

Preparation and Solid-State Polyamidation of Hexamethylenediammonium Adipate: The Effect of Sodium 5-Sulfoisophthalic Acid

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ABSTRACT: The effect of sodium 5-sulfoisophthalic acid (NaSIPA) on the solid-state polymerization of hexamethylenediammonium adipate was studied. In particular, different polyamide salt grades, such as a model salt of hexamethylenediamine and NaSIPA and a polyamide 6,6 salt containing NaSIPA, were prepared through alternative procedures based on the solution–precipitation technique. Furthermore, selected salt grades were solid-state-polymerized in a thermogravimetric analysis chamber under static and flowing nitrogen. Critical reaction parameters, such as the

reaction temperature, surrounding gas, and presence of NaSIPA, were investigated to determine the rate-controlling mechanism of the process. More specifically, NaSIPA significantly influenced solid-state polyamidation by reducing the reaction rate and changing the prevailing mechanism. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1609–1619, 2007

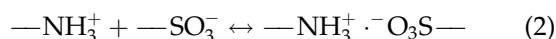
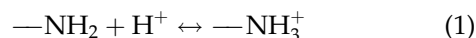
Key words: ionomers; polyamides; solid state polymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Modifying polymers with ionic groups (ionomers) constitutes a very effective approach to changing significantly both the chemical and physical properties of the parent polymers over a broad range. Regarding polyamides and polyesters, such as polyhexamethylenedipamide (PA-6,6) and poly(ethylene terephthalate) (PET), the most commercially important ion-modified resins contain 1–5 mol % sodium 5-sulfoisophthalic acid [NaSIPA; Fig. 1(a)]; in particular, PET containing NaSIPA was originally commercialized by DuPont in 1958 under the trade name Dacron 64.¹

From a commercial and industrial point of view, the main advantage of sulfonated copolymers is the improvement of the polymer dyeability to cationic dyes, since fibers or films with deep and brilliant colors and resistance to stains, fading, and yellowing throughout their life cycle.^{2–9} More specifically, the incorporation of NaSIPA sulfonate groups (SO_3^-) into the polymer chains favors each step of the dyeing process: the uptake of the dyestuff cations by the fiber surface, the diffusion of the dyestuff cations

into the fiber interior, and the binding of the cations into the fiber.^{2,3} The introduction of NaSIPA also improves the polymer resistance to acid stains because the SO_3^- units block the polymer basic groups (e.g., $-\text{NH}_2$) for polyamides [eqs. (1) and (2)], which can no longer react with the acid stains;^{3–9} the latter is really important for applications such as flooring covers (e.g., carpets). Finally, the ionic units of NaSIPA reduce permanently the fiber tendency to static electricity, thus improving the quality of the textile.⁵



Apart from the use of NaSIPA in polyamide fiber applications, its presence also improves polymer operability during subsequent processing, which often deteriorates in the presence of both pigments and copper. For this reason, the preferred range of NaSIPA to be used is 1–2 wt % (added at the salt stage, i.e., before polymerization) for most combinations of pigments and copper; meanwhile, above 4 wt %, the additive itself begins to lower the relative viscosity of the polymer and gives poorer operability.¹⁰ In summary, the commercial and industrial importance of NaSIPA-containing polyamides becomes evident because NaSIPA is added in the majority of nylon production lines. Its significance is even

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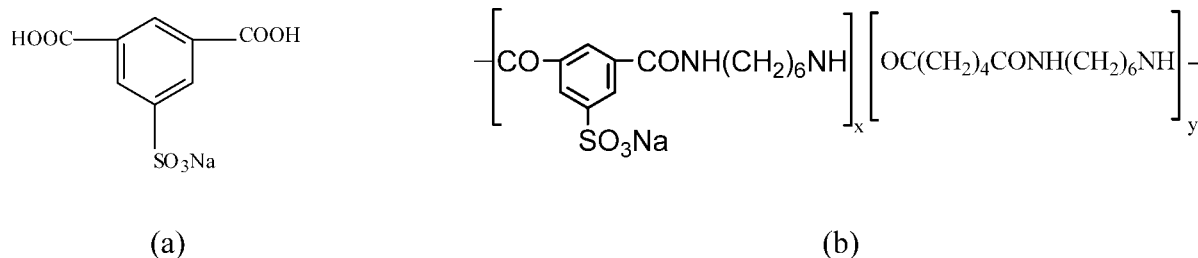


Figure 1 (a) NaSIPA and (b) the NaSIPA-modified PA-6,6 copolymer.

enhanced because nowadays the nylon industry has moved away from the PA-6,6 homopolymer and is seeking modified polyamides with dramatically better properties at comparable prices.

As for the preparation of sulfonated polyamides, NaSIPA consists of a difunctional compound (diacid) and is introduced into the polymer chain through copolymerization. In Figure 1(b), the structure of NaSIPA-modified PA-6,6 is presented; x varies between 0.01 and 0.05, corresponding to 1–5 mol % NaSIPA, and y varies between 0.95 and 0.99.^{1,11,12} The modifier is usually added during the initial stages of conventional solution–melt polyamidation^{5,6,8,9,13} or through the melt polymerization of the PA-6,6 homopolymer with a master batch containing NaSIPA.⁴ However, the sulfonated PA-6,6 copolymers generally have high melt viscosities, which limit the extent of melt polymerization and hinder the effective discharge of the polymerized melt from the reactor.^{1,4} As a result, the conventional solution–melt polymerization is interrupted at a low- or medium-molecular-weight product; when higher molecular weights are required, the sulfonated PA-6,6 prepolymers may be further polymerized in the solid phase [solid-state polyamidation (SSP)]. In general, SSP is widely used as an extension of the melt polymerization process and involves heating the starting material (prepolymer) in an inert atmosphere at a temperature well above its glass-transition point but below the melting temperature, increasing the degree of polymerization while the material retains its solid shape.^{14–16} Alternatively, direct SSP starting from a dry PA-6,6 salt has been also studied with different techniques^{17–19} and presents considerable practical interest because all the problems associated with the high temperatures of melt technology are avoided.¹⁷

