

Investigating alternative routes for semi-aromatic polyamide salt preparation: The case of tetramethylenediammonium terephthalate (4T salt)

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ABSTRACT: In the current article, the effect of different techniques was investigated on the preparation of tetramethylenediammonium terephthalate (4T salt), which consists of an industrially important precursor of high-performance polyamides. In particular, 4T salt was synthesized through solution, slurry, and solvent-free techniques. In each case the salt was isolated as a solid, correlating for the first time the salt preparation/isolation method with attained properties and morphology. This correlation led to a generalized comparison between all synthesized 4T salt grades, aiming at understanding the preparation mechanism of 4T salt. Accordingly, highly pure 4T salt, free of any unreacted diacid traces, can be only obtained from a clear salt solution either by cooling or by nonsolvent addition. Furthermore, by altering the crystallization conditions of the salt, thermal and morphological properties can be significantly affected, which further result in a qualitative correlation with the rate of subsequent direct solid-state polymerization (DSSP). The DSSP reactions were carried out in the microscale of a thermogravimetric chamber, where the different 4T salt grades were heated isothermally until full conversion. Polyamide grades of different thermal and analytical properties were received, underlining that the quality of the salt is a corner stone for subsequent DSSP. These findings can be further exploited also to the DSSP of other semi-aromatic polyamides. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42987.

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INTRODUCTION

Polyamides (PAs) are step-growth polymers having repeating amide bonds in their backbone. PAs can be classified into (a) aliphatic polyamides, derived only from straight chain monomers (e.g., poly(hexamethylene adipamide), PA 66), (b) aramides which have more than 85% of their amide bonds directly connected to two aromatic groups, and (c) semi-aromatic polyamides, consisting of aliphatic monomers and monomers with aromatic moieties. Commercially important semi-aromatic PAs are those in which terephthalic acid (TA) and/or isophthalic acid (IA) comprise at least 55% mol of the dicarboxylic acid moiety in the repeating unit.¹ These materials are often referred to as high-performance engineering polymers, due to their high melting temperature, high heat and chemical resistance, excellent dimensional stability, low water absorption, and high mechanical strength and stiffness. Thus, they are widely used in electronics (e.g., connectors, sockets, switches, surface mount devices, reflectors, and portable electronics housing) and light-

weight automobile applications (e.g., powertrain components and electrical systems).² In this article, the emphasis is given to poly(tetramethylene terephthalamide) (PA 4T), which is a component of commercial grades produced by DSM (Stanyl[®] Fortii[™]), a high-performance polyamide resin with a T_g around 125°C and a melting point in the range of 325°C.³

The first step for preparing diamine/diacid polyamides (-AABB- type) is usually the synthesis of the respective salt in order to ensure the proper end-group stoichiometry for achieving high-molecular-weight polymers.⁴ The salt is a distinct ionic compound, which is formed through proton exchange (neutralization reaction) between the diamine and the diacid. Due to its crystalline and neutral state, it is stable and almost harmless especially compared to the relevant diamines, and it permits safer, easier, and lower cost storing and transportation in large shipments.^{4,5} In addition, a stable salt may comprise the starting material for direct solid-state polymerization (DSSP).

Accordingly, the target in DSSP is to effect considerable polymerization progress, while maintaining the solid character of the reacting mass throughout the whole process.^{6,7} However, keeping the system in the solid state is not always achieved, although the applied temperature is lower than both the melting point of the salt and the polymer. In other words a distinct but strange transition from the solid to the melt state (SMT) occurs. This SMT phenomenon has been extensively studied by Paspaspyrides *et al.* and correlated to the role of the polycondensation water formed during reaction.^{8–12}

Typically, in most common industrial applications (e.g., synthesis of PA 66), salt formation is carried out in water. The reactants are added in the desired ratios in the salt preparation vessel along with water and optionally other additives. The resulting salt solution is stored temporarily or it is transferred to an autoclave reaction vessel to perform polymerization.⁵ The autoclave is then heated up while water is being removed gradually, until a highly concentrated (>85% wt) aqueous salt solution is obtained, which is further subjected to typical solution-melt polymerization.^{13–20} This means that at the late stages of the process, the reaction temperature exceeds the melting point of the polyamide formed. So this approach is characterized as a high-temperature polymerization route.

On the contrary, DSSP is in principle a low-temperature process and applies different technologies. The interest for DSSP so far is oriented mainly to aliphatic polyamide salts and still attracts the interest from both Academia and Industry, as all the problems associated with the high-temperature disadvantages of melt technology are completely excluded. In addition, due to the low temperature involved and the absence of solvents, DSSP is widely considered these days as a “green” polymerization route.^{8–10,21–30}

Especially for the case of PA 4T, there is extensive experimental evidence that it cannot be directly polymerized from tetramethylenediamine (TMD) and TA by melt or solution technique.³¹ Therefore, especially for PA 4T, DSSP is a potentially interesting polymerization technology; therefore, the necessity to prepare high quality 4T salt arises. Three preparation routes can be applied for preparing 4T salt, referred to as solution, slurry, and solvent-free technique.

The solution route involves mixing of alcoholic or aqueous solutions of the reactants.^{6,7,11,32,33} The salt may precipitate as soon as it is formed either by cooling or the precipitation is accomplished by adding a nonsolvent to the salt solution (i.e., “striking”). Typically, isopropyl alcohol or methanol is used as water miscible nonsolvents for the salt precipitation. Aliphatic salts, such as hexamethylenediammonium adipate (66 salt), can be easily prepared through the aforementioned technique, exhibiting high yields, mainly due to the sufficient solubility of not only the diamine but also the dicarboxylic acid monomer in the solvents used. This provides such a high reaction-specific surface that mixing of the reactants occurs on molecular level. Typical examples are given by Coffman *et al.*⁴ for several polymethylenediammonium dicarboxylates, by Gaymans *et al.*³⁴ for the preparation of 46 salt, and by Paspaspyrides *et al.*^{7,8,12,32} for

a variety of aliphatic salts including also long-chain cases, such as 126 and 6Y (Y = 6, 12, 13, 14) salts.

