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HALS in Polyamide 6 Polymerization

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Summary: The use of Hindered Amine Light Stabilizers (HALS) directly in polyamide 6 polymerization can cause some problems. The following two problems were the focus of our project:

1) We investigated, from a theoretical point of view, the results of introducing directly one of the precursors of HALS into polyamide 6 polymerization. For the investigation, 4 amino-2,2,6,6-tetramethylpiperidine (triacetondiamine or TAD) was chosen. We considered the TAD chain-ending effects and their influence on the total amount of amino chain-endings that can be titrated, a parameter of primary importance in the fibre field.
2) We examined the amide interchange reaction in the case of an HALS containing two amide groups, using a product available on the market, N,N'-bis(tetramethyl-4-piperidyl)isophtalamide. In this case we were able to generate a couple of equations that allows one to calculate the quantity of amide interchanged HALS. This was done by comparing the results (molecular weight and chain-endings analysis) of polymerization with and without HALS.

Keywords: HALS, light stabilizers, polyamide, polymerization, transamidation

Introduction

In the last decades, the spinning technology has required a considerable increase of the spinning speed both in the POY (pre-oriented yarn) and in the FDY (full draw yarn) technologies. This evolution has forced industries to be more selective in the choice of the polymers. An excellent polymer for high spinning speed is a polyamide 6 that contains a suitable quantity of thermal and light stabilizers.

The possibility to add amine or amide light stabilizers (HALS) during polyamide 6 polymerization should be investigated from the producers of these polymers.

The chain-ending reactions of the HALS containing amine groups and the amide interchange reactions of the HALS containing amide groups are very important from both theoretical and technological point of view.

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Experimental Part

Relative Viscosity Determination

Relative viscosity is determined by dissolving the polyamide samples in a solution of sulfuric acid 95.7%±0.2% (w/w) at a temperature of 50÷55°C, at a polyamide concentration of 0.01 g/mL. When the polyamide is completely dissolved, let the solution cool down to 20°C and measure the flow-time in a suitable Ubbelohde Viscometer, placed in a thermostatic bath regulated at 20.0±0.1°C. Relative viscosity is calculated by dividing this flow time by that of the solvent measured in the same viscometer.

Number-Average Molecular Weights

The number-average molecular weights we used to determine the percentage of amide interchange through the equation (12), are calculated from the relative viscosity (η_{rel}) through the equations (1) and (2):

$$\overline{M}_n = 11500\left(\eta_{rel} - 1\right) \qquad (1)$$

$$\overline{M}_n = F\left(\eta_{rel} - 1\right) \qquad (2)$$

These equations have been used for a long time and have been verified many times.

Equation (1) must be used with a non-chain-ended polyamide 6 or with a monofunctional chain-ending.[1] Equation (2) must be used with a polyfunctional chain-ending, when the molecular distribution index is other than D=2.

Factor F depends on the molecular weight distribution,[1][2] following equation (3):

$$F = \frac{4.044 - D}{1.777 \mathrm{x} 10^{-4}} \qquad (3)$$

In case of bi-functional chain-endings index D will be obtained from the ratio R between non-terminated and terminated chains[3] as showed in equation (4):

$$D = 2 - 2\left[1/(2 + R)\right]^2 \qquad (4)$$

Titration of Amino and Carboxyl End-Groups

We dissolved the polyamide in 2,2,2 trifluoroethanol and we titrated the amino end-groups with 0.02N aqueous hydrochloric acid and then we back-titrated with 0.02N aqueous sodium hydroxide to detect the carboxyl end-groups.[4]

Industrial Polymerization

To carry out our experiment, we generated two series of three polymerization batches.

All the polymerizations were carried out in industrial batch plant.