As it involves both chemical and physical steps, SSP presents a complex reaction process. On the basis of the reversible polyamidation reaction and the restrictions set by the nature of SSP, one can identify the rate-determining stages: the intrinsic kinetics of the chemical reaction, the diffusion of the reactive end groups, the diffusion of the condensate in the solid reacting mass (interior diffusion), and the dif-

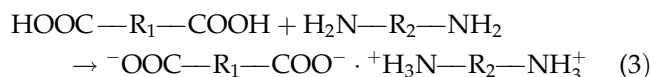
fusion of the condensate from the reacting mass surface to the inert gas (surface diffusion). Therefore, a large number of parameters, such as the temperature, prepolymer molecular weight, crystallinity, reacting particle geometry, and gas flow rate, have been reported to affect the SSP overall rate, suggesting also the relevant mechanism.¹⁶

This article sets the grounds for the investigation of the mechanism prevailing during ionomer-based SSP processes. In particular, the effect of NaSIPA on SSP of polyamide salts is examined, and we take into account its commercial and industrial significance. Therefore, the model salt of NaSIPA/hexamethylenediamine (HMD) and a dry PA-6,6 salt containing NaSIPA were first prepared and characterized, and this permitted the development of an efficient technique for NaSIPA incorporation into the PA-6,6 salt. The latter is very interesting because the preparation, isolation, and characterization of solid NaSIPA-modified nylon salts have not so far been described in the literature on account of the routine use of aqueous salt solutions during the production of ionomers. Selected salt grades were afterwards solid-state-polymerized on a very small scale, that is, in a thermogravimetric analysis (TGA) chamber. TGA chambers have been used in a number of studies to simulate polyamidation reactors, permitting thus the investigation of the process mechanism when it starts from the monomer (PA-6,6 salt).^{20–25}

EXPERIMENTAL

Polyamide salt preparation

Polyamide salt preparation, in general, involves the exothermic creation of ionic bonds between the end groups ($-\text{NH}_2$ and $-\text{COOH}$) of the reactants.²⁶



The reactants used here were HMD, NaSIPA, and adipic acid (AA), which were obtained from Merck (Darmstadt, Germany). The experimental procedure

TABLE I
Experimental Procedure for the Preparation of Polyamide Salt Grades

| Salt grade | Ethanol approach | | Aqueous approach | |
|--|--|--|--|--|
| | Method 1 | Method 2 | Method 2 | Method 3 |
| PA 6,6 salt | Mixing AA and HMD ethanol solutions | Mixing solid AA and HMD aqueous solution and adding ethanol as a nonsolvent | Mixing solid AA and an HMD aqueous solution and adding isopropyl alcohol as a nonsolvent | Mixing solid AA and an HMD aqueous solution and adding isopropyl alcohol as a nonsolvent |
| Mass yield | 97% | 82% | | 50% |
| Aqueous approach | | | | |
| | Method 1 | Method 2 | Method 3 | |
| HMD/NaSIPA salt | Mixing NaSIPA and HMD aqueous solutions and adding isopropyl alcohol as a nonsolvent | Mixing solid NaSIPA and an HMD aqueous solution and adding ethanol as a nonsolvent | Mixing solid NaSIPA and an HMD aqueous solution and adding isopropyl alcohol as a nonsolvent | Mixing solid NaSIPA and an HMD aqueous solution and adding isopropyl alcohol as a nonsolvent |
| Mass yield | 20% | 25% | | 22% |
| Ethanol approach | | | | |
| | Method 1 | Method 2 | | |
| NaSIPA-containing (1% w/w) PA 6,6 salt | Dispersion of NaSIPA in the AA ethanol solution and mixing diacids and HMD ethanol solutions | Dry-mixing solid AA and NaSIPA, mixing solid diacids and an HMD aqueous solution, and adding isopropyl alcohol as a nonsolvent | | |
| Mass yield | 97% | 30% | | |

applied for the preparation of the solid salts was based on the solution–precipitation technique^{5,17–19,27} and involved the use of ethanol or aqueous solutions of the reactants. More specifically, in the ethanol approach, the salt precipitated as soon as it was formed; meanwhile, in the aqueous approach, the precipitation of the salt was accomplished by the addition of a nonsolvent to the solution, such as isopropyl alcohol or ethanol. In each preparation run, the salt solution was cooled for 24 h at 5°C to achieve complete precipitation; it was then filtered, and the sediment was dried for 4 h at 50°C *in vacuo*. Accordingly, solid and pure PA-6,6 salt (hexamethylenediammonium adipate), a model salt derived from HMD and NaSIPA, and a PA-6,6 salt containing 1% (w/w) NaSIPA were prepared (Table I), resulting in mass yields between 20 and 97%.

