

New Process for the Production of Dry Hexamethylenediammonium Adipate

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Received 14 January 2002; accepted 29 May 2002

Published online 19 February 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.11795

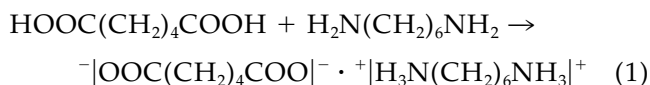
ABSTRACT: A simple and easy technique is proposed for the preparation of dry hexamethylenediammonium adipate (HMA salt), using conventional dry-blending equipment. The process includes contacting adipic acid and hexamethylenediamine, in the presence of a cryogenic medium, which is used to depress the exothermic of the salt formation. The purpose is the formation of free-flowing HMA salt with good homogeneity and balanced end groups, which can be used as a starting intermediate in the polyamide industry. Critical parameters were studied, such as the nature and

amount of cryogenic agent and the presence of water traces in the reacting mixture. Application in an industrial scale seems feasible so that all advantages of handling dry HMA salt instead of its components (adipic acid powder and hexamethylenediamine liquid) can be utilized. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1252–1257, 2003

Key words: polyamides; blending; solid-state polymerization

INTRODUCTION

Traditional production of one of the most commercially important polyamides (PAs), polyhexamethylenedipamide (or PA 6,6), uses as a starting intermediate an aqueous solution of the salt of adipic acid (AA) and hexamethylenediamine (HMD). The use of the salt allows manufacturers to achieve an accurate dosage of the starting monomers and ensures their stoichiometric proportions, which is extremely important to achieve the required molecular weight of the polymer.¹ The salt formation reaction involves the creation of ionic bonds between the end groups (–NH₂ and –COOH) of the reactants and it is highly exothermic. The reaction is shown in the following equation²:



The hexamethylenediammonium adipate (or PA 6,6 salt) formed is a distinct chemical compound; it forms white, diamond-shape monoclinic crystals; it is hygroscopic, readily soluble in water (47% w/v at 18°C); and, when heated, it melts in the range of 190–191°C with partial polymer formation. The salt is stable either dry or in solution at room temperature, but above 140°C it polymerizes.^{3,4}

Typically, reaction (1) is carried out in water. An aqueous salt solution is prepared containing stoichiometric amounts of the diamine and diacid (which is about 56 wt % AA and 44 wt % HMD), so that the resulting salt solution usually contains water in the range of about 50 wt %. The salt solution is then stored temporarily or it is transferred to a prepolymerization vessel to await polymerization.^{1,5}

The industrial batch process for the manufacture of the polyamide, using an aqueous HMA solution as starting intermediate, occurs in two stages. In the first stage, the HMA solution is concentrated in an evaporator. Upon reaching a concentration in the range of 10–30 wt % water, the reaction mixture is transferred to an autoclave for the second stage, where it is heated to elevated temperatures (175–200°C), under increasing pressure to minimize loss of volatile organic compounds. The temperature is further increased (250–270°C) and the pressure is released at a slow rate to bleed off steam and to drive the condensation reaction toward polymerization. While being maintained at approximately the same temperature, the melt reaction mixture is held at a low constant pressure for a sufficient time to obtain the desired degree of polymerization.^{1,4,6}

The aforementioned process is commonly used for the preparation of polyamides on an industrial scale. However, because melt viscosity increases very rapidly with increasing molecular weight, this process results in only relatively low molecular weight products. High melt viscosity leads to various problems: the temperature control and removal of water of reac-

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tion becomes more difficult and the high temperatures encourage, to an increasing extent, side reactions and gel formation, which can drastically impair the quality of the end product.⁷ An additional disadvantage is that large amounts of water have to be transferred in the evaporation stage; furthermore, substantial amounts of energy have to be consumed.

These problems in the conventional industrial manufacture of polyamides are of critical importance. A supplementary technique has been proposed and involves first polymerizing the polyamide salt in the melt stage and then completing the reaction by post-polymerization in the solid state. The latter is achieved by heating the polymer formed in an inert atmosphere to a temperature well above its glass-transition point, but below melting temperature. This so-called solid-state finishing (SSF) can produce a substantial increase in the degree of polymerization of the polymer, while the material retains its solid shape.^{8,9} However, a "direct" solid-state polyamidation (SSP) of dry HMA salt has been also studied, using different techniques,^{10–22} and still attracts the interest of many polymer technologists, given that all the problems associated with the high temperature disadvantages of melt technology are completely absent.¹⁵ In fact, because of the much lower reaction temperatures at which SSP is performed, the danger of undesirable side reactions and gelling is reduced, resulting in polymers with improved properties, such as increased capability of spinning. In addition, SSP uses simpler technology, given that the expensive removal of the water added before polymerization is avoided, thus ensuring significant energy savings.^{3,10,15}