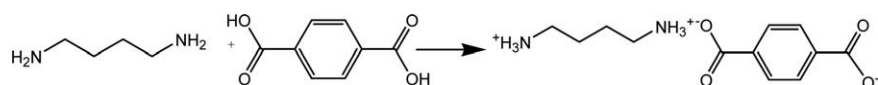
Regarding semi-aromatic polyamide salts, attempts using solution technique on lab scale were firstly described in 1961 by Volokhina *et al.*³⁵ and on large scale were firstly described in a patent of BP Chemicals.³⁶ According to BP, salt components were mixed in equimolar ratios in water under inert atmosphere. The resulting suspension was heated to boil until a salt solution was obtained, which was then rapidly cooled to its critical saturation temperature. Further cooling to ambient temperature occurred at a very slow rate until the salt was sufficiently precipitated. The semi-aromatic salt was then filtered and dried under vacuum. This process included no use of organic solvents and could be applied in a wide range of salts; however, in some systems, such as hexamethylenediammonium isophthalate (6I salt) or *m*-xylenediammonium terephthalate (MXDT salt), mass yield was found relatively low and precipitation proceeded further only with the addition of crystalline seeding materials. In another paper for long-chain semi-aromatic salts (e.g., XT salts, X = 10–13),^{37,38} similar process to³⁵ was employed; however, high ratios of nonsolvent (1:4–1:8 v/v) were added to the cooled salt solution in order to reach high yields.

In addition, Novitsky *et al.*^{39,40} proposed a preparation technique for several long-chain semi-aromatic salts (e.g., 10T or 12T salt), which includes mixing of both reactants in water and resulting in a slurry from the beginning, which was further heated up to reflux temperature until salt solution was obtained. Then, the received hot solution was added to a nonsolvent and left overnight in the refrigerator until the salt had precipitated. This particular technique is considered efficient in terms of the use of low nonsolvent amount; however, it cannot be easily adopted to salts of shorter diamines (e.g., TMD) due to their high volatility.

Gaymans *et al.*^{41,42} described a solution preparation route for 4T and 4I salts, according to which solid diacid (TA or IA) was added slowly into a dilute aqueous solution of TMD, resulting in the pertinent salt solution. The product was then precipitated at high yields by adding a nonsolvent (1:2 v/v in respect to solvent) and it was obtained as a colorless powder after filtration and drying. The main advantages of this process are the absence of external heating, permitting the use of short-chain and more volatile diamines, and the use of low nonsolvent amount, since the total amount of the water added was limited by the addition of solid TA.

Turning to slurry technique, one may say that it is more applicable to 4T salt case due to the low TA solubility in water or ethanol (solubility in water 1.7 mg/100 mL at 25°C).⁴³ This second route involves slurries of the reactants and the resultant salt remains in suspension. It, however, does not provide satisfactory specific surface for molecular mixing and may consequently leave upon filtration unreacted components in the sediment, leading to products of low purity and yields.

Finally, in order to completely exclude solvents during salt formation and to develop the solvent-free preparation technique, attempts to bring the pure components directly in contact with each other have been achieved. A first approach was made by Paspaspyrides *et al.*^{5,44} for the synthesis of 66 salt, in which a



Scheme 1. Neutralization reaction between TMD and TA.

simple technique of reacting adipic acid (AA) and hexamethylenediamine (HMD) in the presence of a cryogenic medium in a conventional dry blending equipment is suggested. More specifically, a highly concentrated HMD aqueous solution (>90%) was brought in direct contact with solid pure AA in the presence of dry ice or liquid nitrogen. The process apparatus comprised a dry blender providing sufficient mass and heat transfer so as to obtain salt in the form of free-flowing powder with a water content of about 4% wt. Finally, DSM Ahead B.V. developed a solvent-free process for preparing 4T salt, in which pure liquefied TMD is added drop-wise onto solid TA powder.⁴⁵

Based on the aforementioned techniques, the herein objective was to develop an optimal route for the preparation of 4T salt, suitable for industrial production. Experimental conditions were varied in order to revoke the major drawback of TA-based semi-aromatic salt preparation. This is the insufficient specific surface of the TA, caused by its low solubility in the applied solvents. Moreover, for the first time, the isolated solid 4T salt grades were thoroughly analyzed and characterized with respect to their morphological structures and correlated to the various types of preparation routes. It was also investigated whether the solvent-free preparation route imparts special characteristics to the formed salt, which cannot be attained by any alternative techniques. The salt characteristics can play a key role in the subsequent DSSP performance. Therefore, the different 4T salt grades were subjected to a micro-scale DSSP in a thermogravimetric analysis (TGA) instrument. The salts were heated isothermally until full conversion and the derived products were characterized and correlated to the initial characteristics of each 4T salt grade.

EXPERIMENTAL

Materials

TA was provided by Merck Chemicals and TMD by Sigma-Aldrich. 2-Propanol and absolute ethanol (abs. EtOH) were also supplied by Merck Chemicals. A 4T salt prepared according to⁴⁵

was kindly supplied by DSM Ahead B.V. and was used as a reference material.

Salt Preparation

4T salt formation involves the reaction of nominal equimolar amounts of TMD and TA according to the Scheme 1. Five different grades (samples 1–5) of 4T salt were prepared in this work and the experimental details are given in Table I. The experimental apparatus used for the preparation of all 4T salt samples is shown in Figure 1.

Solution Technique. The term salt preparation in solution herein means that after mixing all monomers along with the proper amount of solvent, there was a particular moment where everything was dissolved and a clear salt solution was obtained. Nonsolvent was further added to this solution in order to precipitate the salt and the product was collected by filtration, drying overnight in the fume hood, and further drying for 4 h in a vacuum oven. Three grades (samples 1, 2, 3) of 4T salt were prepared accordingly.

Sample 1 was prepared by adding drop-wise a warm (50°C) 67% wt. TMD aqueous solution into a warm (50°C) aqueous TA slurry under vigorous stirring. During TMD addition, the system was kept under reflux. The slurry of the reactants turned gradually to a clear salt solution. The warm clear solution was cooled by adding it drop-wise to cold 2-propanol, which was kept cool by a water/ice bath. The salt precipitated in the form of thin needle like crystals at a yield of 93%.