Polyamide salt characterization

Amine end group analysis

Amine (–NH₂) end groups were determined by potentiometric titration. The dry salt (0.1 g) was dissolved in 100 mL of 75% (v/v) ethanol/water, and the solution was titrated with perchloric acid in methanol. For each salt grade, the theoretical amine end group concentration $\{[-\text{NH}_2]_{\text{theor}} \text{ (mequiv/kg)}\}$ was calculated with eq. (4), and the deviation be-

tween the experimental and theoretical values revealed the deviation of the balance of the end groups in the prepared salt.²⁸

$$[\text{NH}_2]_{\text{theor}} = (1000 \times 2 \times m_{\text{HMD}}) / (\text{MW}_{\text{HMD}} m_{\text{salt}}) \quad (4)$$

where MW_{HMD} is the molecular weight of HMD (116 g/mol), m_{HMD} is the amount of the dissolved diamine (g), and m_{salt} is the theoretical amount of the formed salt equal to the amount of the reactants $[m_{\text{HMD}} + m_{\text{AA}} \text{ (kg)}]$, where m_{AA} is the amount of the dissolved adipic acid.

pH measurements

The pH was measured (pH 211 microprocessor pH meter, Hanna Instruments, Leighton Buzzard, UK) by the dissolution of the polyamide salt in water to make a 1% (w/v) solution. Normally, an aqueous solution of the balanced salt has a pH of 7.6.²⁸

FTIR analysis

FTIR spectra were obtained from Nujol mulls of the dry salt spread onto a KBr crystal with a Nicolet Magna IR 560 spectrometer (Thermo Fischer Scientific, Waltham, MA).²⁸

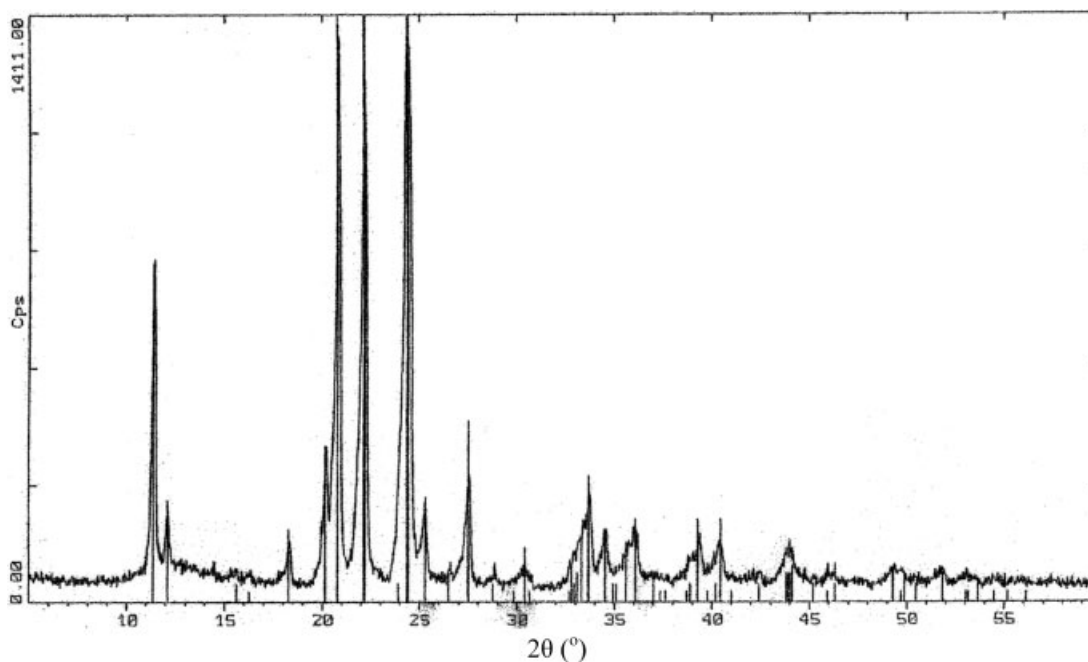


Figure 2 XRD spectrum of the pure PA-6,6 salt prepared with method 1 (Table I). The vertical lines correspond to the reference spectrum for the PA-6,6 salt.

X-ray diffraction (XRD)

XRD data were collected on a Siemens D 5000 X-ray diffractometer (Munich, Germany) with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation.

X-ray fluorescence (XRF)

XRF served as a tool to assess the effectiveness of the NaSIPA incorporation technique. Quantitative XRF was performed on an ARL Advant XP fluorometer (Thermo Fischer Scientific, Waltham, MA), and it was used to determine the concentration of sulfur present in the NaSIPA-containing salt grades.

Differential scanning calorimetry (DSC)

The DSC analysis was performed under a nitrogen flow in the range of 30–300°C at a heating rate of 10°C/min. The system used was PerkinElmer DSC 4 (Wellesley, MA).

SSP

Two polyamide salt grades (pure PA-6,6 salt and PA-6,6 salt plus 1% w/w NaSIPA), prepared from alcoholic solutions of the reactants (Table I, method 1), were subjected to SSP. Both salt grades were in the form of a colorless powder and presented a uniform size distribution (400 mesh). The runs were car-

ried out in a TGA chamber (2100 thermal analysis, DuPont, Wilmington, DE), with small amounts of a salt sample (ca. 30 mg). The SSP runs were conducted at 170 and 177°C under both dry static and flowing (30 mL/min) nitrogen. More details on this approach to investigating the mechanism of the SSP reaction are given elsewhere.²¹

The weight loss [ΔW (g)] at any given time during SSP is anticipated to be equal to the amount of polycondensation water, which escapes, and may be expressed as a function of the polymerization conversion (p_t), the initial concentration of amine end groups $\{[\text{NH}_2]_0$ (g equiv/kg)}, and the amount of the reacting salt at any given time [m_t (kg)]:

$$\Delta W = 18m_t[\text{H}_2\text{O}] = 18p_t m_t [\text{NH}_2]_0 \quad (5)$$

The theoretical total weight loss at the end of the SSP reaction is calculated with eq. (5), for which p_t is equal to 1. In addition, the total reduced weight loss $[(\Delta W)_r]$, expressed as a percentage, is based on the initial weight of the sample (kg). $\frac{\partial(\Delta W)_r}{\partial t}$ (%/min) is the rate of the SSP reaction, assuming no diamine loss. However, the latter assumption is hardly valid for SSP reactions starting from the diamine–diacid salts, and therefore the aforementioned ratio indicates the rate of the decomposition of the starting material.²¹ Finally, in each run, a TGA diagram was deduced, in which the rate of the weight loss was plotted versus the reaction time, including also the warming-up period of the reacting mass.

