Preparation of Polyhexamethyleneadipamide Prepolymer by a Low-Temperature Process

C. D. Papaspyrides,[1] S. N. Vouyiouka,[1] I. V. Bletsos[2]

[1]Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou, Athens 157 80, Greece
[2]E. I. DuPont de Nemours and Co., P.O. Box 27001, Richmond, Virginia 23261

ABSTRACT: The polyhexamethyleneadipamide (PA 6,6) prepolymer is prepared starting from dry hexamethylenediammonium adipate (PA 6,6 salt) by a low-temperature polyamidation technique, which ensures balanced and free-of-thermal-degradation products. The operating temperature is chosen in the vicinity of the melting point of the polyamide salt, to avoid thermal decomposition, which accompanies the higher temperatures of the conventional polyamidation processes. Two stages of prepolymerization are suggested: First, the reaction is carried out under autogenous conditions (pressurized system) to or beyond the point where diamine ends have reacted; hereafter, the system is vented so as to remove the produced water and to drive the condensation reaction toward a higher degree of polymerization. The process is demonstrated using both shaker tubes and a modified, intensively stirred autoclave. The products have balanced ends and no detectable thermal degradation effects and are used as a starting material for solid-state finishing toward high molecular weight polyamides. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 301–306, 2004

Key words: polyamides; Nylon® 6,6; solid-state polymerization; transition

INTRODUCTION

The traditional production of one of the most commercially important polyamides (PAs), polyhexamethyleneadipamide (PA 6,6), uses as a starting intermediate an aqueous solution of the salt of adipic acid (AA) and hexamethylenediamine (HMD).[1] Hexamethylenediammonium adipate (PA 6,6 salt) is a distinct chemical compound; it forms white, diamond-shaped monoclinic crystals, it is hygroscopic, and 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 dry or in solution at room temperature, but above 140°C, it polymerizes.[2]

The predominant and well-known industrial process for PA 6,6 production involves, first, solution polymerization starting from the aqueous PA 6,6 salt solution, removal of the water from the reactor, and, finally, polymerization in the melt state.[3,4] This technique results in the production of PA 6,6 resins, which can be directly used in applications with low requirements regarding the macromolecular chain length.[5] However, the increase of the degree of polymerization may be accomplished by subjecting the products to solid-state (post)polymerization (SSP). The latter is achieved by heating the polyamide grains in an inert atmosphere at a temperature well above their glass transition point, but below their melting temperature.[5–10]

The high temperatures employed (250–270°C) in the conventional polymerization/prepolymerization process encourage, to an increasing extent, side reactions and gel formation, which can drastically impair the quality of the end product.[11] Thus, thermal degradation becomes inevitable and deteriorates the properties of the polyamide produced, which is further molded or solid-state postpolymerized. The problem is enhanced when dealing with more thermosensitive polyamides (i.e., polyamide 4,6), due to the high processing temperatures required.[12]

The herewith-suggested prepolymerization process uses as starting material dry PA 6,6 salt instead of a salt solution, which is subjected to low-temperature polyamidation, to prevent thermal decomposition. This technique is based on polyamide salt SSP studies,[2,13–17] which indicate, depending on the reaction conditions, a typical transition of the process from the solid to the melt state [solid–melt transition (SMT)], where a very fast agglomeration of the reacting grains takes place. As a result, the monomer is transformed to a polymer by a reaction which rarely takes place in a real solid phase: The salt grains start to melt even if the operating temperature is below the initial melting point of the salt. The phenomenon can be seen microscopically since the sharp-edged crystals are trans-
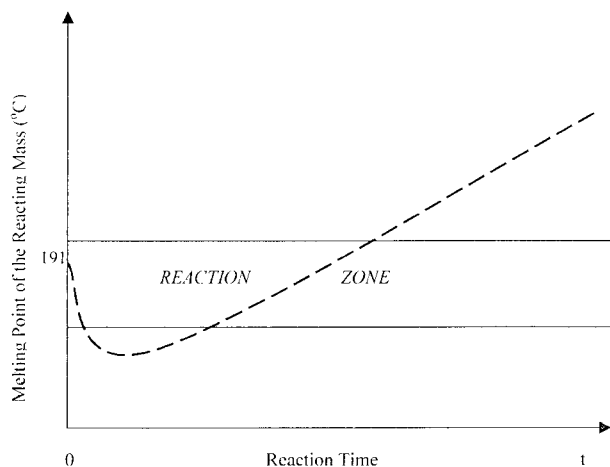
Figure 1 Melting point of the reacting mass versus reaction time and operating temperature zone suggested.