Sample 2 was prepared according to the method described in literature by Gaymans *et al.*¹⁰ More specifically, a diluted TMD aqueous solution (~10% w/v) was prepared, in which the equimolar amount of solid TA was added slowly. Following this way, the pure TA particles were rapidly consumed by the intense basic environment created by the TMD, while the accompanying reaction temperature increased to about 60°C, indicating the exothermic neutralization reaction. At the end of TA addition, a

Table I. Experimental Conditions of 4T Salt Preparation Processes

4T salt samples	TMD amount in		TA amount in		Solvent amount (mL)	Reaction T (°C)	Solvent/nonsolvent (v/v)	Mass yield (%)
	(g)	(mol)	(g)	(mol)				
Solution technique								
1	14.13	0.16	26.67	0.16	80 H ₂ O	50	1/4 2-propanol	93
2					145 H ₂ O	25	1/2 abs.EtOH	92
3	14.13	0.16	26.67	0.16	40 H ₂ O	1-3	1/2 2-propanol	19
Slurry technique								
4	14.13	0.16	26.67	0.16	40 H ₂ O	1-3	-	67
5					50 abs.EtOH	1-3	-	98
Solvent-free technique								
6	178.35	2	326.65	1.97	-	60	-	100

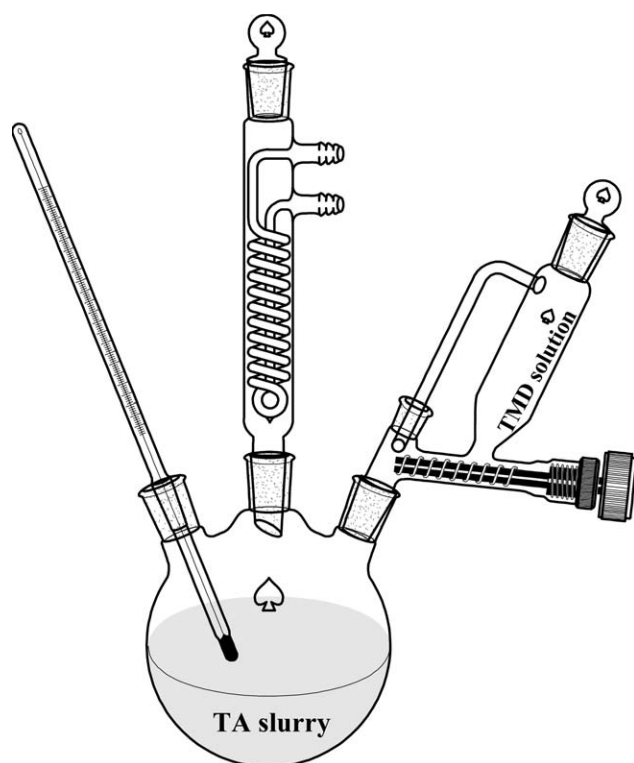


Figure 1. Experimental apparatus for the preparation of 4T salts.

clear salt solution was obtained. This was cooled down to room temperature. The precipitation of the salt occurred by the addition cold abs. EtOH while the solution was vigorously stirred. The product was filtered, dried overnight under the fume hood and further dried at 50°C under vacuum for 4 h. The procedure yielded 92% 4T salt in the form of a white powder.

Slurry Technique. Regarding salts developed in slurries, there was no macroscopical evidence of salt formation during mixing of the reactants, since particles remained constantly in suspension. Accordingly, a 4T salt grade was prepared by adding drop-wise a concentrated aqueous TMD solution to a vigorous stirred aqueous TA slurry, while the apparatus was kept in an ice bath and under reflux, so as to absorb the heat of the exothermic neutralization reaction and avoid potential TMD escape. At the end of TMD addition, a salt slurry was formed, the product was filtered under vacuum, dried overnight in the fume hood and further dried in a vacuum oven at 50°C for 4 h (sample 4, slurry route). The 4T salt was obtained in the form of a fine colorless powder at a relatively low yield (67%), indicating incomplete precipitation. Therefore, the filtrate salt solution was subsequently added drop-wise to 1:2 v/v cold 2-propanol. The received salt was in the form of large transparent crystals at a 19% yield (sample 3) and is considered to be delivered from solution technique by striking.

Sample 5 was prepared by adding drop-wise an ethanolic TMD solution into an ethanolic TA slurry in an ice bath, resulting in a highly viscous salt slurry. The product was filtered and dried as described above. The procedure yielded 4T salt in the form of very fine thin powder (yield 98%).

Solvent-Free Technique. Finally the solvent-free technique delivered Sample 6 and was kindly supplied by DSM Ahead B.V.⁴⁵

Characterization

Structure Verification. All 4T salt grades were analyzed through Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) analysis so as to verify the chemical and morphological salt structure of these chemical compounds. The FT-IR spectra of all salt grades were obtained with a Nicolet 6700 thermoscientific spectrometer, connected to an attenuated total reflection (ATR) accessory. For each region, a series of spectra were recorded and every spectrum consisted of 100 co-added spectra at a resolution of 4 cm⁻¹.

XRD spectra were obtained for all 4T salt grades using a Bruker d2 phaser ed-XRD diffractometer, scanning the 2θ scale from 2° to 60° with 0.08° increment and 1s/step scanning rate. During the measurements, 15 rpm rotation was also applied.

Salt Morphology. Microscopy. Morphological characteristics of all 4T grades were observed by scanning electron microscopy (SEM) with a Hitachi Tabletop 3000 microscope, with distance measuring capability.

Particle size analysis. Particle size distribution and shape analysis measurements were performed using a Sympatec QICPIC particle size analyzer.

Analytical Properties. End-group analysis. The prepared 4T salts samples were subjected to end-group titration measurements, in order to determine their amine and carboxyl content. The potentiometric titrator used for all measurements was the Metrohm 716 DMS Titrino instrument. A total of 50 mg of dry salt was dissolved in 100 mL of 3:2 v/v abs. EtOH/H₂O solution. Regarding the amine content [NH₂], the solution was titrated with perchloric acid in 2-propanol, while the respective carboxyl content [COOH] was titrated with a solution of tetrabutylammonium hydroxide in benzyl alcohol. Measurements were performed in duplicates at least, in order to check that the end groups were evenly spread.

Nuclear Magnetic Resonance (NMR) analysis. ¹H-NMR spectra of 4T salt grades prepared were received in a Bruker Advance 300 MHz instrument and the solvent used was deuterated sulfuric acid (D₂SO₄). ¹H-NMR spectra of PA 4T products were also received and the products were characterized herein with their corresponding repeating unit formulas), where all characteristic peaks can be assigned to hydrogen atoms in the polymer chain and in the polymer end groups.

pH measurements. 1% Aqueous salt solutions were prepared and the respective pH at 25°C was determined by using an ORION 250A digital pH meter. Measurements were performed in duplicates so as to ensure reproducibility.