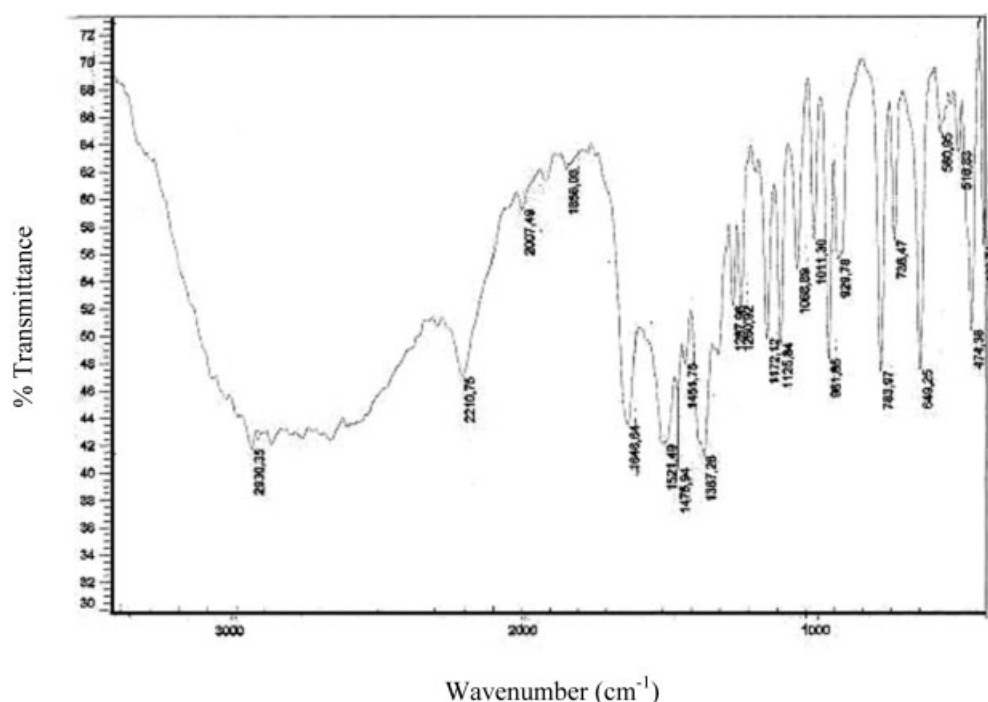


Figure 3 FTIR spectrum of the pure PA-6,6 salt prepared with method 3 (Table I).

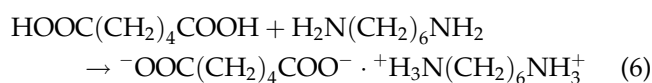
RESULTS AND DISCUSSION

Preparation of the polyamide salts

Case of the pure PA-6,6 salt

Three methods (Table I) were followed for the preparation of the pure PA-6,6 salt, and in all cases, the analysis made by XRD and FTIR (Figs. 2 and 3) verified the formation of the organic salt according to eq. (6), which obeys the general reaction scheme of eq. (3). In particular, the XRD spectra agreed with the one listed in the database of the instrument; meanwhile, the FTIR spectra included the characteristic peaks of the PA-6,6 salt at 2210 cm^{-1} corresponding to the strength vibration of the ionized amine groups ($-\text{NH}_3^+$), at 1521 cm^{-1} corresponding to the deformation vibration of $-\text{NH}_3^+$, and at 1648

and 1451 cm^{-1} corresponding to the vibration of the COO^- group.^{29,30}



The properties of the pure PA-6,6 salt are presented in Table II. For each preparation technique, the experimental amine end group concentration ($[-\text{NH}_2]_{\text{exp}}$) deviated slightly from the theoretical one, revealing the effectiveness of the three applied methods for salt preparation. The pH of the salt aqueous solution (7.5) was close to the theoretical value of 7.6,^{21,28} verifying the formation of a balanced salt proper for step-growth polymerization; meanwhile, the melting points varied between 193 and 195°C , being close to the melt-

TABLE II
Properties of the Polyamide Salt Grades Prepared According to Table I

| Salt grade | Method | $[-\text{NH}_2]_{\text{theor}}$ (mequiv/kg) | $[-\text{NH}_2]_{\text{exp}}$ (mequiv/kg) | Melting point ($^\circ\text{C}$) | $[\text{S}]_{\text{theor}}$ (ppm) | $[\text{S}]_{\text{exp}}$ (ppm) |
|---|--------|--|--|---------------------------------------|--------------------------------------|------------------------------------|
| PA-6,6 salt | 1 | 7629 | 7553 ± 10 | 193.2 | | |
| | 2 | 7642 | 7590 ± 20 | 193.7 | | |
| | 3 | 7623 | 7493 ± 120 | 195.2 | | |
| HMD/NaSIPA salt | 1 | 5212 | 5157 ± 32 | 144.3 | | |
| | 2 | 5200 | 5126 ± 34 | 141.5 | | |
| | 3 | 5200 | 5021 ± 26 | 152.8 | 58,100 | 56,400 |
| NaSIPA-containing (1% w/w) PA-6,6 salt | 1 | 7551 | 7563 ± 25 | 193.9 | 1,040 | 857 |
| | 2 | 7591 | 7395 ± 60 | 194.5 | 840 | 110 |

