

Solid state post-polymerization of PA 6,6: The effect of sodium 5-sulfoisophthalic acid

S.N. Vouyiouka^a, C.D. Papaspyrides^{a,*}, J.N. Weber^b, D.N. Marks^c

^a Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou, Athens 157 80, Greece

^b University of Delaware, 303 Old College, Newark, DE 19716, USA

^c E.I. DuPont de Nemours and Co., Experimental Station, Wilmington, DE 19898, USA

Received 7 November 2006; received in revised form 9 May 2007; accepted 14 June 2007

Available online 21 June 2007

Abstract

Solid state polymerization (SSP) starting from polyhexamethylenedipamide (PA 6,6) precursors was studied in the temperature range of 160–200 °C in a solid bed reactor. Process parameters, such as temperature, time and inert gas flow rate were investigated, meanwhile emphasis was given on the effect of a dyeability modifier (sodium 5-sulfoisophthalic acid, NaSIPA) on the SSP rate, due to the importance of the pertinent sulfonated ionomers in the polyamide industry. Under the specific experimental conditions, the copolyamides with NaSIPA exhibited lower SSP rates than PA 6,6 homopolymer and their retarding behavior was found proportional to the comonomer content. A possible retardation mechanism related to the NaSIPA ionic species has been suggested and verified through modifying the kinetics so as to describe and predict the copolyamide SSP performance.

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Keywords: Nylon 6,6; Solid state polymerization; Ionomers

1. Introduction

With condensation polymers, such as polyamides (PAs) and polyesters (PES), one of the routes to high molecular weight products has been through solid state polymerization (SSP) [1,2]. Starting materials (prepolymers) are heated to a temperature higher than the glass transition point (T_g) but lower than the onset of melting (T_m) and polycondensation progresses through chain end reactions in the amorphous phase of the semicrystalline polymer; reaction by-products are removed by maintaining reduced pressure or through convection caused by passing inert gas [3–10]. As both chemical and physical attributes are involved, SSP comprises a complex process. Based on the reversible polycondensation reaction and on the restrictions set by SSP nature, one can identify several rate-determining steps (Table 1), estimating also the influence

of the main process variables, e.g. temperature, prepolymer molecular weight (MW_0), crystallinity (x_c), reacting particle geometry and catalyst, on the overall process rate [3].

The aforementioned parameters are thoroughly investigated in the literature, regarding homopolymers' SSP, and associated with the pertinent reaction mechanisms [3,7,8,10]. On the other hand, the amount of published SSP data on ion-modified PAs (e.g. sulfonated copolymers) is quite limited, and thus the effect of the polyamide chemical composition on the process has not been yet fully investigated. On this basis, the compositional effects caused by the incorporation of sodium 5-sulfoisophthalic acid (NaSIPA) (Fig. 1a) in polyhexamethylenedipamide (PA 6,6) are herewith studied during SSP, taking into account the expansion of the pertinent sulfonated ionomers in the polyamide industry. In particular, polymers modified with ionic groups constitute a very effective approach of changing significantly both chemical and physical properties of the parent polymer over a broad range. Regarding polyamides and polyesters, e.g. PA 6,6 and poly(ethylene terephthalate) (PET), the most

* Corresponding author. Tel.: +30 210 7723179; fax: +30 210 7723180.
E-mail address: kp@softlab.ece.ntua.gr (C.D. Papaspyrides).

Table 1
Dependence of the most important variables on the SSP controlling mechanism in the absence of gas phase resistance [3]

Controlling mechanism	Parameters				
	Reaction temperature (T)		Particle size	MW_0 and x_c	Catalyst
	At low T	At high T			
Chemical reaction	Yes (strong influence)	Yes (weak influence)	No	No	Yes
End group diffusion	Yes (weak influence)	Yes (strong influence)	No	Yes	No
Interior by-product diffusion	Yes (weak influence)	Yes (strong influence)	Yes (strong influence)	Yes	Yes

commercially important ion-modified resins contain 1–5 mol% NaSIPA, and, in particular, PET containing NaSIPA was originally commercialized by DuPont in 1958 under the trade name of Dacron[®] 64 [11].

From a commercial and industrial point of view, the main advantage of the sulfonated copolymers is the improvement of the polymer dyeability to cationic dyes, resulting in fibers or films with deep and brilliant colors and resistance to stains, fading and yellowing throughout their life cycle [12–15]. More specifically, the incorporation of NaSIPA sulfonate groups (SO_3^-) in the polymer chain favors each step of the dyeing process, through considerably increasing the negative charge (zeta potential) of the fiber surface and thus the electrostatic interactions associated with this [12,13]. In addition, NaSIPA introduction improves the polymer resistance to acid stains, since the SO_3^- units “block” the protonated polyamide terminal groups, i.e. NH_3^+ ($[NH_3^+] = [NH_2]$), which are present in the melt and solid states [16,17] (Eq. (1)). Thereby, the amine groups are no longer available to absorb acid stains (e.g. wine and soft drinks) [13–15], which is really important for applications like flooring covers. Finally, the ionic units of NaSIPA reduce permanently the fiber tendency to static electricity, improving the quality of the textile [15].



