP) together with pyridine has an active role in the progress of the reaction, and high molecular weights are obtained.

The use of DMAc as solvent instead of NMP represents an additional improvement on the reaction conditions yielding to an increase on the viscosity up to 10%. Furthermore, this method can lead to high molecular weight polyimides derived from very unreactive aromatic diamines, much higher than those obtained by any one- or two-step polyimidation reaction.

Experimental Section

The synthesis of aromatic polyimides of different molecular weights was carried out by reacting the dianhydride 6FDA and diamines DDSO and 6FpDA through a *in situ* silylation base-assisted or nonassisted process. For each experimental setup, a flask was charged with a solution of 5.0 mmol of diamine in 5.0 mL of solvent. The solution was cooled to 0 °C, and the required amount of TMSCl (1 mol/mol amino group) was added to the experiment, followed by the corresponding amount of base or mixture of bases. After that, 5.0 mmol of 6FDA was rapidly added along with 5.0 mL of solvent. The reaction mixture was then stirred for 15 min at 0 °C, and then the temperature was raised up to room temperature and left overnight. Polyimides were obtained by chemical cyclodehydration of the formed polyamic acid. A more detailed experimental section, including measurements of molecular weight by gel permeation chromatography (GPC), is included in the Supporting Information.

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Supporting Information Available: A more detailed experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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