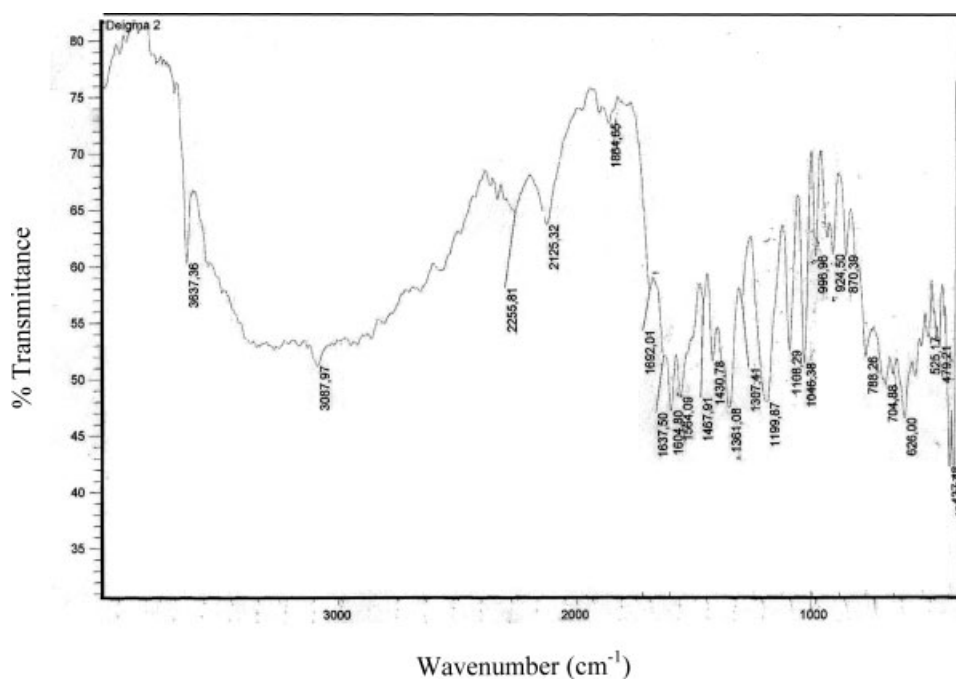


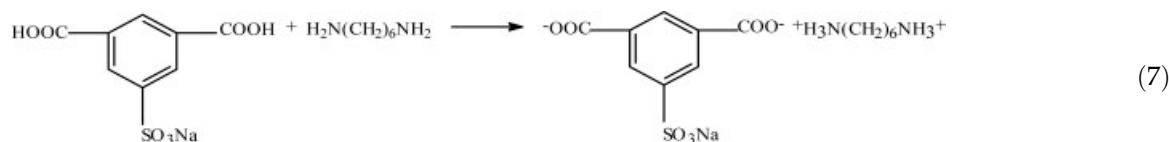
Figure 4 FTIR spectrum of the model salt HMD/NaSIPA prepared with method 3 (Table I).

ing range found in the literature (191–200°C).^{20,31} On the basis of the higher mass yield (97%), method 1 (ethanol approach) was proved to be the most suitable technique, in agreement with our previous studies.^{17–20}

Case of the model salt HMD/NaSIPA

Turning to the model salt HMD/NaSIPA, we applied only the aqueous approach because NaSIPA is not soluble in ethanol. The FTIR spectrum (Fig. 4)

verified the ionic character of the salt structure according to eq. (7). The absorption band found at 2125 cm⁻¹ was attributed to the strength vibration of —NH₃⁺, that at 1564 cm⁻¹ was attributed to the deformation vibration of —NH₃⁺, and those at 1637 and 1430 cm⁻¹ were attributed to the vibration of COO⁻.^{29,30} The absorptions at 1604 and 996 cm⁻¹ were characteristic of the aromatic structure; meanwhile, the strong transmittance at 2255 cm⁻¹ could be attributed to the sulfonate groups (—SO₃⁻),³² as also found in the pure NaSIPA FTIR spectrum.



The properties of the model salt are quoted in Table II. The amine end contents ensured the formation of a balanced salt structure; meanwhile, the melting points varied between 141 and 153°C. On the basis of the XRF analysis, the determined sulfur concentration (56,400 ppm) and the low deviation from the theoretical content (58,100 ppm) verified the homogeneous NaSIPA distribution in the formed salt and the efficiency of the preparation technique through the suggested aqueous approach. However, all three methods presented extremely low mass yields (20–25%, Table I), probably because of the

low reactivity of NaSIPA and the instability of the formed salt. The latter may be the main reason, especially because of the difficulties faced during salt preparation: during the addition of the nonsolvent (ethanol or isopropyl alcohol) to the aqueous salt solution, two different phases were formed, which potentially inhibited high mass yields. This phase separation may be attributed to a decrease in the solubility of alcohol (ethanol and isopropyl alcohol) in water because of the presence of NaSIPA ionic species (SO₃⁻ and Na⁺). The latter is known as the salting-out effect, and it is widely used in the