Thermal Properties. All 4T salt samples considered were first dried at 50°C under vacuum overnight. Differential scanning calorimetry (DSC) measurements were carried out in a Mettler Toledo DSC 700 module from 30°C to 500°C with 10°C/min heating rate under nitrogen flow (20 mL/min), in order to determine the thermal properties of the salts, such as melting

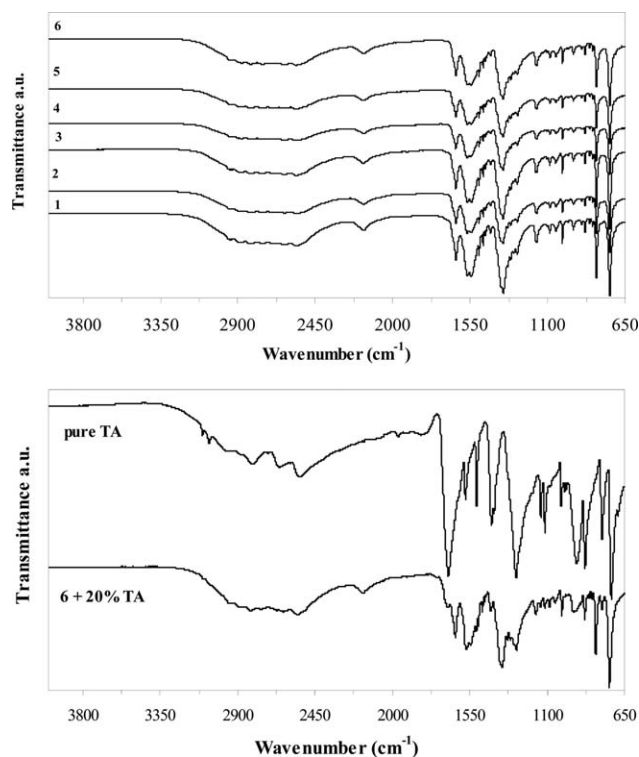


Figure 2. (a) FT-IR spectra of 4T salt samples and (b) FT-IR spectra of pure TA and spiked with TA sample 6 salt.

point (T_m) and enthalpy of fusion (ΔH_f). In addition, TGA was conducted in a Mettler Toledo TGA/DSC 1 HT module from 30°C to 500°C, with 10°C/min heating rate, under nitrogen flow (10 mL/min), so as to study the thermal stability of the produced salts. DSC and TGA measurements were performed in duplicates. The PA 4T products were heated from 30°C to 500°C with 20°C/min. in a Mettler DSC 700 instrument, with simultaneous nitrogen flow controlled at 20 mL/min. From the DSC scans the values of melting points (T_m), enthalpy of fusion (ΔH_f) and decomposition temperature (T_d) were determined.

Preliminary DSSP runs. The herein synthesized 4T salt samples were subjected to DSSP in a TGA instrument. The DSSP runs were performed in a TGA/DSC 1 HT instrument. Sample holders used for DSSP were 40 μ L standard aluminum crucibles, sealed with lids having a perforated hole (50 μ m) on top, both provided by Mettler. 15 mg of each salt sample was placed in a crucible and was inserted in the TGA chamber at 30°C (T_0) and was rapidly preheated to 150°C (T_1) so as to sweep off any possible humidity trapped in the salt. Subsequently, the sample was further heated to 260°C (T_{DSSP}) at a lower heating rate. Finally, the sample was heated isothermally at T_{DSSP} until a constant plateau was reached (2–3 h).

RESULTS AND DISCUSSION

In the current article, a comparison between three different 4T salt synthesis techniques was performed for the first time, aiming to explore the effectiveness of each process in terms of yield, amounts of solvent/nonsolvent employed, morphological characteristics and attained properties as obtained by DSC, TGA,

titrations, NMR, XRD, SEM, FT-IR measurements of the final product. The latter attributes are of high importance since the formed salt can be used as a monomer in DSSP, the only feasible polymerization route for the production of pure PA 4T. Accordingly, polymerization data are presented showing the effect of the different salt preparation methods on DSSP.

Structure Verification

Salt formation was firstly studied by means of FT-IR spectroscopy [Figure 2(a)] for all 4T salt samples. The characteristic peaks of ionized amine and carboxyl groups were found: the wide peak at 2200 cm^{-1} assigned to the stretching vibration of the ionized amine groups (NH_3^+), the peak at 1660 cm^{-1} attributed to NH_3^+ antisymmetric stretching vibration, and the weak peak at 1125 cm^{-1} corresponding to NH_3^+ transverse rolling vibration. The formation of ionized carboxyl groups COO^- was indicated by the strong peak at 1410 cm^{-1} attributed to symmetric stretching vibration.⁷ The spectrum of pure TA was also received for comparison reasons [Figure 2(b)]. Apart from the peak at $\sim 800 \text{ cm}^{-1}$, which corresponds to the π -band of the aromatic ring,⁴¹ and was also found in the salt grades, no other similarities exist. In order to determine any possible free amount of TA kept in the salt due to the diacid insolubility, a significant TA amount ($\sim 20\%$ wt) was added to sample 2 and the respective spectrum was found similar to the pure one, indicating that FT-IR analysis cannot detect any unreacted TA residues.

XRD results are shown in Figure 3. The salt samples were initially ground down to fine powder in order to avoid possible orientation phenomena. The received spectra exhibited the same crystal structure independently of the applied salt formation technique. Moreover, the XRD pattern matches with the 4T crystal structure reported by Moritani and Kashino⁴⁶, where it was also mentioned that 4T salt crystallizes in an anhydrous form.

Salt Morphology

Microscopy. The morphological characteristics of the 4T salt samples from experiments 1–5 were studied by SEM. Based on the received SEM images (Figure 4), different morphologies and crystal sizes of 4T salt were obtained and were correlated to the respective preparation process used and more specifically to the salt precipitation technique and rate.