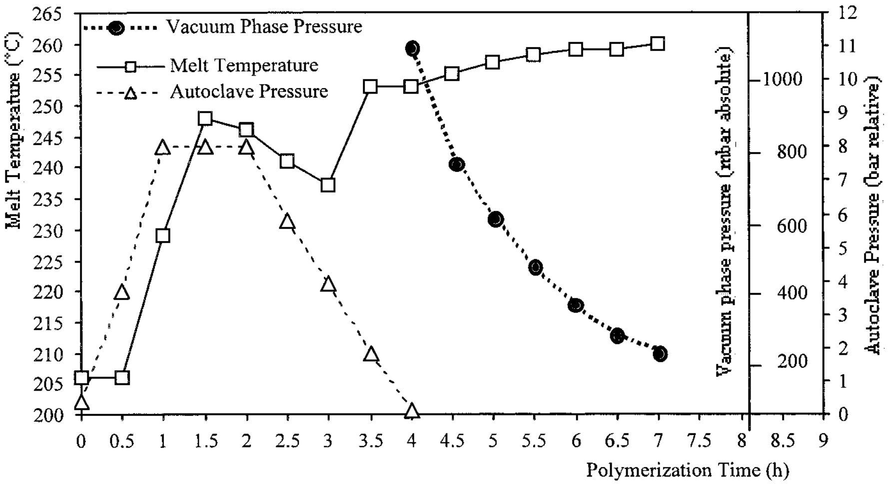


Fig. 1. Melt temperature, autoclave pressure in the pressure and vacuum phases as function of polymerization time.

The conditions of batch polymerization were identical to those used in industrial plants and were kept the same for all the polymerizations. In Figure 1 we graphed the variables relevant to these conditions such as the polymer temperatures and the pressures in the pressure and vacuum phases.

Table 1. Recipes and final compositions relevant to the two series of batches polymerized with and without TAD-IPA.

	Blank polymerizations without TAD-IPA				Polymerization with TAD-IPA			
	Autocl. charge	Extract. dried PA6	Percent in final PA6	Chain-endings conc.	Autocl. charge	Extract. dried PA6	Percent in final PA6	Chain-endings conc
Components	*Kg*	*Kg*	*wt.-%*	*mmoles/ /kg*	*Kg*	*Kg*	*wt.-%*	*mmoles/ /kg*
Caprolactam	1400.00	1225.00	98.986	-----	1400.00	1225.00	98.599	-----
Benzylamine	2.80	2.27	0.184	17.20	2.80	2.27	0.183	17.10
Acetic acid	1.40	1.21	0.098	16.33	1.40	1.21	0.098	16.33
TAD-IPA	-----	-----	-----	-----	4.20	4.62	0.372	8.40
Antifoam	0.88	0.40	0.032	-----	0.88	0.40	0.032	-----
CL+Oligom.	-----	8.04	0.650	-----	-----	8.28	0.666	-----
Water	50.00	0.62	0.050	-----	50.00	0.62	0.050	-----
TOTAL	1455.08	1237.54	100.000	-----	1459.28	1242.40	100.000	-----

In Table 1 we reported the recipes for three batches without HALS and for three batches with the presence of 0.3 wt.-% (weight percent) on caprolactam of the HALS.

In Table 2 we reported the results of the analysis on the extracted and dried polyamide, for the six batches and the average values.

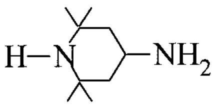
Table 2. Analysis relevant to the final polyamides 6 obtained in the two series of batches polymerized with and without TAD-IPA.

		Blank polymerizations without TAD-IPA				Polymerization with TAD-IPA			
		Batches				Batches			
Properties	Unities	1st	2nd	3rd	Average	1st	2nd	3rd	Average
η_{rel}	------	2.674	2.665	2.679	2.673	2.606	2.624	2.617	2.616
[COOH]	*meq/kg*	34.4	35.7	34.6	34.9	35.3	33.9	33.4	34.2
$[NH_2]$	*meq/kg*	35.7	36.6	36.3	36.2	54.6	51.9	53.7	53.4
CL+Olig.	*wt.-%*	0.60	0.67	0.56	0.61	0.72	0.59	0.65	0.65
Water	*wt.-%*	0.048	0.054	0.053	0.052	0.054	0.061	0.064	0.060

Results and Discussion

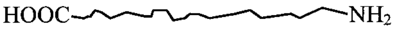
HALS as Chain-Ending

Because the use of additives containing HALS is ideal to provide thermal and light resistance, different producers of these chemicals (generally HALS are obtained from tetramethylpiperidine) have tried to make appropriate derivatives and relevant polyamide based master-batches. Among these producers, BASF[5][6] and Allied[7] have patented the use of triacetondiamine (TAD - 4amino2,2,6,6 tetramethyl-piperidine) and relevant derivatives. TAD contains in its molecule a perfectly polycondensable primary amine and a sterically hindered secondary amine which does not polycondensate under usual melt-polycondensation conditions but which is perfectly dyeable as chain-endings. Moreover the molecule is thermically stable at the polymerization conditions.