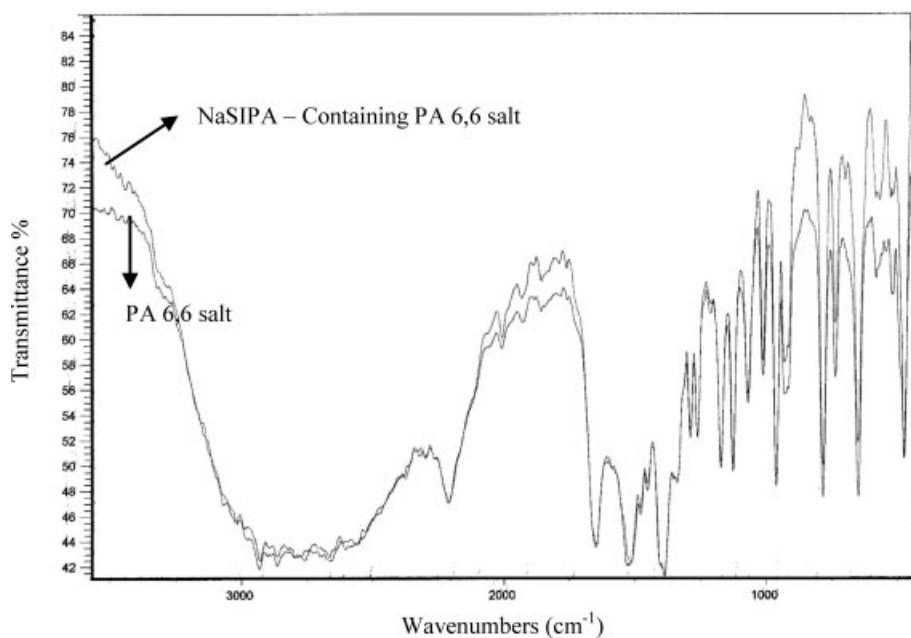


Figure 5 FTIR spectrum of the NaSIPA-containing 1% (w/w) PA-6,6 salt prepared with method 1 (Table I).

purification of proteins, in which water and ethanol become immiscible by the addition of a salt, such as potassium carbonate or ammonium sulfate.^{33,34}

Case of the NaSIPA-containing PA-6,6 salt

Regarding the NaSIPA-containing PA-6,6 salt, first of all, it should be mentioned that the FTIR spectra were exactly the same as those of the pure PA-6,6 salt (Fig. 5), indicating the presence of the ionized end groups. The same prevailed for the XRD analysis; meanwhile, the properties of the NaSIPA-containing salts (Table II), such as the melting point ($\sim 194^\circ\text{C}$) and the pH (7.5–7.6), were also found close to those of the pure PA-6,6 salt, indicating the end-group balance in the monomer.

When we studied the applied techniques, the quantitative incorporation of NaSIPA into the solid PA-6,6 salt was successfully accomplished through method 1 (Table I), which was based on the ethanol approach and involved the addition of the solid additive in the ethanol solution of AA, mixing with the HMD ethanol solution, and finally precipitation of the salt as soon as it was formed. The efficiency of this technique was proved by the much higher mass yield (97%) in comparison with the aqueous approach (method 2; 30%) and, more importantly, by the high sulfur contents of the salt formed (Table II): the salt prepared through method 1 contained 857 ppm sulfur, deviating not too much from the theoretical value of 1040 ppm. On the contrary, the salt formed through method 2 presented an extremely high deviation between the theoretical (840

ppm) and experimental values (110 ppm) of the concentration of sulfur, revealing that a significant amount of NaSIPA ($\sim 87\%$) did not precipitate with the PA-6,6 salt. Some preliminary runs were also carried out with method 2 for higher NaSIPA contents (2 and 3% w/w), and again the mass yields were found to be significantly low (31%).

The success of method 1 over method 2 as a NaSIPA incorporation technique may be attributed to the absence of water; when aqueous salt solutions were prepared containing the additive and then alcohols were used as nonsolvents, the aforementioned phase separation (salting-out effect) hindered the precipitation of the formed salt. The latter was not the case for the ethanol approach (method 1), in which NaSIPA was obligatorily incorporated into the PA-6,6 salt, which precipitated as soon as it was formed.

SSP runs of the prepared salts

Two polyamide salt grades (pure PA-6,6 salt, as a reference, and PA-6,6 salt plus 1% w/w NaSIPA), prepared through the ethanol approach (method 1, Table I), were subjected to SSP in a TGA chamber, and the results are presented in Table III. $(\Delta W)_r$ at the end of all SSP runs varied between 23 and 28%, and it was thus found to be higher than the stoichiometric amount of water [$(\Delta W)_{r,theor}$, eq. (5)] formed for $p_t = 1$ and for equimolar amounts of the reactants. This deviation reveals that the weight loss of the reacting mass during SSP was not only due to the removal of polycondensation water but also due

TABLE III
 $(\Delta W)_r$ at the End of the SSP Runs Starting from Polyamide Salts in a TGA Chamber at 170 and 177 °C under Flowing and Static Nitrogen

| Salt grade | TGA conditions | Time (min) | $(\Delta W)_{r,theor}$ (%) | $(\Delta W)_r$ (%) |
|---|-----------------------------------|------------|----------------------------|--------------------|
| PA-6,6 salt | 170 °C and flowing N ₂ | 79 | 13.59 | 25.16 |
| | 170 °C and static N ₂ | 79 | 13.59 | 24.36 |
| | 177 °C and flowing N ₂ | 79 | 13.59 | 28.14 |
| | 177 °C and static N ₂ | 79 | 13.59 | 25.38 |
| NaSIPA-containing (1% w/w) PA-6,6 salt | 170 °C and flowing N ₂ | 79 | 13.61 | 23.32 |
| | 170 °C and static N ₂ | 79 | 13.61 | 24.23 |
| | 177 °C and flowing N ₂ | 79 | 13.61 | 25.97 |
| | 177 °C and static N ₂ | 79 | 13.61 | 25.15 |

to the decomposition of the polyamide salt and thus the partial volatilization of HMD. The readily volatile diamine escaped along with water, as already observed during SSP of PA-6,6 and PA-6,10 salts^{21,35} and also different aromatic polyamide salts.²² In a previous joint study from our laboratory and DuPont Co.,²¹ the HMD loss during SSP under flowing nitrogen was studied with IR spectroscopy. Accordingly, HMD and water were identified by IR analysis of the TGA effluent gas, and their evolution was monitored throughout the SSP process at a constant reaction temperature. It was then shown that the diamine loss dominated early in the reaction, after which water was rapidly formed. This early HMD volatilization was found to contribute to the SSP mechanism and, more specifically, to the nucleation stage of the reaction through increasing defective surfaces in the crystal lattice and thus the active

centers for the nucleation of the generated polymer phase.