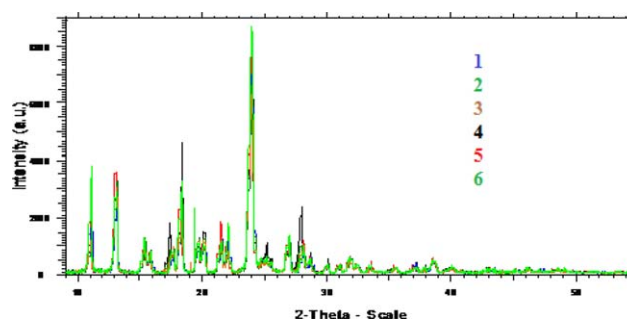


Figure 3. XRD spectra of 4T salt samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

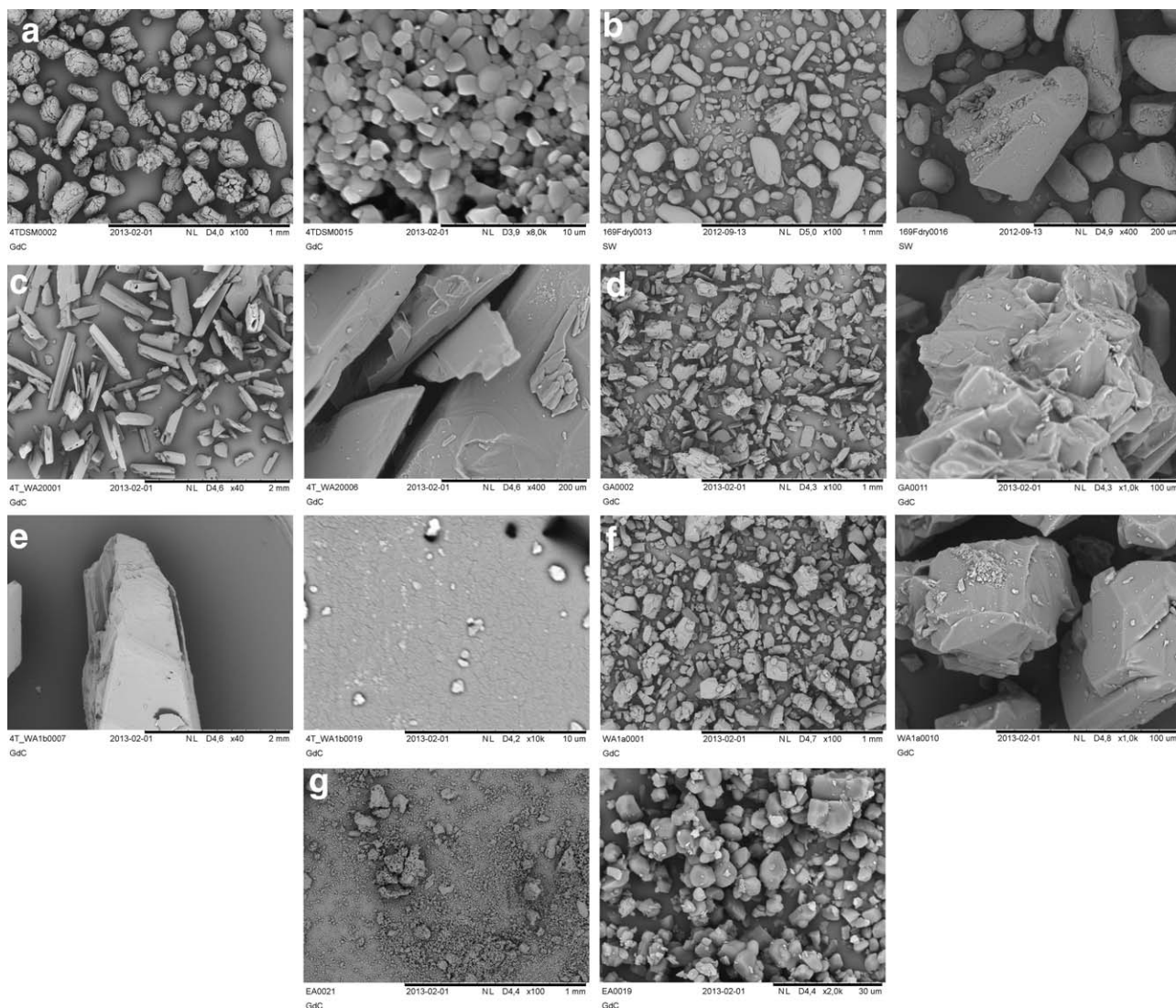


Figure 4. SEM photos of the prepared 4T salt samples. TA particles also given for comparison.

Regarding the salts prepared by the solution technique, samples 1 and 3 were obtained after adding drop-wise the filtrate solution to a large amount of 2-propanol. This procedure yielded large, sharp-edged, and perfectly formed crystals [Figure 4(c,e)]. However, in the case of sample 2, fragmented medium-sized irregular crystals [Figure 4(d)] were obtained, which can be attributed to the fact that the whole amount of the nonsolvent (abs. EtOH) was abruptly added to the salt solution, resulting in a very fast and violent crystallization.

Turning to the slurry technique, in sample 4 the precipitation of the salt was achieved spontaneously, resulting in fragmented medium-sized crystals of irregular shape [Figure 4(f)], as in sample 2. Similarly, the precipitation of sample 5 was much more abrupt since it was performed upon salt formation in ethanolic environment, resulting in even smaller irregular-shaped particles [Figure 4(g)].

On the contrary, regarding the solvent-free technique, sample 6 presented a totally different morphology [Figure 4(a)], since it was found to be consisted of crystals shaped like “cracked

potatos”. However, when the magnification was further increased, it was noticed that these crystals were not compact, but consisted of agglomerated smaller micrometer sized particles. In addition, it should be highlighted that these potato-shaped salt particles resembled the general shape of the initial TA particles [Figure 4(b)].

Summarizing the above findings and in harmony with crystallization theory, the morphology of the obtained salt can be dramatically altered depending on the imposed preparation conditions, i.e., (a) rapid crystallization (e.g., samples 2 and 4) results in medium-sized compact crystals with rough surface, (b) spontaneous salt formation and abrupt precipitation (e.g., samples 5 and 6) reduces the obtained particle size, while the slow precipitation in a nonsolvent (e.g., samples 1 and 3) delivers perfectly shaped, compact, and smooth large crystals.

Particle Size Analysis. Completing morphology characterization, particle size distribution data of each 4T salt sample is given (Table II) supplementary to the SEM. The d_{50} value is considered most important since it represents the size of the

Table II. Particle Size Analysis Results

4T salt samples	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Aspect ratio
1	263	477	765	0.4
2	42	100	344	0.7
3	536	1049	1713	0.5
4	53	129	324	0.7
5	23	183	513	0.7
6	64	174	295	0.7

50% of the particles measured, while the aspect ratio value given shows the spherical character of those particles. From the particle distribution curves (Figure 5), it is obvious that the most homogeneous crystals were 1 and 6, while the worst case was found for sample 5, which exhibited inhomogeneous irregular particles of several sizes. This is completely in line with the observed morphology obtained by SEM.