The advantages of the SSP process starting from dry salt urgently raise the need to find a simple way of making salt. Although techniques are known for precipitating the salt from its aqueous solution, such as by adding a nonsolvent to the solution [e.g., isopropanol or methanol (solubility 0.4% w/v at 25°C)], such processes require the subsequent recovery of all solvents involved.⁴

For this purpose, efforts have been made to prepare highly concentrated aqueous salt solutions. According to U.S. Patent 4,442,260,⁵ an aqueous solution of 73.5–77.5 wt % AA and 22.5–26.5 wt % HMD is prepared at 55–60°C and contains solute in the range of 60–69 wt %. Evaporation follows by boiling the solution at 110–160°C, until the solute concentration reaches 89–96 wt %. When this concentrated salt solution is ready to be polymerized, HMD, which may contain 0–20% water, is added under heating until reaching stoichiometric proportions of AA and HMD. On the other hand, U.S. Patent 4,213,884²³ describes the preparation of HMA solution containing 70–90 wt % salt plus polyamide oligomer. The starting material of the process is a less concentrated salt solution (40–65 wt % salt) where solid AA is added in the temperature range of 60–

110°C. The resulting solution, with free carboxylic ends, is then reacted with the equivalent amount of molten HMD. The reaction is carried out under pressure (2–15 bar) and the final reaction temperature is kept in the range of 140–210°C.

It should be mentioned here that both starting materials for PA 6,6 production are classified as hazardous: adipic acid is commercially available in the form of a white crystalline powder and its finely dispersed particles (dust) may form explosive mixtures in air. The explosive potential in combination with the health effects that this material may cause renders AA difficult and dangerous to handle during shipping and storing.²⁴ On the other hand, hexamethylenediamine is available as an aqueous solution in a concentration range from 70 to 100 wt %. Aqueous solutions of 70 to 80% are liquids, whereas higher concentrations are solids at room temperature, but shipped as warm liquids. In either case, HMD is a corrosive and caustic material, which demands extreme caution during loading and unloading procedures.²⁵

The difficulties mentioned concerning the shipping and storing of AA and of HMD are overcome when HMA salt is used instead. The salt is almost harmless in comparison with AA and HMD and weighs much less, given its very low water content. These benefits ensure a safer, easier, and cheaper way of shipping and storing the monomer for the manufacture of polyhexamethylenedipamide.

In this study, we describe a much simpler process of direct mixing of AA and HMD in the presence of critical amounts of water and a cryogenic medium; the simplicity of the process also derives from the equipment required (a typical sigma blender).²⁶ Thus, having in mind the significant impact of the HMA salt on the polyamide industry, the goal of the technique proposed here is the preparation of low water content HMA salt in the form of a free-flowing powder, with good homogeneity and balanced end groups.

EXPERIMENTAL

Materials

A batch procedure was used to prepare HMA salt. The reactants used for the formation of the salt were solid AA in the form of white powder and a concentrated aqueous solution of HMD (91.3 wt %). Liquid nitrogen and solid carbon dioxide were selected as cryogenic media. A commercial HMA salt from Rhone-Poulenc Co. (France) was used as reference.

Equipment

The reaction was carried out in a 1.5-L mixing chamber of a double arm-kneading mixer with sigma blades (Werner Co., Greenville, PA). Such a mixer

TABLE I
Experimental Conditions

Run	Cryogenic medium	Amount of cryogenic medium (g)	Form of added hexamethylenediamine
1	No	—	Aqueous solution
2	Solid CO ₂	73	Aqueous solution
3	Solid CO ₂	146	Aqueous solution
4	Liquid N ₂	Half the mixing chamber	Aqueous solution
5	Solid CO ₂	146	Solid

easily created the torque required to achieve better homogenization of the reactants. On the other hand, the device was suitably modified with rubber gaskets to ensure a tight seal and to prevent the evaporation of HMD.

Preparation of low water content HMA salt

AA (146 g) and a quantity of the cryogenic agent were placed in the mixer. The aforementioned aqueous HMD solution (127 g), heated to 45°C, was then added to the mixer through a funnel. The reactants were then blended for 1 h and the salt was finally collected.

Different runs were carried out, to study critical parameters of the process and to determine the proper conditions for satisfactory products. The solid carbon dioxide amount employed was varied and the effect of the presence of water traces in the reacting mixture was considered. The different conditions of each experimental run are presented in Table I. For each experimental run, three replicates were performed.