Apart from NaSIPA use in polyamide fiber applications, it has been also found that its presence improves the polymer operability during subsequent processing, which is often deteriorated by the presence of both pigment and copper. For this reason, the preferred range of NaSIPA to be used is 1–2 wt.% (added at the salt stage, i.e. prior to 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 [18].

NaSIPA consists of a difunctional compound (aromatic sulfodicarboxylic acid) and is introduced in the polymer chain through copolymerization. In Fig. 1b, the structure of the NaSIPA-modified PA 6,6 is presented, where y varies between 0.95 and 0.99 and x between 0.01 and 0.05 corresponding to

1–5 mol% NaSIPA [11,19,20]. The comonomer is usually added during the initial stages of the conventional solution-melt polyamidation [15,21] or through melt polycondensation of PA 6,6 homopolymer with master-batch containing NaSIPA [14]. However, the sulfonated PA 6,6 copolyamides generally have high melt viscosities, which limit the extent of melt polymerization as well as hinder the effective discharge of the polymerized melt from the reactor [11,14]. As a result, the conventional solution-melt polycondensation is interrupted at a low or medium molecular weight product, meanwhile, in cases where higher molecular weights are required, the sulfonated PA 6,6 prepolymers are further polymerized in the solid phase (SSP).

The current paper investigates the mechanism prevailing during the ionomer-based solid state polymerization processes. The effect of NaSIPA on PA 6,6 SSP is thoroughly examined, considering the importance of the additive in industrial scale and that its presence affects the majority of nylon production lines. Even more, this effort is of significant interest, since, nowadays, the nylon industry has moved away from PA 6,6 homopolymer and seeks for modified polyamides with dramatically better properties at comparable prices.

2. Experimental

2.1. Starting materials

PA 6,6 resins were supplied by DuPont Co. (Wilmington, Delaware). The prepolymers were prepared through polycondensation of aqueous salt solutions. PA 6,6 homopolymer was made using an aqueous PA 6,6 salt solution and PA 6,6 copolyamides with NaSIPA at three different concentrations (1, 2 and 3% w/w) were prepared through polycondensation of aqueous PA 6,6 salt and HMD/NaSIPA salt solutions. In all grades preparation, no other additive was used. The samples were in the form of flakes and, prior to any SSP runs, they were sieved and dried under vacuum (80 °C, 4 h). The particle size selected for the SSP runs was 10–12 mesh (1.7–1.4 mm).

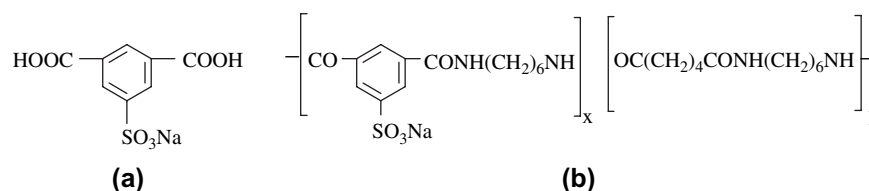


Fig. 1. Structure of (a) sodium 5-sulfoisophthalic acid (NaSIPA) and (b) PA 6,6 copolyamide with NaSIPA.

2.2. SSP runs

A bench scale reactor, assembled by DuPont Co., with a 50 g resin capacity was used to solid state polymerize all polyamide grades in the temperature range of 160–200 °C (0–4 h) under flowing and static nitrogen. The cylindrical, stainless steel reactor was equipped with a gas inlet below the sample chamber, to permit preheated purge gas (nitrogen, N₂ purity 99,999%) to pass through the polymer bed during reaction. The purge gas was used to distribute heat evenly throughout the sample chamber and to remove volatile reaction products. The nitrogen, controlled at a constant predetermined flow rate (260 mL/min), was preheated while passing through a coil of 1/8 in stainless steel tubing. Thermocouples at two individual locations within the reaction chamber were used to monitor polymer temperature during SSP. A fluidized sand bath (Techne Corporation) was used to heat the reactor and the purge gas. Four heating elements were used to heat the sand, fluidized by air, to the SSP temperatures.

The reactor was first filled with dried and sieved prepolymer (30 g), closed and examined for leaks through a pressure test. It was then left overnight under a constant nitrogen flow (18 mL/min) in order to remove oxygen. The temperature of the sand bath was raised to the SSP temperature (T_R) and the reactor was immersed in the fluidized bath, and in case the run corresponds to “0 h”, the SSP reactor was immediately removed from the bath as soon as the temperature reached T_R . This way, the effect of the heating time was included in the current study and the properties of the grades at zero time were considered as the initial ones. For longer reaction time (2 and 4 h), the experiment was considered to begin from the point where the reactor interior temperature was T_R . After the completion of the reaction, the reactor was cooled ($T < 40$ °C), the product was removed from the reactor vessel, placed in a plastic container, sealed and stored in a dessicator.

2.3. Polyamide characterization

PA 6,6 prepolymers and SSP products were analyzed to determine end group contents, relative viscosity (RV), molecular weight distribution (MWD) and their melting characteristics. The reproducibility of the results was estimated on the values of the standard deviation of the mean (SDM).