Analytical Properties

End-Group Analysis. Solid-state chemical characterization of salts is challenging. At present, the salt was dissolved and by means of titration the amine and acid end-group concentration was determined (Table III). In all salt samples, during amine end titration, one equivalence point (EP) was reached corresponding to $[\text{NH}_2]$ content in the range of 7606–7928 meq/kg. This is close to the theoretical value (7865 meq/kg) of equimolar anhydrous 4T salt. Only in the case of sample 4, a much lower value of 7079 meq/kg was titrated. In the carboxyl end-group titration curve, two distinct EPs were determined in sam-

ples 4, 5, and 6, indicating the existence of two types of acid moieties in the formed salt, with sample 4 exhibiting the higher excess of acid. The experimental $[\text{COOH}]$ content was found in the range of 7293–7782 meq/kg, similar to the respective $[\text{NH}_2]$ contents.

This experimental acid excess should be attributed to unreacted TA, which as insoluble species can be “trapped” in the formed salt during precipitation but also during filtration. This entrapment seems dependent on the preparation process, as it may happen at a significant extent when the specific surface for reaction was kept low, due to the limited solvent volume (e.g., samples 4 and 5). When a dilute TMD solution was used in sample 2, the TA was added slowly as a solid and the TA powder was consumed rapidly by the TMD, while the formed salt was gradually dissolved with no TA excess. The same applies in the cases of samples 1 and 3, where the salt has been properly formed in solution, and then precipitated by the nonsolvent addition.

pH Measurements. pH measurements of 1% aqueous salt solutions (Table III) were also found in harmony with the respective end-group data. More specifically, the aqueous solutions of samples 1, 2, and 3, which showed no acid excess, exhibited neutral pH value (6.8–7.0), while sample 4 with the higher acid excess presented an acidic pH (5.6). The latter finding was verified by performing a spiking experiment with TA: in 1% aqueous solution of sample, 12% wt solid TA was added and the pH measured was found at the same value of 5.6. It is also worthwhile mentioning, that the 1% aqueous solutions of the samples which presented this free TA excess, were not completely dissolved, proving that this excess is indeed free TA, since the latter is practically insoluble in water.

$^1\text{H-NMR}$ Analysis. $^1\text{H-NMR}$ spectra of all synthesized 4T salt samples were received in order to reinforce and to verify the aforementioned end-group data and the existence of unreacted TA in the specific salt grades. Interpreting the resulting spectra (Figure 6), the sharp peaks at 3.4 and 4.7 ppm corresponded to the aliphatic protons of the TMD, the short broad peak at 7.5 ppm corresponded to the protonated amine cations (NH_3^+) and the sharp high peak at 9.9 ppm represented the protons of the aromatic ring of the TA. The acid excess can be calculated, through integrating the intensity of TA and TMD protons, revealing significant deviation from 1:1 ratio in the samples 4, 5, and 6. The calculated values from NMR are presented in Table IV and are in good agreement with end-group analysis, showing NMR sensitivity to detect quantitatively salt imbalance.

Thermal Properties

The synthesized 4T salt samples were subjected to DSC and TGA analysis. The determined thermal properties values (T_m , ΔH_f , T_d) are given in detail in Table V. In all cases, it was found that upon heating in the DSC, all 4T salt grades presented an endotherm at ca. 285°C, accompanied by mass loss signal in the respective TGA curves at ca. 280°C as shown in Figure 7. This indicates that upon 4T salt melting, also salt decomposition and water formation by $\text{NH}_2\text{-COOH}$ condensation reaction (i.e., polymerization) occur at the same time. Furthermore, by integrating these endotherms, enthalpy values of 500–550 J/g were determined. If these values are compared, the respective

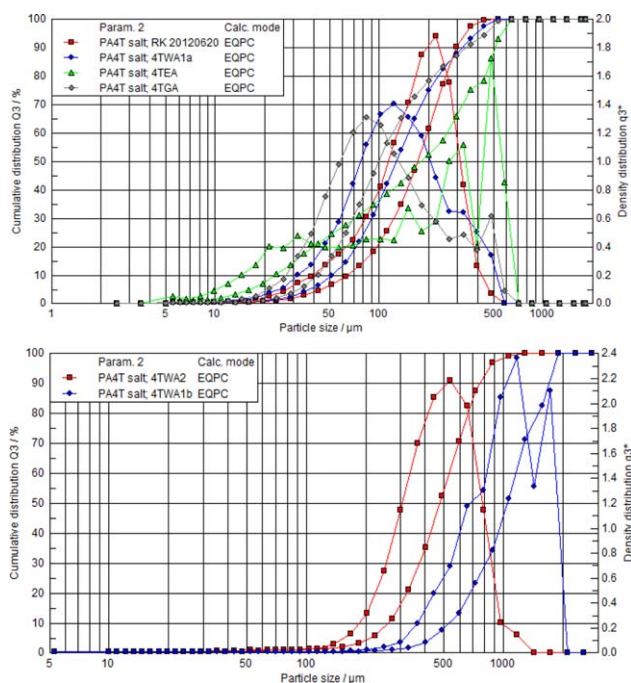
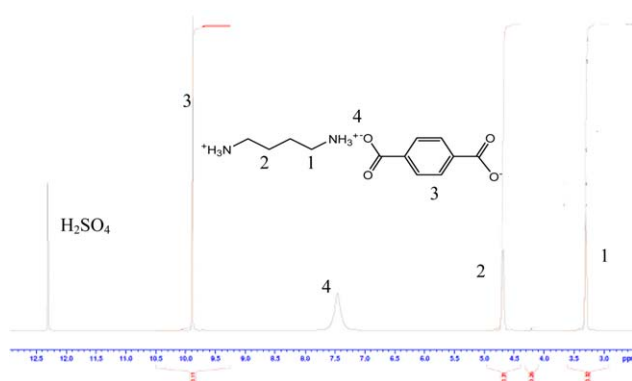


Figure 5. Particle size distribution curves of the 4T salt samples prepared. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Analytical properties of 4T salt samples. End-group analysis and solution pH determination