formed to nearly spherical particles. It has been suggested that the water produced during the solid-state polycondensation reaction hydrates the polar groups of the reactant, and as the amount of water increases, the crystal structure of the salt is destroyed by the formation of highly hydrated regions. After the formation of these melt areas, the reaction proceeds mainly in the melt, even at temperatures below the initial melting point of the salt and the reaction rate is considerably increased. The above behavior occurs more drastically at higher reaction temperatures. As the polymerization proceeds further, the molecular weight increases, the hygroscopicity of the reacting system decreases, and, eventually, the solid character of the process is restored.

Based on the above, under conditions of reasonable reaction kinetics, the transition to the melt and the tendency to agglomerate become inevitable. Consequently, the operating temperature, for the herewith prepolymerization process, is chosen a few degrees below or above the melting point of the salt. In fact, operating even below the latter, due to the aforementioned SMT phenomenon, the melting point will be reduced and the salt grains will agglomerate and turn again to a semimelt mass. In any case, however, the lower temperatures used are beneficial, since undesirable side reactions are not apt to occur and degradation is minimized, in comparison to the conventional polyamidation processes, where the operating temperature is much higher. The suggested reaction temperature profile is presented in Figure 1, where the variation of the melting point of the reacting mass versus reaction time is also shown.[13–18]

The main concern now is that the transitions between solid and melt require careful design of the experimental apparatus. The problem of an appropriate reactor arises, since it should be capable of handling (stirring and agitating) all these physical forms

for an adequate period of time. The same reactor should be capable of keeping the reacting mass from hardening into a single mass and therefore producing a granular prepolymer instead.

An additional feature of salt polyamidation is the need to compensate for or to reduce the loss of the readily volatile diamine from the reaction composition. Several measures have been adopted for this purpose, such as the introduction of HMD from the beginning of the polycondensation reaction in an amount sufficient to counteract diamine loss,[19] the use of nitrogen gas containing HMD and its return to the starting material feed line, and, finally, the decrease of the reaction temperature to minimize the HMD loss.[20]

The problem of the HMD loss is also treated here and the production of a balanced prepolymer without the need for HMD recovery is allowed. An "autogenous" route is suggested: The use of a closed, intensively stirred, vessel, under pressure during the initial stages of the polymerization, is appropriate to ensure that a feed consisting of dry salt with balanced ends would result in a stable and balanced prepolymer. After all the HMD has reacted to form amide bonds, the pressure can be released to allow water removal and shift the reaction to a higher degree of polymerization. The critical parameters studied are the time and the temperature required for HMD to react before releasing the pressure of the closed vessel, without the need for an elaborate control strategy to maintain the proper stoichiometry.

Concluding the above, the significant advantages of this low-temperature polyamidation of dry salt, derived from the polymer thermal protection and from the easy handling–storage of the salt, render its commercial application feasible.[18] The suggested technique intends to overcome the drawbacks of the traditional prepolymerization process, taking also into account a simple and easy technique for the preparation of dry PA 6,6 salt that has been already proposed by the authors.[21]

EXPERIMENTAL

Starting materials

The PA 6,6 salt used in all tests was obtained from the Rhone–Poulenc Co. (France).

Experimental apparatus

A batch procedure in a small and larger scale was applied to convert dry PA 6,6 salt to polyamide prepolymers, which were afterward solid-phase postpolymerized. Accordingly, the prepolymerization process was carried out first in shaker tubes and in small quantities and then in a properly modified autoclave. The required equipment is described below:

(a) A *shaker tube* is a small steel vessel about the size of a large test tube, which is mounted in a metal member capable of heating and vibrating, rapidly and forcefully, the tube.