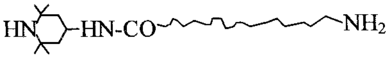


The dosage of TAD is critical when adding a small quantity of this product to the polymerization process. This is due to its strong chain-ending effect, which is similar to that of a monofunctional amine, and to its strong repercussion on the total number of amino chain-endings. The effect is so strong that in order to reduce the number of these total amino groups (primary of the macromolecule chains and secondary of TAD), it is almost always necessary to add a bicarboxylic acid and consequently another chain-ending (in addition to TAD). The following example is given to illustrate this point.

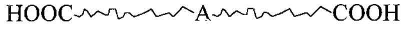
Taking into consideration a polyamide 6 with a molecular weight of 19000 (52.6 mmoles/kg) chain-ended with 0.2 wt.-% of TAD (12.8 mmoles/kg) and a sufficient quantity of adipic acid to obtain 42 meq/kg of titratable amino group, the chain situation will be the following (all the concentrations are relevant to the final polyamide 6, extracted and dried):



not chain-ended chains = 16.4 mmoles/kg



chains containing TAD = 12.8 mmoles/kg



chains containing adipic acid = 23.4 mmoles/kg

Thus, the use of two chain-endings, one of them being TAD, allow us to reach a good molecular weight stability during spinning (by the use of large quantity of chain-endings) and a good thermal stability during high speed spinning (by the presence of TAD).

In addition the dyeability can be predicted because of the presence of the 42 meq/kg of dyeable groups: 29.2 meq/kg supplied by the primary amino group and 12.8 meq/kg supplied by the secondary amino group of TAD.

Effectiveness as Light Stabilizer

When we started this research, there were some questions on the effectiveness of using TAD as a light stabilizer in lieu of low molecular weight HALS. These questions were related to TAD's reduced mobility when linked to a macromolecular chain.

In another paper we showed that the light stabilization is identical for a polyamide 6 with TAD as chain-ending and a polyamide 6 blended with HALS containing the same concentration of sterically hindered amine.[8]

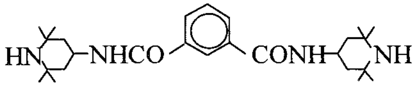
Amide Interchange Determination

When feeding HALS during polymerization, one has to take into account the many possible interferences with the polymerization reactions by thermal and thermo-oxidative reactions. Many degradation by-products of the thermal or thermo-oxidative reactions can interfere during the polymerization process and therefore selecting thermally stable HALS for the polyamide 6 polymerization is critical.

In addition to the chain-ending effect of an HALS having a reactive primary amino group in its structure, the interference created by the amide interchange between the amide group of an amide type HALS and the polyamide chains has to be taken into consideration. This interference is not negligible and can produce unexpected variation in terms of molecular weight.

The HALS we have to take into account must be a primary amide and there are many products available on the market.

We decided to test both experimentally and theoretically one of the products available on the market. N,N'-bis(tetrametyl-4-piperidyl)isophthalamide (TAD-IPA) can be easily purchased and is broadly used in polyamide 6 spinning:



This HALS is stable under standard polymerization conditions but the amount that will transamidate is strictly dependent on the polymerization conditions (temperature, time, pressure, catalysts) and must be evaluate on a case-by-case basis.

To evaluate this parameter by analysis is quite complicated due to the low solubility of polyamide and, moreover, it requires sophisticated instrumentation such as NMR, GC/MS, etc.