4T salt samples	Analytical properties					
	Theoretical ends (meq/kg)	[NH ₂] (meq/kg)	[COOH] ^a (meq/kg)	Acid excess		pH (1% aq. solution)
				(meq/kg)	(% wt)	
1	7865	7866 ± 52	7697 ± 157	-	-	6.95 ± 0.02
2		7891 ± 31	7782 ± 32	-	-	6.77 ± 0.10
3		7928 ± 63	7712 ± 48	-	-	6.99 ± 0.01
4		7079 ± 23	7089 ± 35	948 ± 70	11.8	5.62 ± 0.02
5		7606 ± 110	7293 ± 158	535 ± 38	6.8	5.73 ± 0.01
6		7846 ± 2	7456 ± 13	326 ± 7	4.4	5.95 ± 0.02

$$^a [\text{-COOH}] = [\text{-COOH}]_{\text{total}} - [\text{Acid excess}] = V_{\text{EP2}} - V_{\text{EP1}}$$

**Figure 6.** Typical ¹H-NMR spectrum of 4T salt received in D₂SO₄. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

enthalpy of vaporization of water at 100°C (i.e., 2.26 kJ/g) and normalized to the theoretical polycondensation water amount of 4T salt (i.e., 14.2% wt), it was found that 65–70% of the absorbed energy corresponds to evaporation of water. This finding is very crucial and indicates that 4T salt is a good candidate for DSSP. Based on these grounds, this DSC endotherm can be considered seen as a combination of endothermic breaking of the crystal structure while reaction water is evaporating as steam. Therefore, it is here referred to as reactive or phenomenological melting point of the salt (T_m) and is correlated to the respective preparation process (Table V): when a more perfect

Table IV. Calculations from the ¹H-NMR Spectra of 4T Salt Samples

4T salt samples	TA excess by ¹ H-NMR (% wt)	TA excess by end-group analysis (% wt)
1	1.6	-
2	1.2	-
3	1.1	-
4	11	11.8
5	6	6.8
6	4	4.4

and larger crystal structure was attained (e.g., samples 1 and 3) T_m increased (ca. 290°C), while when the obtained crystals were small, imperfect and fragmented it significantly decreased (e.g., samples 5 and 6) to ca. 283°C, indicating a higher reactivity to condensate. The preparation processes which led to crystals of intermediate size (e.g., samples 2 and 4) showed respective intermediate melting points (ca. 285°C). From TGA analysis, the salt decomposition temperature (T_d) followed the same trend with DSC results.

It is also interesting to note that all 4T salts polymerized during the DSC scan, as evidenced by the endotherms at temperatures above 400°C corresponding to polymer structure (PA 4T) (Figure 7). In particular, a two overlapping endotherms at ca. 425°C and 460°C were detected and in literature this is recognized as a double melting peak for the polyamide 4T.⁴¹ However, when combining TGA and DSC analysis, the first sharp peak corresponds in fact to the melting point of PA 4T, while the second at 460°C is accompanied by intense mass loss in the TGA and exhibits the decomposition point of this particular polyamide. This is an additional proof, that PA 4T is not a melt processable resin, since the polymer melting and decomposition overlap. Finally, as observed in TGA scans above 300°C, PA 4T derived from salt 4 presented lower thermal stability, which can be attributed to the high content of free TA (~12% wt) and to its subsequent sublimation.

Table V. Thermal Properties of All 4T Salt Samples as Obtained by DSC and TGA Analysis

4T Salt samples	Thermal properties		
	DSC		TGA T_d (°C)
	T_m (°C)	ΔH_f (J/g)	
1	287.7 ± 0.4	551.1 ± 3.3	290.0 ± 0.1
2	285.0 ± 0.4	527.9 ± 19.8	282.7 ± 0.1
3	290.0 ± 1.0	544.7 ± 3.2	289.7 ± 0.2
4	285.3 ± 0.6	540.7 ± 13.4	290.1 ± 0.2
5	283.2 ± 0.9	502.9 ± 14.6	283.0 ± 0.3
6	283.1 ± 0.3	546.2 ± 10.7	280.6 ± 0.4

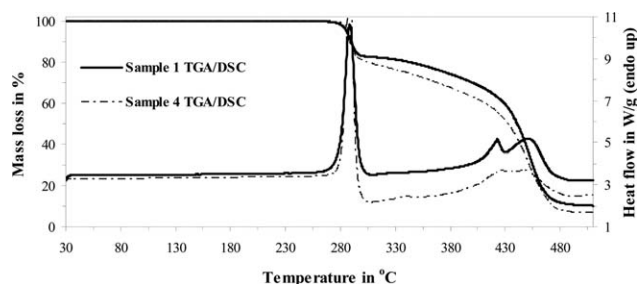


Figure 7. Indicative DSC and TGA curves of the 4T salt samples, showing the simultaneous phenomena occurring at 285°C.

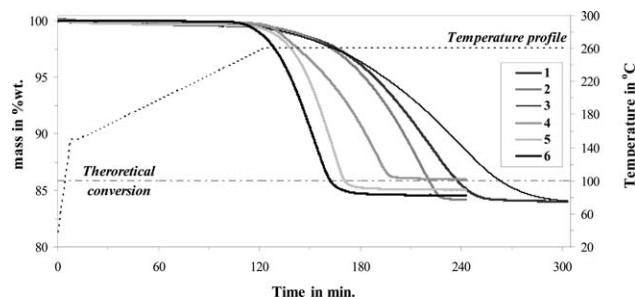


Figure 8. TGA curves of the DSSP of the different 4T salt samples 1–6.

Preliminary DSSP of 4T Salt Samples. The TGA chamber was used as a micro polycondensation reactor, since the progress of the polymerization could be indirectly monitored by the weight loss of the water formed.^{5,35} According to the thermal properties of the synthesized 4T salts (Table V) the “phenomenological” melting point varied from 283°C to 290°C; therefore, the DSSP temperature was selected ca. 25°C lower (i.e., $T_{\text{DSSP}} = 260^\circ\text{C}$), trying to retain the solid character during polymerization, i.e., to avoid SMT in accordance with the literature sources.^{8,11,12,26,35}

From the obtained TGA curves of this preliminary DSSP evaluation (Figure 8), it can be concluded that all curves reach a constant plateau. In all salt samples, the recorded mass loss values (Table VI) were higher than the theoretical loss of 4T salt (i.e., 14.2% wt) indicating that the total mass loss should be attributed to evaporation of both the polycondensation water formed and also to the volatile component of the salt (i.e., TMD). A reactiv-

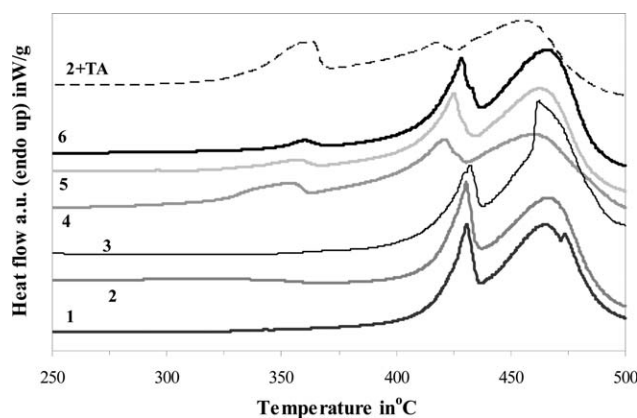


Figure 9. DSC scans on the received PA 4T products.