2.3.1. End group analysis

The end group concentrations were determined by potentiometric titration. For amine end determination ([NH₂]), the samples were dissolved in a mixture of 85% phenol–15% methanol (w/w) and titrated with a solution of perchloric acid in methanol. For acid end analysis ([COOH]), the polymer was dissolved in a mixture of 5:1 *o*-cresol–5% *o*-dichlorobenzene:20% LiCl/methanol and titrated with a solution of tetrabutyl ammonium hydroxide in benzyl alcohol.

2.3.2. Viscosity measurements

The relative viscosity (RV) of PA 6,6 is the ratio of the viscosity of a solution of 8.4% (w/w) polymer in a solution of

90% formic acid to the viscosity of the formic acid solution (ASTM D789 (1978)). Viscosity measurements were performed using a Cannon–Fenske viscometer at 25 °C.

2.3.3. Molecular weight distribution (MWD)

The samples were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with 0.01 M sodium trifluoroacetate and then analyzed by size exclusion chromatography, using the system Model Alliance 2690 (Waters Corporation, Milford, MA).

2.3.4. Differential scanning calorimetry (DSC)

The DSC analysis was performed in the range of 30–300 °C, using a heating rate of 10 °C/min. The system used was Perkin–Elmer DSC 4.

3. Results and discussion

3.1. Theoretical

SSP kinetics were studied using a simple 3rd order Flory theory-based model (Eq. (2)), considering only the polycondensation reaction, due to the low reaction temperature and due to the constant by-product removal through convection caused by passing nitrogen. The pertinent rate expression fits end group-based SSP data very well and it is adequate to describe the overall process. In particular, in a previous publication of ours [22], it was effectively used for the SSP of PA 6,6 prepolymers with carboxyl end group excess, as in our case regarding the starting materials (Table 2), meanwhile it was also satisfactorily tested for different polyamides under various conditions.

$$\begin{aligned} -\frac{d[\text{COOH}]}{dt} &= k_3[\text{COOH}]^2[\text{NH}_2] \Rightarrow \frac{dx}{dt} \\ &= k_3([\text{COOH}]_0 - x)^2([\text{NH}_2]_0 - x) \\ &\times \int \rightarrow \frac{1}{D_0^2} \ln \frac{[\text{COOH}]_0 - [\text{NH}_2]_0 p_t}{[\text{COOH}]_0 (1 - p_t)} \\ &- \frac{1}{D_0} \left(\frac{1}{[\text{COOH}]_0 - [\text{NH}_2]_0 p_t} - \frac{1}{[\text{COOH}]_0} \right) \\ &= k_3 t \end{aligned} \quad (2)$$

where, x is the concentration of the reacted groups (meq/kg), $[\text{COOH}]_0$ and $[\text{NH}_2]_0$ the initial concentrations of the carboxyl and amine end groups (meq/kg), D_0 the initial carboxyl end group excess (meq/kg), p_t the polymerization conversion calculated at any given reaction time based on the amine concentration and k_3 the apparent SSP rate constant for 3rd order kinetics ((kg/meq)² h⁻¹).

The application of this simple kinetic model led to values of the apparent rate constants at any given reaction time; on this basis, a mean value was determined and the standard deviation of the mean (SDM) was calculated indicating the model's effectiveness.

Table 2
Characterization of the SSP starting materials

	C_s (meq/kg)	T_m (°C)	ΔH_m (cal/g)	RV	[NH ₂] (meq/kg)	[COOH] (meq/kg)	\overline{M}_n (g/mol)
PA 6,6 homopolymer (PA)	0	261.6	13.4	64.24 ± 0.05%	48.904 ± 0.194	69.048 ± 0.290	16,956
PA 6,6 copolyamide with 1% w/w NaSIPA (PA1)	34	260.7	12.0	60.33 ± 0.08%	52.016 ± 0.114	71.907 ± 0.585	16,139
PA 6,6 copolyamide with 2% w/w NaSIPA (PA2)	67	261.1	10.8	56.57 ± 0.07%	51.710 ± 0.350	79.360 ± 3.126	15,259
PA 6,6 copolyamide with 3% w/w NaSIPA (PA3)	100	257.2	10.1	51.93 ± 0.02%	55.580 ± 0.129	84.614 ± 1.706	14,266

3.2. SSP results under flowing nitrogen

The characterization of the SSP starting materials is presented in Table 2, in which the concentrations of the sulfonate (SO₃⁻) groups (C_s) in the PA 6,6 copolyamides with NaSIPA were also calculated, based on the amount of NaSIPA used during prepolymerization. The prepolymer grades were characterized by relative viscosity (RV) in the range of about 52–64 and they exhibited \overline{M}_n values of about 14,300–17,000 g/mol, which, however, decreased as a proportion of the NaSIPA content, implying slower polycondensation rates regarding the melt technique, as also mentioned in literature [11,14]. Regarding DSC data, the melting points ($T_m = 257.2$ – 261.6 °C) were rather declining with NaSIPA content and this was clearly the case for enthalpy of fusion (ΔH_m). Apparently, the presence of the comonomer in the polymer chain molecules makes the structure less compact and organized, as it is also confirmed in the literature [12,19] by the higher diffusion rate of the dye-stuff in the sulfonated copolyamides.