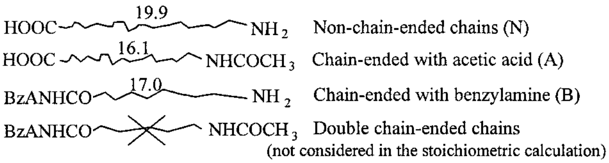
A simpler way to get this result was obtained by comparing the results of two series of three polymerizations carried out under identical conditions. The comparison terms were the number-average molecular weight (or relative viscosity) and the concentrations of different types of terminated chains, values that can be calculated by knowing the end-groups (amino and carboxyl) and the HALS concentrations in the final polyamide.

Simulation

Let us consider a polyamide 6 produced with this recipe:

Caprolactam = 99.7 p. Benzylamine = 0.2 p. Acetic acid = 0.1 p. Water = 3.0 p.

The following leakage was predicted during the polymerization: benzylamine = 18 wt.-% acetic acid = 13 wt.-%. It is assumed that the extraction plant can extract 10 wt.-% of caprolactam and its oligomers. Therefore the chain situation will be illustrated in Figure 2.



Non-chain-ended chains (N)
Chain-ended with acetic acid (A)
Chain-ended with benzylamine (B)
Double chain-ended chains
(not considered in the stoichiometric calculation)

$[NH_2]$ = 19.9+17 = 36.9 meq/kg
$[COOH]$ = 19.9+16.1 = 36 meq/kg
P_T= 36.9 x 36 = 1328 $(meq/kg)^2$
n° of chains = 53 mmoles/kg
$\overline{M}_n$= 18868 dalton η_{rel}= 2.64

Fig. 2. Situation of the chains in case of a PA6 terminated with a pair of chain-ending.

If, in the initial recipe, we add 0.25 wt.-% of TAD-IPA (MW=442.6 dalton), this will correspond to 0.278 wt.-% or 6.28 mmoles/kg in the final polyamide 6.

If no amide interchange occurs during the polymerization, the only change would be in the titratable amino group: $[NH_2]_{TIT} = [NH_2]_{PC} + [NH]_{TAD\text{-}IPA}$ = 36.9+6.28x2 = 49.46 meq/kg

Molecular weight, relative viscosity, carboxyl end-groups and polycondensable amino end-groups remain unchanged.

If some amide interchange occurs during the polymerization, the chain situation will get more

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim and more complicate because a large number of possible reactions between the TAD-IPA and the different chains have be to considered. Specifically, six types of amide interchange reactions can occur.

Taking into account the whole schema, we can obtain a total of twelve type of chains with different terminations and ten types of non-macromolecular products. The possible cyclic oligomers are not taken into consideration because they do not affect chain-endings.

Fortunately, this complicated schema can be simplified in the calculation. This is because, from a stoichiometrical point of view, the number of chains to be taken into consideration is small. Linear monomeric products and chains with double terminations can all be incorporated in the chains we take into consideration for the calculation.

For this simulation, the following parameters were taken into account:

(1) The chain ending and the dyeable amino-group situation in the polyamide after the possible amide-interchange.

(2) The case when amide-interchange reactions occurred either completely or at only 50%.

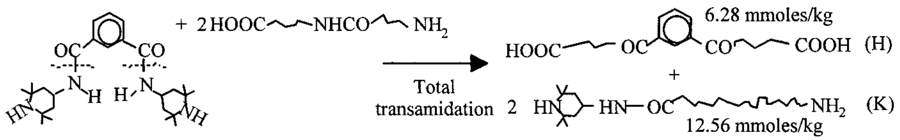
(3) The possibility that the transamidation occurred only by one of the two amide groups of TAD-IPA.

It should be noted that in reality the situation is always a mixture of these three possibilities. However, interesting conclusions can be drawn from these simplified assumptions.

Case A – Complete amide interchange

In this situation, in order to perform our calculation, we only have to add chains H and K to the previously considered chains N, A and B. In fact, as already mentioned, from a stoichiometrical point of view, a lot of chains can be merged with the previous types.