Salt characterization

Samples of the HMA salt formed, according to Table I, were tested to examine their homogeneity based on pH and end group data. Regarding the sample of Run 1, the pH was only measured, since the salt here was not made according to the procedure proposed; it was formed in the absence of a cryogenic medium and the resulting salt had the form of a paste (Table II).

In the following test methods, the end product was dried for 2 h at 50°C except for the "wet samples," which were not dried.

pH measurements

pH was measured by dissolving 10 g of the wet product in the necessary amount of water to make a 9.5 wt % solution. Normally, a 9.5% aqueous solution of the balanced salt has a pH of 7.6.⁴ In all cases, the average value of five pH measurements is reported, whereas the coefficient of variation [c.v. = (standard deviation/mean pH) × 100] is calculated and reveals the homogeneity of each salt grade.

Analysis of end groups

Amine (–NH₂) and carboxyl (–COOH) end groups were determined by potentiometric titration. Dry salt (0.1 g) was dissolved in 100 mL of 75% (by volume) ethanol/water. The solution was titrated for amine ends with 0.1N hydrochloric acid (HCl). The same solution was then back titrated through two end points with 0.1N sodium hydroxide (NaOH) for acid end groups.

FTIR analysis

FTIR spectra were obtained from Nujol mulls of the dry salt spread onto a KBr crystal using a Nicolet 20SX FTIR spectrometer (Nicolet Instruments, Madison, WI).

The corresponding values (pH and concentrations of amine/acid end groups) for the commercial HMA salt were also determined, to compare it with the HMA grades formed.

TABLE II
Characteristics of HMA Salts: Concentration of –NH₂ and –COOH, Mean pH, Coefficient of Variation of pH (pH c.v.), and Form

Sample	–NH ₂ (meq/g)	–COOH (meq/g)	Mean pH	pH c.v. (%)	Form
Commercial HMA salt	7.62	7.73	7.6	—	Powder
Run 1	—	—	7.70	19.48	Paste
Run 2	7.32	7.42	6.39	3.60	Powder
Run 3	7.20	7.56	6.00	1.50	Powder
Run 4	7.84	7.00	9.90	0.61	Powder
Run 5	6.93	7.91	7.58	20.71	Powder

RESULTS AND DISCUSSION

As mentioned previously, the formation of the HMA salt is a particularly exothermic reaction. For the conventional manufacture of the salt, where solvents are involved (water or methanol), the liquids act as heat-transferring and heat-controlling media. Therefore, in their absence, the increase of temperature is not easily controlled and the reacting mixture tends to agglomerate into a single mass rather than remaining in a solid, free-flowing form. This is exactly the case of Run 1, which was performed in the absence of a cryogenic medium (Table I), resulting in a paste (Table II). Furthermore, the salt of Run 1 was not homogeneous, as revealed by the pH c.v. of 19.5%.

The results of Run 1 indicate that sufficient heat transfer from the reaction mixture is needed and may be accomplished by using cryogenic agents; thus, in Runs 2–5, the reaction was successfully carried out in a solid particulate state, resulting in free-flowing powder products (Table II). An alternative route may also be suggested that constitutes the circulation of a heat transfer medium along the reaction assembly. The agitation of the reacting mixture also helped to maintain the solid character of the particulates, in that it made heat transfer more efficient from the reacting particles to the cryogenic medium, thus keeping the formed salt as powder rather than paste.

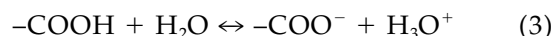
Regarding Runs 2–4, the analysis made by FTIR verifies that in all cases HMA salt was formed. The FTIR spectrum (Fig. 1) includes the characteristic peak of the PA 6,6 salt, at 2200 cm^{-1} , which is the strength vibration of the ionized amine groups ($-\text{NH}_3^+$).²⁷ Nevertheless, the appearance of some polyamide peaks has been also observed, in particular the characteristic peaks at 3300 cm^{-1} (attributed to the N–H stretching vibration of the secondary amide), at 1640 cm^{-1} (attributed to the carbonyl stretching vibration), and at 1540 cm^{-1} (attributed to the N–H deformational vibration).⁴ The intensity of these peaks is quite small, although this indicates clearly that even the presence of cryogenic media does not exclude completely the formation of polyamide oligomers. Although FTIR shows conclusively that HMA was formed in Runs 2–4, some salt still began to polymerize to form oligomers, especially in the so-called dead points of the mixing chamber, where mixing was inadequate (e.g., corners).