The SSP runs under flowing nitrogen were carried out at three reaction temperatures and the results are shown in Tables 3–5. In all cases, the effectiveness of SSP as a post-polymerization technique was proved independent of the nature of the reacting grade. After 4 h of SSP, the RV and \overline{M}_n values increased by 3–116% and 4–31%, respectively (in comparison to the initial values for $t = 0$ h). The same trend

was valid with the reaction temperature (T) rise; as anticipated, T emerged as the most important process parameter, due to its interaction with almost all aspects of the process: an increase of the SSP temperature speeds up the chemical reaction, the mobility of the functional end groups and the by-product diffusion.

Examining the melting characteristics of the SSP products ($t = 4$ h), it can be seen that, in most cases, the enthalpy of fusion (ΔH_m) slightly decreased throughout SSP; apparently, under the specific experimental conditions, the increase of molecular weight during SSP inhibited the chain folding in the crystalline phase, clearly due to mobility reasons. The macromolecules obtained higher molecular weight, which impeded their segmental mobility and arrangement in the lattice, meanwhile favored the creation of crystal defects, causing also a slight decrease in T_m . Synergistic action for the observed slight crystallinity decrease may have the potential interchange reactions occurring during SSP, which could also cause an increase in the lattice defects. The pertinent reactions, such as amine–amide and acid–amide interchanges, are considered to play a fundamental role during SSP, by providing a mechanism for end group functionality to migrate and thus facilitate polymerization [23]. However, they induce morphological changes in the polymer structure, through creating loops and bridges and therefore producing a structural reorganization of the amorphous and crystalline regions of the polymer.

Table 3
SSP results at 160 °C under flowing nitrogen

T (°C), t (h)	T_m (°C)	ΔH_m (cal/g)	RV	[NH ₂] (meq/kg)	[COOH] (meq/kg)	\overline{M}_n (g/mol)	p_t
<i>PA 6,6 (PA)</i>							
160, 0	261.6	13.4	65.81 ± 0.04%	46.750 ± 0.095	68.675 ± 0.149	17,327	0.000
160, 2			82.12 ± 0.03%	43.619 ± 0.245	67.436 ± 0.777	18,009	0.067
160, 4	261.1	13.4	90.72 ± 0.03%	40.706 ± 0.181	62.680 ± 1.300	19,345	0.129
<i>PA 6,6 + 1% w/w NaSIPA (PA1)</i>							
160, 0	260.7	12.0	68.17 ± 0.03%	50.576 ± 0.160	72.354 ± 0.681	16,269	0.000
160, 2			68.20 ± 0.04%	47.345 ± 0.218	72.367 ± 0.313	16,707	0.064
160, 4	261.0	11.7	70.20 ± 0.10%	44.755 ± 0.128	67.611 ± 0.465	17,799	0.115
<i>PA 6,6 + 2% w/w NaSIPA (PA2)</i>							
160, 0	261.1	10.8	57.57 ± 0.02%	49.603 ± 0.146	77.592 ± 1.862	15,724	0.000
160, 2			60.60 ± 0.03%	47.045 ± 0.312	75.798 ± 1.457	16,281	0.052
160, 4	260.0	10.6	67.10 ± 0.03%	44.655 ± 0.028	73.134 ± 1.777	16,980	0.100
<i>PA 6,6 + 3% w/w NaSIPA (PA3)</i>							
160, 0	257.2	10.1	52.32 ± 0.06%	54.822 ± 0.809	81.169 ± 1.177	14,707	0.000
160, 2			53.88 ± 0.03%	52.885 ± 0.995	82.761 ± 0.635	14,744	0.035
160, 4	258.3	9.3	59.90 ± 0.01%	49.951 ± 0.616	80.328 ± 1.852	15,352	0.089

Table 4
SSP results at 180 °C under flowing nitrogen

T(°C), t(h)	T_m (°C)	ΔH_m (cal/g)	RV	[NH ₂] (meq/kg)	[COOH] (meq/kg)	\bar{M}_n (g/mol)	p_t
<i>PA 6,6 (PA)</i>							
180, 0	261.6	13.4	65.55 ± 0.02%	44.307 ± 0.024	67.344 ± 1.459	17,913	0.000
180, 2			86.12 ± 0.00%	37.738 ± 0.043	60.107 ± 0.354	20,440	0.148
180, 4	261.2	12.8	105.16 ± 0.09%	34.472 ± 0.031	59.204 ± 0.427	21,350	0.222
<i>PA 6,6 + 1% w/w NaSIPA (PA1)</i>							
180, 0	260.7	12.0	63.80 ± 0.03%	48.616 ± 0.024	67.093 ± 2.750	17,285	0.000
180, 2			75.50 ± 0.04%	42.073 ± 0.114	62.282 ± 2.736	19,165	0.135
180, 4	260.8	11.0	94.11 ± 0.30%	39.188 ± 0.368	60.838 ± 0.476	19,995	0.194
<i>PA 6,6 + 2% w/w NaSIPA (PA2)</i>							
180, 0	261.1	10.8	59.92 ± 0.10%	47.927 ± 0.223	77.211 ± 0.362	15,982	0.000
180, 2			71.32 ± 0.01%	42.332 ± 0.111	68.177 ± 0.891	18,098	0.117
180, 4	260.0	10.2	91.04 ± 0.28%	38.860 ± 0.010	63.917 ± 0.554	19,460	0.189
<i>PA 6,6 + 3% w/w NaSIPA (PA3)</i>							
180, 0	257.2	10.1	53.46 ± 0.07%	53.520 ± 0.217	83.660 ± 0.809	14,579	0.000
180, 2			73.92 ± 0.03%	47.600 ± 0.182	79.147 ± 0.523	15,779	0.111
180, 4	257.9	10.2	81.56 ± 0.25%	43.344 ± 0.029	73.487 ± 0.404	17,119	0.190