(b) Regarding the *autoclave* experiments, a horizontally mounted cylindrical vessel was preferred, because it would tumble the reacting mass and, hence, provide better mixing. For this purpose, a 1-gal stainless-steel Autoclave Engineers autoclave was suitably modified, in order to be stirred, and the rotor was at first protected from excessive torque by a magnetic coupling. However, stirring problems because of the insufficient torque appeared and we eliminated the magnetic coupling and protected the equipment by electrical means, so that the drive would shut off in the case of mechanical overload.

Prepolymerization experimental procedure

(a) *Shaker tube experiments:* First, we loaded 75 g of dry PA 6,6 salt into the shaker tube (400 mL), ensuring the absence of oxygen by filling it with inert gas. We then heated the tube to the specified temperature (in the range of 180–210°C), following which we maintained the autogenous condition (225 psig) for 30–55 min. Subsequently, the tube was vented, while heating at the same temperature for 30–60 min. Prepolymer samples were afterward solid-phase polymerized under a nitrogen current (0.225 L/min) for 6 h at 180°C.

(b) *Autoclave experiments:* We placed 300 g of dry salt in the suitably modified autoclave (1 gal), to produce larger quantities of the PA 6,6 prepolymer of the same quality as in the shaker tubes. The salt grains were heated at 210 and 225°C (150–220 psig) for 30–70 min and, hereafter, the venting conditions lasted for 5–12 min at the same temperature.

The different conditions of each experimental run are presented in Table I. The samples formed during these runs are named based on the equipment used and on the temperature/time (°C/min) conditions during the first autogenous stage. Thus, the runs ST were conducted in the shaker tubes, and, meanwhile, runs A in the autoclave. In Run A225/70, the torque capacity of the motor, was enhanced, since there is no magnetic coupling to protect the motor, but it is protected by electrical means.

Characterization of PA 6,6 prepolymer

Samples of the PA 6,6 prepolymer formed, according to Table I, and their SSP products were analyzed to determine end-group content, relative viscosity (RV), molecular weight distribution (MWD), water content, bishexamethylene triamine (BHMT) content, and their melting–crystallization characteristics. The conden-

TABLE I
Experimental Conditions of Prepolymerization Runs

Samples	Apparatus used	Autogenous conditions	Venting conditions
ST180/30	Shaker tube	$T = 180°C$ $P = 225$ psig $t = 30$ min	$T = 180°C$ $t = 30$ min
ST210/55	Shaker tube	$T = 210°C$ $P = 225$ psig $t = 55$ min	$T = 210°C$ $t = 60$ min
A210/45	Autoclave	$T = 210°C$ $P = 150$–165 psig $t = 45$ min	$T = 210°C$ $t = 7$ min
A210/30	Autoclave	$T = 210°C$ $P = 165$–170 psig $t = 30$ min	$T = 210°C$ $t = 5$ min
A225/70	Autoclave direct coupling to motor	$T = 225°C$ $P = 170$–220 psig $T = 70$ min	$T = 225°C$ $t = 12$ min

sate collected during venting was also analyzed for end-group concentration and water content.

End-group analysis

The end-group concentrations were determined by potentiometric titration. For —NH_2 determination, the samples were dissolved in a mixture of 85% phenol–15% methanol and titrated with a solution of perchloric acid in methanol. For —COOH analysis, the polymer was dissolved in a mixture of 5:1 *o*-cresol–5% *o*-dichlorobenzene:20 % LiCL/methanol and titrated with a solution of tetrabutylammonium hydroxide in benzyl alcohol.

Viscosity measurements

The RV of PA 6,6 is the ratio of the viscosity of a solution of a 8.4% (by weight) polymer in a solution of 90% formic acid at 25°C to the viscosity of the formic acid solution, measured at 25°C.

MWD

The samples were dissolved in *ortho*-chlorophenol and then analyzed by size-exclusion chromatography.

Water content

The samples were dispersed in methanol and titrated with the "Karl Fischer" reagent.

Figure 2 DSC trace of ST180/30.