In Runs 2 and 3, solid carbon dioxide was employed in different quantities to depress the exothermic of the reaction. The results in Table II indicate that the characteristics of the prepared salts in Runs 2 and 3 deviate slightly from those of the commercial HMA salt. The end-group content seems slightly lower, which is, however, in agreement with the findings of the FTIR spectra (i.e., it might be attributed to the oligomerization of the salt). The latter also seems responsible for

the slightly reduced pH of Run 2. On the other hand, there are no significant variations in the quality of the resulting salt when we varied the amount of solid carbon dioxide. As a result, a balanced salt (Fig. 2) with good homogeneity and in the form of free-flowing powder was produced in both runs.

In Run 4, liquid nitrogen was employed as a cryogenic medium instead of solid carbon dioxide (Table I). Here, the number of carboxyl ends is significantly reduced (Table II) compared with that of the other runs, resulting in an unbalanced salt (Fig. 2). This can be explained by the loss of some adipic acid powder when it comes into contact with the evaporating liquid nitrogen as it was added to the sigma blender. Nevertheless, pH measurements again reveal a homogeneous product (c.v. = 0.61%).

Finally, in the case of Run 5, the resulting salt lacks end-group balance (Fig. 2) and homogeneity (c.v. = 20.71%). These properties are apparently attributable to the absence of water during the preparation stage, given that HMD was added as a solid into the mixer (Table I). Therefore, it becomes evident that a critical amount of water plays a positive role for salt formation. This finding is consistent with the fact that proton transfer between water and carboxyl or amine end groups results in the ionization of the latter, as shown in the following reactions²:



Thus, even trace amounts of water are indispensable for the creation of the ionic bonds between the end groups and for establishing a well-defined interface with good molecular mobility.

CONCLUSIONS

Dry hexamethylenediammonium adipate can be prepared by direct contact of adipic acid and hexamethylenediamine in a typical dry-blending mixer, in the presence of cryogenic media. The absence of a cryogenic agent resulted in salt formation in the form of a paste, with insufficient homogeneity, whereas when a cryogenic medium was used, the product was obtained as free-flowing powder with good homogeneity and balance of end groups. Concerning the nature of the cryogenic agent, solid carbon dioxide appeared to be effective because it succeeded, acting as a heat-controlling medium, in depressing the exothermic of the reaction and in preserving the solid character of the reactants and the good properties of the product. On the other hand, the use of liquid nitrogen contributed to the formation of an unbalanced salt because of the loss