Furthermore, SEC was performed on PA and PA3 regarding the high reaction temperature (200 °C) and the polydispersity index (PDI) reached 2.28 and 2.48, respectively, after 4 h of SSP, presenting a suitable material for processing. The PDI increased (initial values: 1.93 and 1.90) similarly for both materials and this rise is in accordance with Flory theory [24], which states that molecular weight distribution (MWD) widens during a typical linear step polymerization. Degradation reactions seem to be avoided, because otherwise they would result in a narrowing of MWD [25].

Turning to the effect of NaSIPA on the PA 6,6 SSP, at each reaction temperature, the copolyamides exhibited reduced SSP rates, as indicated by the lower, in each case, final RV, \bar{M}_n and p_t values. For example, at 160 °C, polymerization was slowed down when increasing the NaSIPA content and PA3 presented the lowest final polymerization conversion: after 4 h of SSP, for PA p_t was 13%, for PA1 $p_t = 12\%$, for PA2 $p_t = 10\%$ and for PA3 $p_t = 9\%$. The same observation has been also made

in the monomers SSP [26], where the presence of the comonomer (NaSIPA) even at the low concentration of 1% w/w reduced the overall rate of the process in comparison to pure PA 6,6 salt.

The aforementioned retarding behavior of the copolyamides becomes even more clear when comparing the apparent rate constants (k_3) for 3rd order kinetics (Eq. (2)): PA 6,6 homopolymer presented the higher rate constant in the temperature range of 160–200 °C (Fig. 2) and, more specifically, k_3 decreased by 11–57% as the amount of NaSIPA increases. Finally, based on the relevant Arrhenius plots (R^2 : 0.9955–1), the activation energy values were found in the range of 65.98–80.51 kJ/mol (Eq. (3)–(6)), lying within the limits referred in literature (42–318 kJ/mol) [22].

$$\text{PA: } k_3 = 4.8 \times 10^{-6} \exp\left(\frac{-70,476}{R} \left(\frac{1}{423} - \frac{1}{T}\right)\right) \quad (3)$$

Table 5
SSP results at 200 °C under flowing nitrogen

T (°C), t (h)	T_m (°C)	ΔH_m (cal/g)	RV	[NH ₂] (meq/kg)	[COOH] (meq/kg)	\bar{M}_n (g/mol)	p_t
<i>PA 6,6 (PA)</i>							
200, 0	261.6	13.4	85.81 ± 0.01%	40.415 ± 0.034	61.307 ± 0.518	19,662	0.000
200, 2			134.72 ± 0.19%	30.557 ± 0.672	56.387 ± 1.002	23,003	0.244
200, 4	262.0	11.8	185.68 ± 0.05%	26.711 ± 0.179	51.171 ± 1.161	25,680	0.339
<i>PA 6,6 + 1% w/w NaSIPA (PA1)</i>							
200, 0	260.7	12.0	84.63 ± 0.05%	44.406 ± 0.020	61.806 ± 0.878	18,830	0.000
200, 2			127.40 ± 0.10%	35.635 ± 0.191	61.148 ± 1.626	20,665	0.198
200, 4	259.3	10.9	169.72 ± 0.49%	31.505 ± 0.031	56.308 ± 2.335	22,776	0.291
<i>PA 6,6 + 2% w/w NaSIPA (PA2)</i>							
200, 0	261.1	10.8	90.40 ± 0.19%	44.504 ± 0.051	67.860 ± 2.038	17,799	0.000
200, 2			121.17 ± 0.10%	35.355 ± 0.117	61.290 ± 2.036	20,694	0.206
200, 4	259.0	10.7	158.25 ± 0.08%	31.518 ± 0.177	58.891 ± 2.027	22,122	0.292
<i>PA 6,6 + 3% w/w NaSIPA (PA3)</i>							
200, 0	257.2	10.1	69.06 ± 0.15%	50.030 ± 0.286	74.693 ± 1.601	16,036	0.000
200, 2			101.38 ± 0.00%	39.845 ± 0.384	69.232 ± 2.069	18,336	0.204
200, 4	259.5	8.8	139.32 ± 0.29%	35.304 ± 0.282	62.103 ± 3.609	20,532	0.294