As for the SSP parameters, the reaction temperature emerged as the most important for both starting materials (Figs. 6 and 7). Specifically, higher rates of weight loss were attained sooner at the elevated reaction temperature, as shown by both the sharpness of the curves of the weight-loss rate and their duration. Regarding the pure PA-6,6 salt (Fig. 6) and comparing the rates of $(\Delta W)_r$ under static and flowing nitrogen at both temperatures, we found that the curves coincided for short reaction times, probably indicating the easy removal of water and/or HMD from the reacting sites at the surface of the monomer during the warming-up period (17 min). On the other hand, for longer reaction times, and especially at the low reaction temperature of 170 °C, the rate of weight loss under flowing nitrogen was slightly

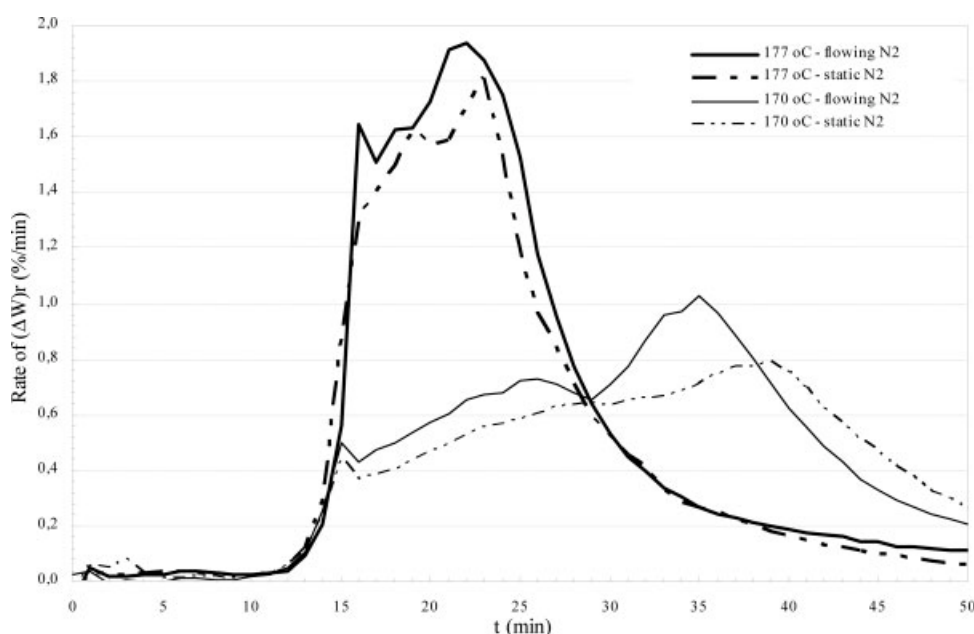


Figure 6 $\frac{\partial(\Delta W)_r}{\partial t}$ for the reacting mass during SSP of the pure PA-6,6 salt under flowing and static nitrogen at 170 and 177 °C.

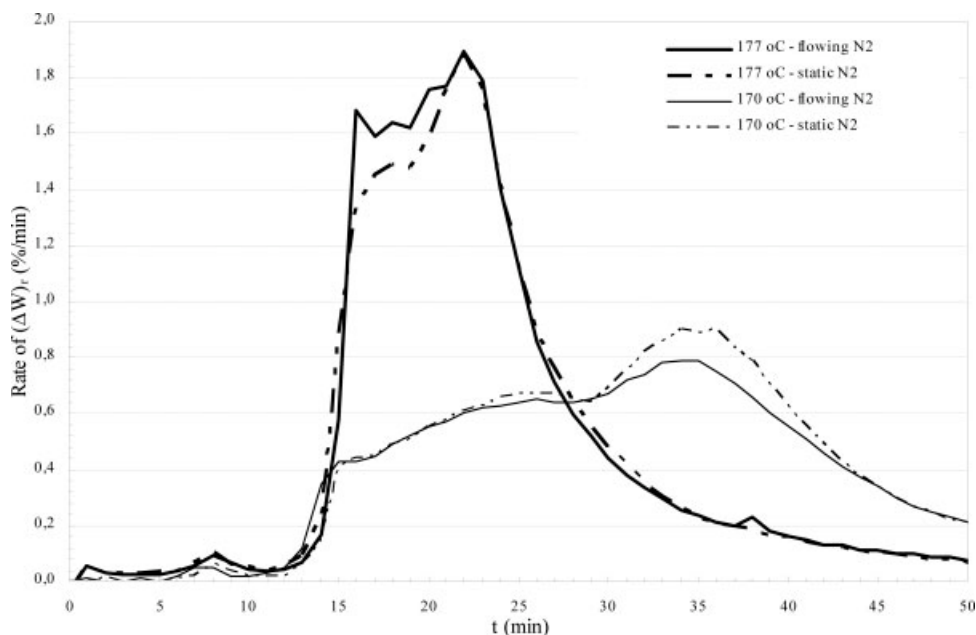


Figure 7 $\frac{\partial(\Delta W)_r}{\partial t}$ of the reacting mass during SSP of the NaSIPA-containing 1% (w/w) PA-6,6 salt under flowing and static nitrogen at 170 and 177°C.

higher, and this revealed that the overall process was affected by diffusion limitations. Indeed, it is a well-known fact that an increase in the nitrogen flow rate not only increases the mass- and heat-transfer rates in a gas–solid system but also reduces the byproduct concentration in the gas phase and accelerates its diffusion from the particle surface into the bulk of the gas phase.²³ In addition, the presence of the nitrogen flow may favor the aforementioned dia-

mine volatilization process and result in a higher number of nucleation sites.²¹ Overall, the pure PA-6,6 salt SSP process and/or the volatilization of HMD may be thus considered to be greatly influenced by mass transport for the temperature range of 170–177°C.