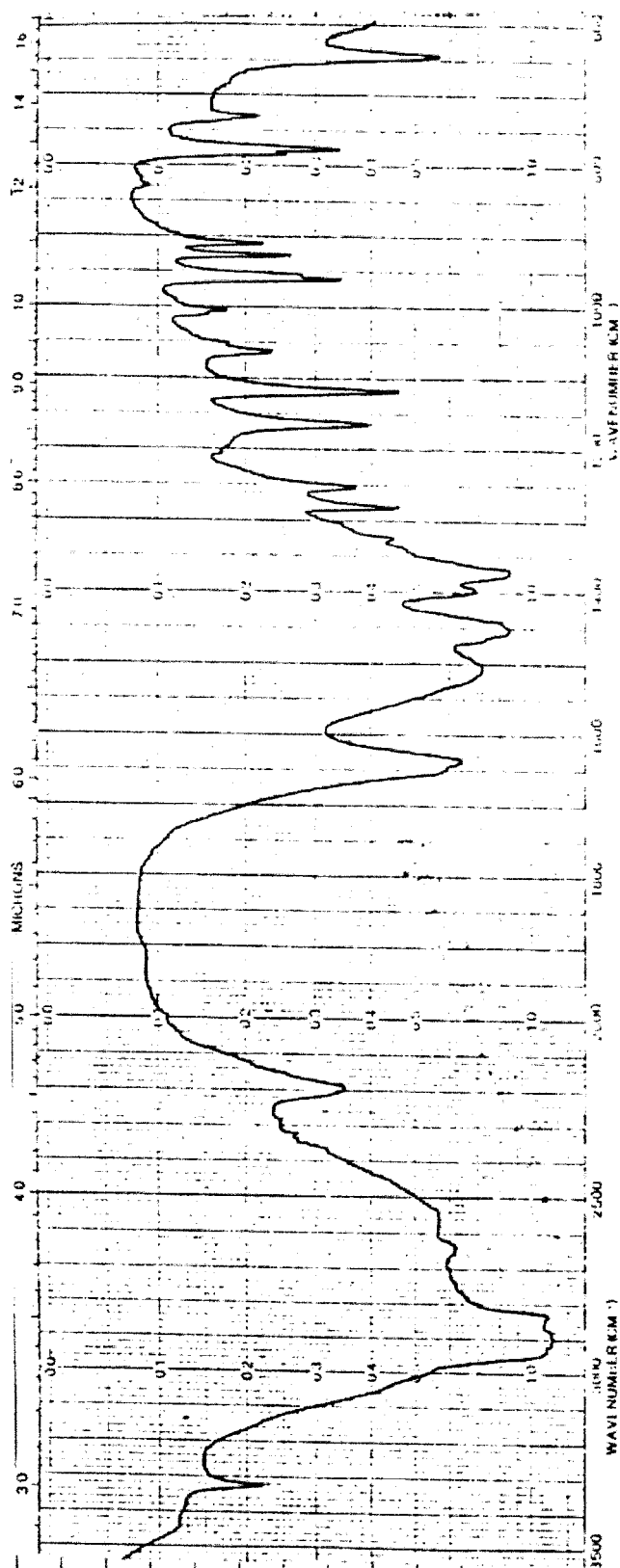


Figure 1 FTIR spectrum of HMA formed.

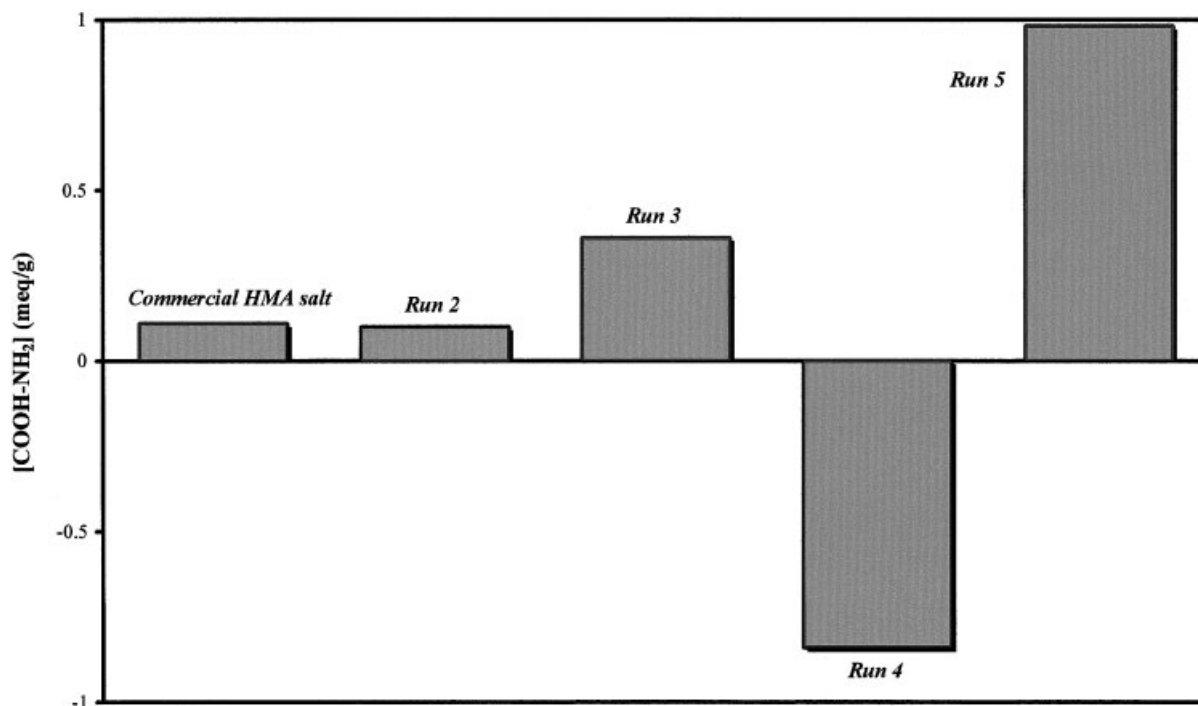


Figure 2 Balance of carboxyl and amine end groups in the HMA salts considered.

of adipic acid during mixing. Regarding hexamethylenediamine, it was revealed that when added in the form of a very concentrated aqueous solution, the water traces present also contribute in obtaining a homogeneous and balanced salt, without substantially changing the solid-state nature of the reaction and the free-flowing characteristics of the product. On the contrary, when added as solid, the salt formed was unbalanced and thus inappropriate for use as a starting material in polyamide manufacture.

The authors thank Robert Burgess for the experimental setup and the salt preparation experiments; Dan Kasprzak for the FTIR analysis; and David Robson for the end-group titrations. C.D.P. also thanks Ray Miller, Joe Weber, and David Marks for providing the opportunity for a sabbatical at the Experimental Station that led to this work.

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