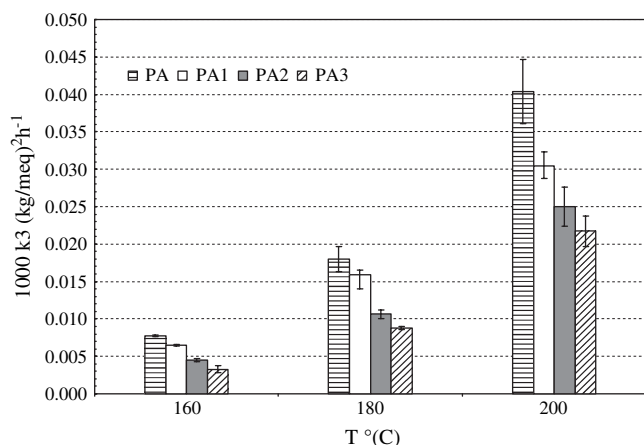


Fig. 2. Rate constants (k_3) during SSP under flowing nitrogen at three reaction temperatures.

$$\text{PA1} \quad k_3 = 4.3 \times 10^{-6} \exp\left(\frac{-65,984}{R}\left(\frac{1}{423} - \frac{1}{T}\right)\right) \quad (4)$$

$$\text{PA2} : \quad k_3 = 2.8 \times 10^{-6} \exp\left(\frac{-72,951}{R}\left(\frac{1}{423} - \frac{1}{T}\right)\right) \quad (5)$$

$$\text{PA3} : \quad k_3 = 1.9 \times 10^{-6} \exp\left(\frac{-80,513}{R}\left(\frac{1}{423} - \frac{1}{T}\right)\right) \quad (6)$$

where, k_3 is the apparent SSP rate constant for 3rd order kinetics ($(\text{kg}/\text{meq})^2 \text{h}^{-1}$) under flowing nitrogen, T the absolute reaction temperature (K) and R the universal gas constant ($\text{J}/\text{mol K}$).

3.3. SSP results under static nitrogen

SSP runs were carried out under static nitrogen, using PA 6,6 homopolymer (PA) and copolymer containing 3% w/w NaSIPA (PA3) at 160 and 200 °C for 4 h. Regarding NaSIPA negative effect on the SSP process, the picture remained the same (Table 6). In addition, the importance of the by-product removal was revealed, since the rate constants under static (k_3^s) decreased by 12–19% in comparison to the flowing nitrogen processes. However, this decrease under static did not significantly vary when comparing PA and PA3, showing that both grades “experienced” similar difficulty in removing the polycondensation water. This observation seems quite useful as discussed below.

Table 6
Rate constants (k_3^s) during SSP under static nitrogen and % decrease of the rate when comparing static and flowing nitrogen processes

Samples	1000 k_3^s (kg/meq) ² h ⁻¹	%($k_3^s - k_3$)/ k_3
160 °C		
PA	0.006577	-15%
PA3	0.003059	-19%
200 °C		
PA	0.031866	-12%
PA3	0.016762	-15%

3.4. Retardation mechanism – kinetics

The SSP behavior of the ionomers was further studied so as to explore the relevant reaction mechanism. The retardation reasons were first of all sought in the different properties of the copolyamides against the homopolymer. Thus, the retarding behavior may be attributed to the anticipated higher by-product removal resistance in the NaSIPA-modified grades, due to the increased hygroscopic sites of the additive structure. Based on the literature findings, the presence of the sodium sulfonate groups hinders drying, meanwhile it may initiate and/or catalyze the hydrolysis reaction. This was suggested in the case of sulfonated PET copolymers that are found to be significantly susceptible to acidic hydrolysis and exhibiting much higher hydrodegradability compared to pure PET [27]. However, our SSP results under static nitrogen indicated that the hygroscopicity of the additive structure cannot fully explain the dramatic rate decrease (almost 57%) observed in the copolyamide samples, since PA and PA3 showed similar difficulty in the removal of the polycondensation water during SSP.

On the other hand, if considering the effect of the aromatic comonomer (isophthalic acid) on the SSP slowdown, it may be assumed that this does not apply here, since in the case of PET copolyesters with isophthalic acid, the SSP performance was exactly the opposite: the rate constants for the copolymers increased as a function of the aromatic diacid content, probably due to the less compact structures and due to the thus increased diffusion of by-products [28].

Further, the SSP process might have been influenced by the morphology of the sulfonated ionomers. According to the model proposed by Eisenberg et al. [29] for random ionomers, the NaSIPA ionic moieties aggregate into “multiplets” (Fig. 3a), which, in turn, aggregate themselves into “clusters” (Fig. 3b), creating finally a contiguous phase of restricted mobility in the polymer mass. Accordingly, during the SSP of the NaSIPA-containing copolyamides, 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 and/or the water escape, slowing down the SSP reaction. However, the herewith experimentally observed rate decrease increased proportionally to NaSIPA amount and this cannot be explained solely by the aforementioned aspects.