BHMT content

BHMT is a trifunctional amine containing a secondary amino group in the molecular chain and its content indicates the degree of polyamide thermal degradation. Samples were heated and hydrolyzed in the presence of hydrobromic acid followed by vacuum drying. The resultant decomposed product was gas-chromatographed.

Differential scanning calorimetry (DSC)

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

RESULTS AND DISCUSSION

Small-scale experiments (shaker tubes)

DSC graphs of ST samples indicated conversion of the PA 6,6 salt to the PA 6,6 prepolymer: The DSC trace showed a sharp peak at 264.92°C, which corresponds to the PA 6,6 melting point (Fig. 2). A smaller peak at 253.09°C was due to the oligomer and appeared as a minor species in the chromatogram. Thermal degra-

dation precursors and branching precursors were not detected.

Table II summarizes the analytical data of the products in the shaker tubes. The values of the RV achieved were in the range of 12–24.5; meanwhile, the molecular weight of the prepolymers varied between 15,300 and 20,900, which shows high conversion even at such low reaction temperatures (180°C, 210°C). No loss of HMD was observed, since there was a small excess of HMD in the prepolymers formed (4 meq/kg). Therefore, the autogenous step hindered the escape of the volatile diamine during venting and to preserve the stoichiometric balance of the end groups in the resulting prepolymer. In addition, the samples had a normal MWD (2.2–4.8) and low water content (2.62–2,81%). The BHMT content of ST210/55 (Table II) was significantly lower than that of ST180/30 and this difference was attributed to localized heating in the beginning of prepolymerization, which led to higher thermal degradation and was corrected in later experiments.

Turning to the parameter of time during the autogenous condition, it seems that 30 min is long enough for the majority of HMD to react before venting, even

TABLE II
Prepolymerization of PA 6,6 Salt in Shaker Tubes

Samples	RV	NH_2 (meq/kg)	COOH (meq/kg)	COOH—NH_2 (meq/kg)	M_n	M_w	MWD	H_2O (wt %)	BHMT (mol/10^6 g)
ST180/30	12.0	175	171	−4	6900	15,300	2.2	2.62	2.8
ST210/55	24.5	87	83	−4	4380	20,900	4.8	2.81	1.0
Condensate		—	—					100	

TABLE III
Solid-state Polymerization (6 h, 180°C, N$_2$) of PA 6,6 Prepolymers Prepared in Shaker Tubes

Samples	RV$_{initial}$	$M_{n,initial}$	$M_{w\ initial}$	MWD$_{init}$	RV$_{SSP}$	$M_{n\ SSP}$	$M_{w\ SSP}$	MWD$_{SSP}$
ST180/30	12.0	6900	15,300	2.2	43.1	11,500	26,700	2.33
ST210/55	24.5	4380	20,900	4.8	42.4	13,800	32,100	2.33

Initial and final characteristic values of the samples are reported.

at the low temperature of 180°C. A further indication of the effectiveness to prevent the loss of the volatile diamine was the composition of the condensate of ST210/55 (H$_2$O: 100%).

As expected, the higher RV was obtained in ST210/55, where the reaction temperature was only 20°C above the melting point of the salt and venting lasted for 60 min. Thus, it becomes evident that high reaction rates can be accomplished even at low reaction temperatures (in comparison to typical polymerization processes), taking advantage of the inevitable decrease of the melting point of the reacting mass (Fig. 1) and the optimized autogenous/venting conditions. In fact, the suggested prepolymerization process is effective and results in high-quality, balanced prepolymers, suitable for SSP, as can be seen in Table III. Prepolymers of ST180/30 and ST210/55 were solid-state postpolymerized (180°C, 6 h) and resulted in PA 6,6 resins of high RV (42.4–43.1) and normal MWD (2.33); such an increase in the RV is significant and favored by the end-group balance of the prepolymers.

Large-scale experiments (autoclave)

The autoclave experiments demonstrated that the same approach employed with the shaker tubes could be used to produce larger quantities of PA 6,6 of the same quality. Polyamide prepolymers were formed

starting from dry PA 6,6 salt and Table IV presents analysis data of the autoclave samples: The bulk product obtained from the middle zone of the reactor, under all conditions, was well balanced, had an RV between 8.5 and 27.1 (average weight molecular weight 12,500–25,500), and a low water content (0.79–3.70 %).