In order to keep things as simple as possible, only the amide interchange with non-terminated chains was considered. The same conclusions, however, can be drawn if the amide interchange occurs on the four types of chains considered in the polymerization without TAD-IPA. If H mmoles/kg will transamidate we obtain H mmoles/kg of chains containing isophthalic acid as regulator and K chains terminated with TAD, being K=2H:



As illustrated in the above reaction, three polymer chains are obtained from two polymer chains. This means a decrease in molecular weight and, at the same time, a variation of the molecular weight distribution index, because the H chains are terminated with a bicarboxylic acid. The final result will be a decrease of molecular weight, while the titratable and polycondensable amino groups, as well as the carboxyl groups, remain constant.

Starting from the initial situation and considering the type of chains we already have described, we can obtain:

$$[NH_2]_{TIT} = N+B+2K = N+17.0+25.12 = \underline{N+45.12} \qquad (5)$$

$$[NH_2]_{PC} = N+B+K = N+17.0+12.56 = \underline{N+29.56} \qquad (6)$$

$$[COOH] = N+A+2H = N+16.1+12.56 = \underline{N+28.66} \qquad (7)$$

The polymerization conditions being the same, the P_T can be considered constant, and thus:

$P_T = (N+29.56)(N+28.66) = 1328$ which yields $N = \underline{7.34\ meq/kg}$

From this value we will obtain: $[NH_2]_{PC} = \underline{36.90\ meq/kg}$ $[COOH] = \underline{36.00\ meq/kg}$

$[NH_2]_{TIT} = \underline{49.46\ meq/kg}$

As predicted, the polycondensable and titratable amino groups as well as the carboxyl groups remained unchanged while the molecular weight and the relative viscosity decreased:

Total number of chains = N+A+B+3H = 59.28 mmoles/kg.

From this value we can calculate the following parameters:

$$\overline{M}_n = {}^{10^6}\!/_{59.28} = 16869 \text{ dalton} \qquad D = 1.982^{(a)} \qquad \eta_{rel} = {}^{\overline{M}_n}\!/_{F} + 1 = {}^{16869}\!/_{11603} + 1 = 2.454^{(a)}$$

$^{(a)}$ D can be calculate from the chain situation [equation (4)], while F is obtained from D [equation (3)]

Case B – 50% of total amide interchange

With a calculation that is very similar to the one outlined in *Case A* and taking into consideration that 50% of the TAD-IPA remains unreacted, we obtain the following:

N = non terminated chains = 13.62 mmoles/kg

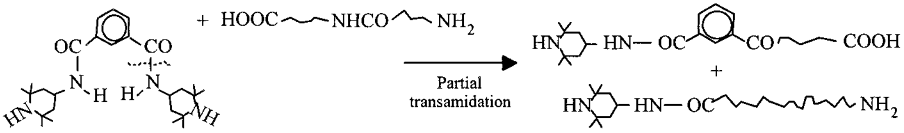
$[NH_2]_{PC} = \underline{36.90\ meq/kg}$ $[COOH] = \underline{36.00\ meq/kg}$ $[NH_2]_{TIT} = \underline{49.46\ meq/kg}$

$$\overline{M}_n = {}^{10^6}\!/_{56.14} = 17812 \text{ dalton} \qquad D = 1.994 \qquad \eta_{rel} = {}^{\overline{M}_n}\!/_{F} + 1 = {}^{17812}\!/_{11531} + 1 = 2.545$$

Also in this case, the only variables are molecular weight and relative viscosity that are intermediate between the previous two already considered.

Case C – 100% of partial amide interchange

For a more complete evaluation, we have taken into account the possibility of a partial transamidation, when only one of the amide groups of TAD-IPA has undergone an amide interchange:



Using the same calculation, we obtained, as predicted, the same results found in *Case A*. Only the MWD index and, consequently the relative viscosity, are a little higher. The difference in viscosity is so small that it can be considered negligible from a practical standpoint. This means that we are not able to distinguish between partial and total transamidation

$$\overline{M}_n = 10^6/59.28 = 16869\,\text{dalton} \qquad D = 2.00 \qquad \eta_{rel} = \overline{M}_n/F + 1 = 16869/11500 + 1 = 2.467$$

Evaluation of Amide Interchange

To determine the percentage of TAD-IPA that will undergo transamidation, we can find a suitable equation by taking the same type of mathematical approach we used in the previous examples. P_T is obtained from the blank polymerization (without TAD-IPA) shown in the experimental part of this discussion. Using the same symbology for the different type of chains we can set an equation based on P_T [equation (8)]:

$[NH_2]_{PC} = (N+B+K)$ $\qquad$ $[COOH] = (N+A+2H)$

$$P_T = (N+B+K)(N+A+2H) = (N+B+2H)(N+A+2H) \qquad (8)$$

Now, if H represents the mmoles/kg of transamidated TAD-IPA, S the total quantity of TAD-IPA in the final polyamide, and T the fraction of transamidated TAD-IPA, we obtain this relation: ST = H.