Based on the above considerations, another mechanism is proposed regarding the ion-modified PA 6,6 SSP. The retardation is correlated to the partial deactivation of the amine ends by the sulfonate (SO_3^-) units (Eq. (1)), which exist in the amorphous regions of the copolyamides. As a result, there are two types of end groups, namely active ($[\text{NH}_2]_{\text{active}}$) and inactive ($[\text{NH}_2]_{\text{inactive}}$) amine ends. The former are able to participate in the polymerization reaction and their concentration in the copolyamides is lower against PA 6,6 homopolymer, resulting in reducing the reactant concentration and thus the reaction rate. The inactive amine groups are attached to SO_3^- in the restricted mobility domains (clusters) and their constant concentration during SSP is assumed to be a fraction of the total amine ends, depending on the SO_3^- content, the reaction temperature and the morphology of the ionomer.

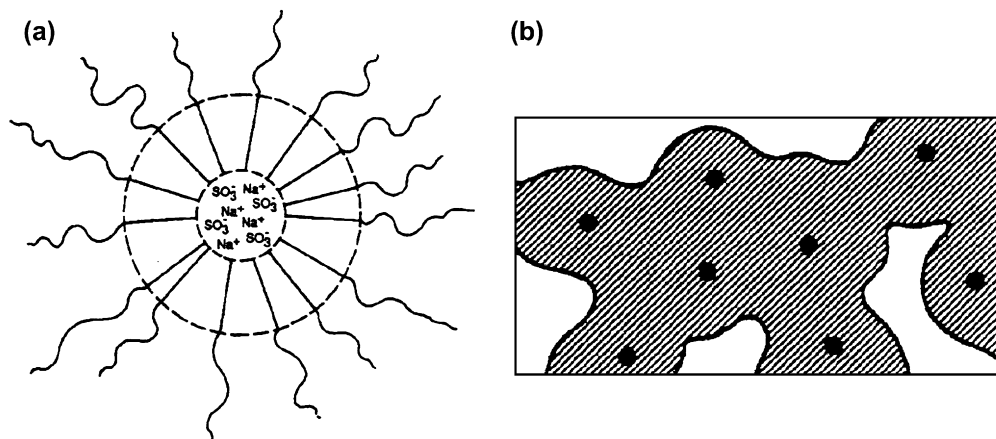


Fig. 3. Scheme of the restricted mobility model regarding the sulfonated random ionomers by Eisenberg et al. [29]. (●) = ionic multiplets, the hatched area = the restricted mobility domain (clusters) and the unmarked area = the unclustered matrix.

According to this mechanism, it is proposed that the active amine ends are less than the experimentally measured value ($[\text{NH}_2]_{\text{total}}$) and more specifically decrease proportionally (Eq. (7)) to a function of the sulfonate groups (C_s), using also a “deactivation factor” ($1/J$). The latter reflects the influence of the different ionomers’ morphology and of the reaction temperature on the concentration of the inactive amine groups.

$$[\text{NH}_2]_{\text{active}} = [\text{NH}_2]_{\text{total}} - [\text{NH}_2]_{\text{inactive}} = [\text{NH}_2]_{\text{total}} - [\text{NH}_2]_{\text{total}} \frac{C_s}{J} \quad (7)$$

where $[\text{NH}_2]_{\text{total}}$ is the amine end concentration measured experimentally (meq/kg), C_s the sulfonate group content (meq/kg) and $1/J$ the deactivation factor (J in meq/kg).

The 3rd order rate expression can be modified (Eq. (2)), so as to involve the $[\text{NH}_2]_{\text{active}}$ and the concentration of the sulfonate ends (C_s), explaining also why the SSP rate retardation increases with NaSIPA content (Eq. (8)).

$$\begin{aligned} \frac{-d[\text{COOH}]}{dt} &= k_{\text{copolyamide}} [\text{COOH}]^2 [\text{NH}_2]_{\text{total}} \\ &= k_{\text{copolyamide}} [\text{COOH}]^2 \frac{[\text{NH}_2]_{\text{active}}}{1 - (C_s/J)} \end{aligned} \quad (8)$$

where $k_{\text{copolyamide}}$ is the apparent SSP rate constant of the copolyamides for 3rd order kinetics ($(\text{kg}/\text{meq})^2 \text{h}^{-1}$).

This modified rate expression implies that the SSP kinetics are the same independent of the starting material, as indicated also by the similar activation energy values deduced (Eqs. (3)–(6)), meanwhile the main retardation reason is the reduction of the reacting species content. As a result, the apparent SSP rate of the copolyamides could be correlated to that of PA 6,6 homopolymer ($k_{\text{PA6,6}}$) through Eq. (9):

$$k_{\text{copolyamide}} = k_{\text{PA6,6}} \left(1 - \frac{C_s}{J} \right) \quad (9)$$

The assumption of the inactive amine ends’ mechanism was tested through examining the fitting of our SSP experimental data to Eq. (9). For all reaction temperatures, the ratio of

$k_{\text{copolyamide}}/k_{\text{PA6,6}}$, based on the data in Fig. 2, was plotted versus C_s (Table 2) and the linearity ($R^2 = 0.9538$) (Fig. 4) verified the validity of the suggested mechanism. The slope of the line represents the deactivation factor and was found to be equal to $-0.0053 \text{ kg}/\text{meq}$, i.e. J is equal to 189 meq/kg. This value of C_s/J may be considered as the fractional decrease of the total amine ends in the copolyamide grades, i.e. for PA1, the active amine ends are 82% of the experimentally measured value, for PA2 65%, and for PA3 47%.