In comparing A210/30 with A210/45, it is shown that, under similar conditions but with a shorter heating time during the pressurized stage and better control of venting, the condensate was primarily water (87.04%) and the polydispersity was narrower (2.3). These two runs indicate also problems related to stirring and heat- and mass-transfer limitations. Lack of homogeneity of the samples obtained from different spots inside the reactor was detected and attributed to insufficient torque capacity. More specifically, good heat and mass transfer was achieved in the middle of the reactor (A210/45), but poor heat and mass transfer was observed between the walls and the middle of the reactor (A210/30). The product collected from the proximity of the back wall showed higher conversion than did the product from the front wall, because the latter was at the lowest temperature as it was the loading end of the reactor.

The homogeneity problems were resolved when the torque capacity was increased and the polymerization time was lengthened (A225/70). Then, the quality of

TABLE IV
Prepolymerization of PA 6,6 Salt in the Properly Modified Autoclave with Stirring

Samples	Sample position in reactor	RV	NH$_2$ (meq/kg)	COOH (meq/kg)	COOH—NH$_2$ (meq/kg)	M_n	M_w	MWD	H$_2$O (wt %)
A210/45	Middle of the reactor	14.2	122	148	26	4260	28,100	6.60	3.03
	(random places without	12.0	146	170	24	3170	16700	5.27	3.70
	contact to reactor walls)	12.4	643	618	−25	3360	16300	4.85	4.05
Condensate			390	290	−100				40.37
A210/30	Back wall	10.1	185	203	18	4970	11,700	2.35	0.64
	Middle of reactor	8.5	604	633	29	5440	12,500	2.30	0.79
	Front wall	2.8	1035	967	−68	1560	3230	2.07	2.44
Condensate			688	595	−93				87.04
A225/70	Middle of reactor	27.1	74.4	104	29.6	10,900	25,500	2.34	1.07
	Reactor walls	21.9	103	106	3	11,100	25,800	2.32	1.38
Condensate			62	11	−51				96.73

the product was improved significantly: Samples taken from different regions of the autoclave had identical MWD (2.32–2.34) and water content (1.07–1.38%); meanwhile, the composition of the condensate (H_2O: 96.73 %) indicated a favored removal of the polycondensation water in comparison to A210/45 (40.37%) and A210/30 (87.04%), where oligomers were also detected in the condensates.

The prepolymers formed in the autoclave were not further solid-state polymerized, since the aim of this work was achieved, that is, the effectiveness of the suggested prepolymerization technique was ensured to a large scale, especially when heat- and mass-transfer problems were resolved in the presence of adequate mixing. It was concluded that the formation of a high-quality prepolymer and the end-balance maintenance are feasible when keeping the reaction temperature in the vicinity of the salt melting point and following a two-stage process, which includes a pressurized and a vented step, in a properly designed reactor.

CONCLUSIONS

Dry balanced salt was converted to the PA 6,6 prepolymer by a low-temperature autogenous process operating in the vicinity of the melting point of the salt. The well-known transition to the melt state was exploited, even at temperatures below the salt melting point. The requirement of developing a reactor capable of handling transitions from the solid to the melt and again to the solid state arises and the first approach is described in this work. To ensure diamine control, two steps are followed: (a) A vessel is charged with dry salt and inert gas and it is sealed, heated, and agitated. The autogenous condition is maintained to or beyond the point where diamine ends have reacted. (b) Water vapor is then vented from the vessel. This autogenous route allows the production of a balanced prepolymer without detectable thermal degradation products and without the need for HMD recovery. The process was demonstrated using both shaker tubes and a customized, intensively stirred autoclave.

Within our experimental conditions, we prepared prepolymers in shaker tubes with an average weight molecular weight range of 15,300–20,900 and with polydispersity ranging from 2.2 to 4.8. Using the autoclave, prepolymers with a molecular weight of 12,500–25,800 and a polydispersity of 2.3 were formed. The quality of these products ensures safe solid-state finishing at higher temperatures toward much higher molecular weights.

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