However, the picture changes in the case of the SSP runs starting from the NaSIPA-modified PA-6,6 salt. For most reaction times, the curves of the rates

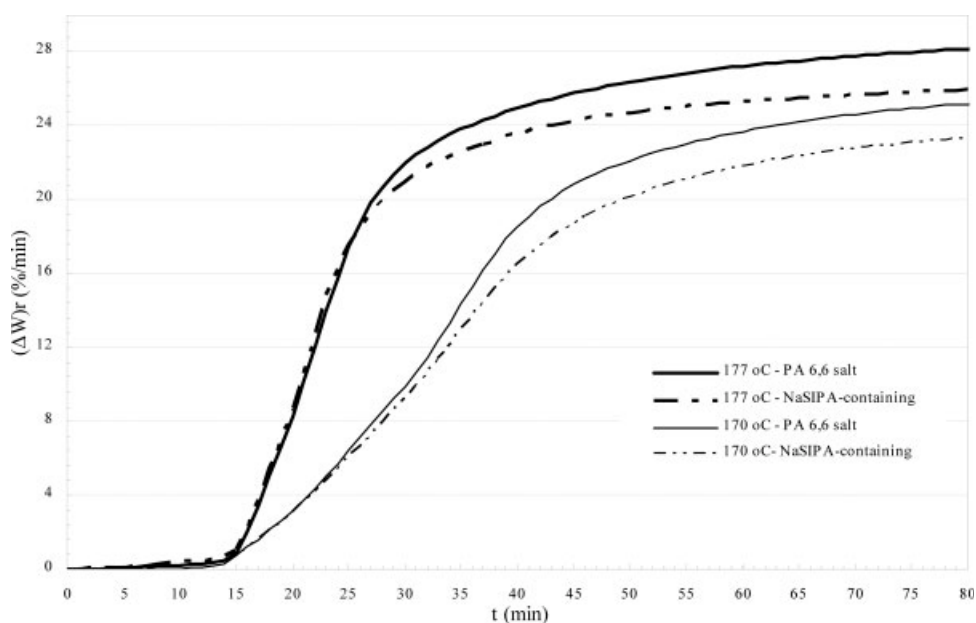


Figure 8 $(\Delta W)_r$ of the reacting mass during SSP of the PA-6,6 salt and NaSIPA-containing 1% (w/w) PA-6,6 salt at 170 and 177°C under flowing nitrogen.

of weight loss under flowing and static nitrogen (Fig. 7) almost coincided, and this indicated that the reaction mechanism was not so much influenced by diffusion, as was the case for the pure PA-6,6 salt. In other words, it seems that NaSIPA interfered with the process by making the diffusion limitations of the water and/or HMD through the particle to the surrounding gas not so important. A relative change in the SSP mechanism was also observed in a previous study of ours,²¹ in which TGA was again used as a small-scale reactor in the case of SSP catalytic runs: the presence of a catalyst changed the controlling step, which was no longer diffusion.

Furthermore, when comparing the curves of $(\Delta W)_r$ of the two starting materials under flowing nitrogen (Fig. 8), we found that the modifier had a slight retarding effect on the weight loss of the reacting mass and slowed down the SSP reaction and/or the diamine loss in accordance with unpublished data of ours.³⁶ This negative effect of the presence of NaSIPA on the process rate may be related to the structure of the sulfonated comonomer. First, according to the model proposed by Eisenberg et al.³⁷ for ionomers, the NaSIPA ionic moieties aggregate into multiplets, which, in turn, aggregate themselves into clusters, creating finally a contiguous phase of restricted mobility in the polymer mass. During SSP of the NaSIPA-containing salt, the ionic groups are localized in the amorphous regions and create a low-mobility area, which obviously acts as a lattice defect and impedes the diffusion of the functional end groups. Even more, the reverse reaction rate is anticipated to be higher in the NaSIPA-modified salt because of the increased hygroscopic sites of the additive structure. This is in agreement with the literature findings, according to which the presence of the sodium sulfonate groups may initiate and/or catalyze the hydrolysis reaction, as suggested for the case of sulfonated PET copolymers found to be significantly susceptible to acidic hydrolysis and exhibiting much higher hydrodegradability than pure PET.³⁸

CONCLUSIONS

The advantages of SSP starting from a dry salt increase the need for the development of a suitable preparation technique of the solid monomer. Therefore, on the grounds of the significant role of NaSIPA in the polyamide industry, an effective NaSIPA-incorporation technique is proposed that involves the precipitation of the sulfonated PA-6,6 salt from ethanol solutions of the reactants. The properties of the prepared solid comonomer were defined for the first time to permit its use as a starting material for SSP. SSP runs were carried out on a small scale starting from the solid and pure PA-6,6 salt and NaSIPA-

containing 1% (w/w) PA-6,6 salt. In the first case, the importance of diffusion limitations was revealed; meanwhile, the presence of NaSIPA had a double effect on the SSP progress: the rate of the overall process was reduced, and the chemical reaction prevailed more intensively. The phenomenon was attributed to the presence of the NaSIPA ionic moieties, in accordance with previous studies on sulfonated PA-6,6 and PET.

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