Considering also the Arrhenius equation for PA 6,6 homopolymer SSP (Eq. (3) as well as Eq. (9)), the compositional effect of NaSIPA on the SSP apparent rate constant can be assessed when knowing C_s and T (Eq. (10)). A further modification of this rate expression can be made (Eq. (11)), in order to include the slight effect of reaction temperature on the deactivation factor. $1/J$ values were calculated for each reaction temperature and were successfully expressed as an exponential function of $1/T$ (R^2 : 0.9773). In particular, $1/J$ decreased to some extent with temperature, apparently due to the induced increase of reacting species mobility in ionomers, resulting in inactive amine ends’ partial rejection from clusters and finally activation with T rise.

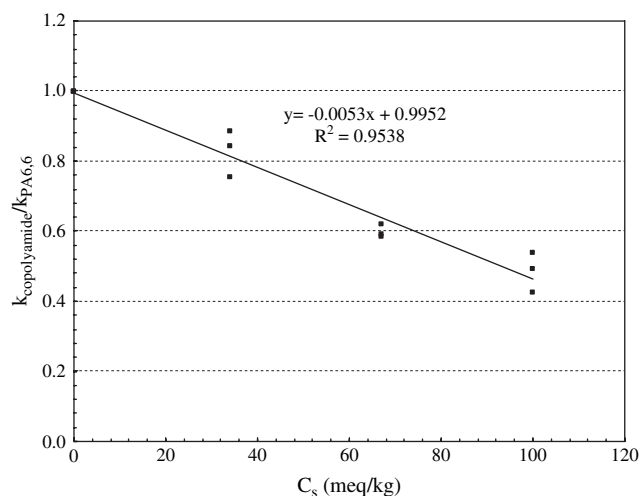


Fig. 4. Fitting of Eq. (9) regarding the SSP of all polyamide grades under flowing nitrogen (160–200 °C).

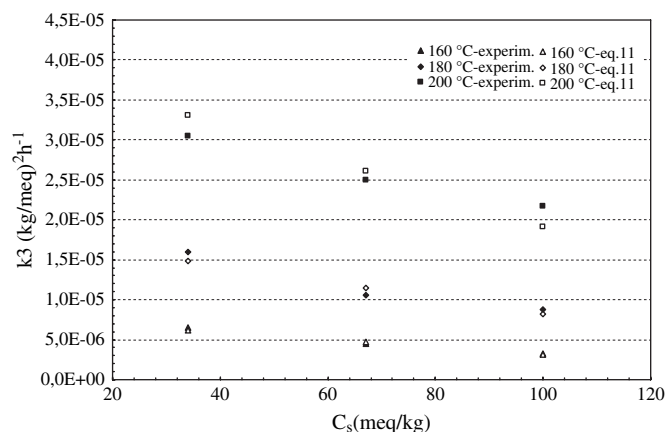


Fig. 5. Fitting of Eq. (11) regarding the SSP of all polyamide grades under flowing nitrogen (160–200 °C).

$$k_{\text{copolyamide}} = 4.8 \times 10^{-6} \exp\left(\frac{70,476}{R} \left(\frac{1}{423} - \frac{1}{T}\right)\right) \times \left(1 - \frac{C_s}{189}\right) \quad (10)$$

$$k_{\text{copolyamide}} = 4.8 \times 10^{-6} \exp\left(\frac{70,476}{R} \left(\frac{1}{423} - \frac{1}{T}\right)\right) \times \left(1 - 6 \times 10^{-3} \exp\left(\frac{-4587}{R} \left(\frac{1}{423} - \frac{1}{T}\right)\right)\right) \times C_s \quad (11)$$

Eq. (11) results deviate slightly from the experimental SSP data (Fig. 5) and this final rate expression may be successfully used in simulation models, especially since the relevant reaction rate constants are usually extrapolated from melt polymerization data despite the very different morphology of the solid polymer.

4. Conclusions

The performance of ion-modified polyamides was examined during solid state polymerization, giving emphasis on sodium 5-sulfoisophthalic acid (NaSIPA) effect due to its significance in polyamide industry. This dyeability modifier was used as a comonomer at different concentrations resulting in PA 6,6 copolyamides, which were submitted to SSP runs in the temperature range of 160–180 °C. The overall SSP rate constants and activation energies (66–81 kJ/mol) were calculated, indicating the retarding behavior of the copolyamides with NaSIPA. A retardation mechanism was herewith suggested and based on the amine ends' partial deactivation, due to their attachment to NaSIPA sulfonate groups. As a result, in copolymer samples, the active amine ends, able to participate in the polymerization

reaction, are less than that in PA 6,6 homopolymer, reducing the reactant concentration and thus the reaction rate. The above mechanism was verified through testing for fitting the modified copolyamide kinetics, where the concentration of the sulfonate groups was incorporated.

Acknowledgements

The authors gratefully thank Dr. C. Tsenoglou for his significant contribution regarding data treatment as well as Mr. T. Karlatiras for his help during the SSP runs.

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