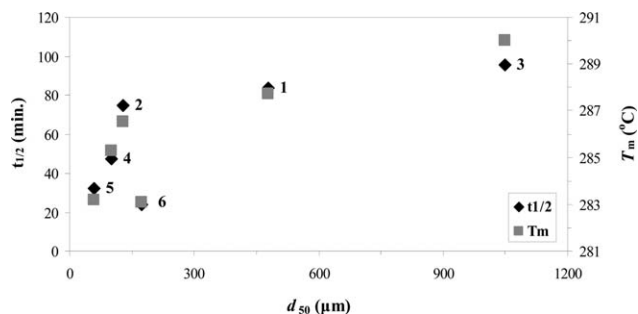


Figure 10. Correlation between salt particle size rate of DSSP ($t_{1/2}$) and melting point of the salt.

ity trend between the different 4T salt samples was found. The $t_{1/2}$ value (i.e., the time required to reach 50% of conversion at T_{DSSP}) was calculated from the TGAs. Figure 9 shows the correlation between the $t_{1/2}$ value (i.e., the time required to reach 50% of conversion at T_{DSSP}) and their respective “phenomenological” melting points of the salts versus the average particle size (d_{50}) of the herein synthesized salts. Accordingly, it seems that both the melting points and the $t_{1/2}$ values are a function of the size of the crystal, rendering that way the preparation procedure as a crucial step for the subsequent DSSP behavior. This behavior will be thoroughly described in an upcoming article of our group, which will focus exclusively on the mechanism of DSSP and parameters influencing thereof.³¹

Furthermore, in order to assess qualitatively the behavior of the residual TA hidden in the salt, during DSSP, the NMR spectra of PA 4T derived by samples 2 and 4 were compared. In particular, sample 2 that was produced through the solution technique and showed no residual TA content while sample 4 by was derived by slurry technique showed 11.8% wt TA. From the interpretation of the spectra (Figure 11), it was obvious that peak 5 and 7 (at ca. 8.5 ppm) corresponding to the protons of the acid end groups and the residual TA in the PA 4T is much higher for the

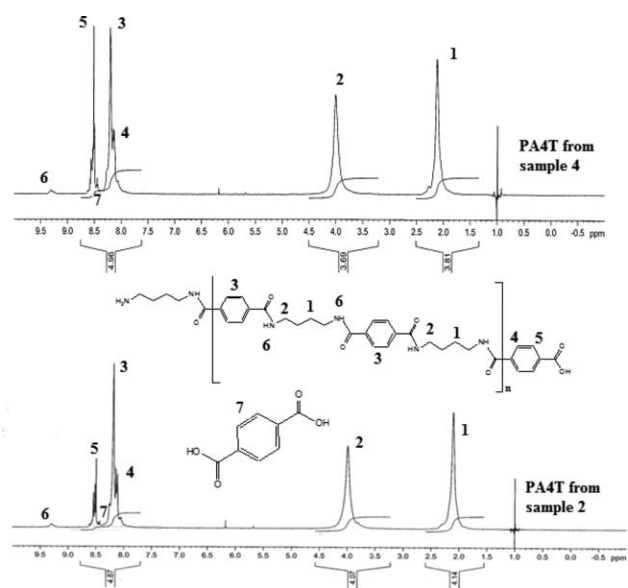


Figure 11. $^1\text{H-NMR}$ spectra of PA 4T products derived from salt samples 2 and 4.

case of the sample 4, proving that it was still kept in the polyamide sample. This results in higher total acid end-group concentration and consequently in a lower final molecular weight.

Finally, in all derived polyamide samples (1–6), thermal properties were analyzed by DSC (Figure 10). The TA shows up in the DSC as an endotherm at ca. 350°C. This was confirmed by a DSC scan of sample 2 spiked with pure TA (sample 2+TA). All PA 4T samples show a double endotherm in the range of 400–500°C, with the first peak (ca. 425°C) corresponding to the PA 4T melting point T_m , while the second peak (ca. 465°C) corresponds to the thermal decomposition T_d of the polyamides as confirmed by TGA. PA 4T samples which were derived from salts 1, 2, 3 which showed no TA excess, exhibited higher T_m and T_d compared to the respective ones of 4, 5, 6 which had a residual TA content ranging from 4.4 to 11.8% wt in the original salts used (Fig. 2). This behavior demonstrates the influence of residual TA content in the starting materials.

Summarizing, all these scouting polymerization prove that there is a strong dependence between the imposed preparation process of 4T salt and the attained morphology and/or properties of the respective samples.

CONCLUSIONS

The objective was to prepare tetramethylenediammonium terephthalate (4T salt) through using three different techniques (solution, slurry, and solvent-free) and to correlate the attained morphology and properties in the perspective of applying subsequently DSSP. The latter is considered as the only industrially viable polymerization route for the production of pure PA 4T, while the 4T salt characteristics determine significantly its overall efficiency. Therefore, with emphasis on the end-group balance, crystal morphology, and thermal properties, the effect of the applied salt preparation technique was discussed. In particular, unreacted TA was found entrapped in salt structures prepared by slurry and solvent-free technique, while crystal morphology and thermal properties were found to be a function of the precipitation rate of the salt: slow rates resulted in perfectly shaped large crystals with higher phenomenological melting points. Nevertheless, it should be noted that the 4T salt prepared through solvent-free technique seems quite interesting, since it exhibited a unique crystal morphology and size, while consisting of nano-scale porous particles, which were not possible to achieve through any other technique. The influence of the salt preparation procedure was evident on the subsequent preliminary DSSP runs. It was found that the particle size in the salt significantly affects its DSSP reactivity. Also it was found that unreacted TA content in the 4T salt leads to high TA and acid end-group content in the PA 4T and affects both T_m and T_d .

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