Therefore we can transform the previous equation (8) in this way:

$$P_T = (N+B+2ST)(N+A+2ST) \qquad (9)$$

From this equation it is easy to obtain other interesting relations between these variables:

$$\text{number of chains (mmole/kg)} = \frac{1}{2}\left[\sqrt{(A-B)^2 + 4P_T} + A + B + 2ST\right] \qquad (10)$$

$$\overline{M}_n = 2x10^6 \Big/ \left[\sqrt{(A-B)^2 + 4P_T} + A + B + 2ST\right] \qquad (11)$$

From the equation (11) is possible to obtain the equation (12), which is the value of the transamidated TAD-IPA fraction:

$$T = \frac{1}{2S}\left[\left(2x10^6/\overline{M}_n\right) - (A+B) - \sqrt{(A-B)^2 + 4P_T}\right] \qquad (12)$$

By substitution with the equation (2) we can obtain the equation (13):

$$T = \frac{1}{2S}\left\{\left[2x10^6/F(\eta_{rel} - 1)\right] - (A + B) - \sqrt{(A - B)^2 + 4P_T}\right\} \qquad (13)$$

F being dependent on T, we need to obtain a much more complicated equation. Usually, due to the small number of chains containing a bifunctional chain-ending (obtained by transamidation), we can use the value 11500 for the factor F. This estimation will produce only a negligible error, quite often lower than the precision of Relative Viscosity measurement itself:

$$T = \frac{1}{2S}\left\{\left[173.913/(\eta_{rel} - 1)\right] - (A + B) - \sqrt{(A - B)^2 + 4P_T}\right\} \qquad (14)$$

These equations are very useful for calculating the quantity of transamidated TAD-IPA. These equations can only be used for polyamide 6 chain-ended with a monoamine, a monocarboxylic acid, and polymerized with TAD-IPA. However, this case being one of the more complicated (double chain-endings), using the same logic, it is very easy to find similar (and usually simpler) equations for different chain-ending (single or couple) applications.

How to Apply the Equations in a Real Case

To illustrate how to use this equation in a real situation, we carried out two series of three polymerizations with and without TAD-IPA as explained in the experimental section of this paper. The polymerization recipes (Table 1) and the relevant average results (Table 2) of the series are also shown in the experimental section.

From the values of the first series of polymerizations (Table 2), we can calculate P_T using the average values of the concentrations of carboxyl and amine groups: P_T=1263 (meq/kg)^2.

The values for A, B and S to be used in equation (14) must be obtained from Table 1. The value for viscosity is obtained from Table 2:

η_{rel}=2.616 A=16.3 mmoles/kg B=17.1 mmoles/kg S=8.40 mmoles/kg

Because there is only a very small concentration of chains containing a bicarboxylic acid in our example, F will be close to 11500 (by iteration: D=1.998; F=11513). Using an estimation of 11500 for F and using equation (14), we obtain a value for T of 0.187. This means that only 18.7% of the original TAD-IPA is transamidated.

With different polymerization conditions, specially in continuous plant where the polymerization times are higher, the quantity of TAD-IPA that will transamidate is higher and can reach values around 40%. In this case the molecular weight will be dramatically reduced and these amide interchange reactions must be took into consideration.

Conclusion

The chain ending reaction of TAD, alone or with other bicarboxylic acids, was discussed for polyamide 6 polymerization. A method for calculating the percentage of transamidation of a light stabilizer, like TAD-IPA, was also presented for polyamide polymerization. This calculation uses the polymer's number-average molecular weight (or relative viscosity in sulfuric acid) and the amino and carboxyl end-groups concentrations.

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