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EFFECT OF POLYMERIZATION CONDITIONS ON THE THERMOOXIDATION OF NYLON 6

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ABSTRACT

The thermally initiated oxidation of cationic, anionic, and hydrolytic polymers of caprolactam (6-hexanelactam) was followed by determination of the oxygen uptake, molecular weight, and concentration of amino and carboxylic groups. In order to establish the effect of catalyst residues, unextracted as well as extracted anionic and cationic polymers were investigated. A series of polymers containing predominantly carboxylic or primary amino groups as well as polymers of different molecular weight having equal concentrations of carboxylic and amino groups were used to determine the specific effects of these groups on the thermal oxidation of hydrolytic polymers.

INTRODUCTION

Polycaprolactam, which is also referred to as nylon 6 and polyamide 6, is one of the most important representatives of recyclable polymers because it can be converted into monomeric caprolactam almost quantitatively. Therefore, from the ecological as well as economical points of view, nylon 6 has to be considered as one of the most important polymers for the future. Consequently, investigation of its properties is of increasing importance, and we should consider whether the degradability of nylon 6 can be affected not only by environmentally adverse additives but also by proper polymerization conditions.

Among the properties determining the quality of nylon 6, stability toward thermal oxidation plays a decisive role. Unfortunately, the service properties of polyamides deteriorate rapidly at rather low extents of oxidation. In the initial stages of thermal oxidation, the tensile strength has been found to decline proportionally to oxygen consumption (Fig. 1), so that continuous measurements of oxygen consumption can be used instead of tedious tensile strength measurements for the evaluation of the relative stability of nylons toward thermal oxidation.

In this article we deal with some factors which could affect the oxidizability of nylon 6, such as the type of catalyst (reaction mechanism), the polymerization temperature, the concentration of end groups, and the extraction of polymerization products.

EXPERIMENTAL

Polymers

Caprolactam purified by several crystallizations from water and benzene and free from impurities affecting radical reactions was polymerized under the conditions given in Table 1.

Thermal Oxidation

Thermal oxidation was carried out at 140°C in equipment suitable for following the kinetics of oxygen consumption under conditions where the rate of oxidation was not controlled by the diffusion of oxygen [2].

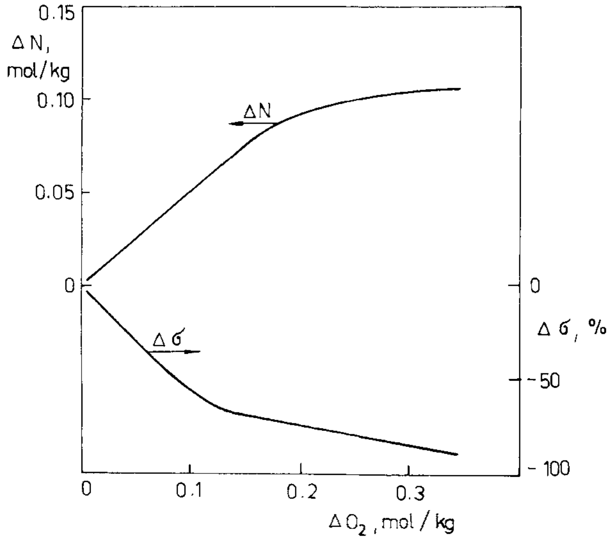


FIG. 1. Changes of the concentration of polymer molecules (ΔN) and decrease in tensile strength (Δσ) during thermooxidation of fibers of hydrolytic nylon 6 (Polymer 1, Table 1) at 140°C.

TABLE 1. Polymerization Conditions and Concentration of Acid (A) and Basic Groups (B), and Polymer Molecules (N) in the Polymer Extracted with Water

Polymer	Initiating system[a]				T, °C	Time, hours	[A]	[B]	[N]
	X	mol%	Y	mol%			mmol/kg		
1	AHA	3.0	–	–	230	21	66	66	66
2	L.HCl	2.0	–	–	230	145	200[b]	128	179
3	PIC	2.0	NaL	0.8	190	4	31	39	107
4	AHA	0.2	DA	1.7	240	170	152	5	155
5	AHA	0.1	DA	1.1	240	170	102	6	108
6	AHA	0.1	DA	0.5	240	170	44	15	57
7	AHA	5.0	–	–	240	170	80	80	79
8	AHA	0.2	DAH	0.3	240	113	11	54	37
9	AHA	0.2	DAH	0.5	240	113	10	96	59
10	AHA	1.1	DAH	2.6	240	170	152	2	155
11	AHA	4.4	DAH	1.1	230	22[c]	100	3	100
12[d]	AHA	3.0	–	–	230	21	66	0	66
13[d]	AHA	4.4	DAH	0.6	230	22[c]	20	0	97
14	AHA	0.2	DA	0.2	240	170	15	15	28
15	AHA	0.3	–	–	240	170	15	35	30
16	AHA	0.2	AO	1.8	240	170	15	30	50
17	AHA	1.2	–	–	240	170	38	38	38
18	AHA	2.4	–	–	240	170	53	53	53
19	H_2O	2.2	–	–	270	30	57	60	62
20	H_2O	3.0	–	–	250	30	57	57	57
21	H_2O	3.0	–	–	240	30	64	64	63
22	H_2O	4.3	–	–	230	30	66	66	65

[a] AHA = 6-aminohexanoic acid, L.HCl = caprolactam hydrochloride, PIC = cyclic trimer of phenyl isocyanate, NaL = sodium salt of caprolactam, DA = dodecanoic acid, DAH = 1,6-diaminohexane, AO = 1-aminooctane.

[b] Value for unextracted polymer: 340.

[c] Additional evacuation to 133 Pa for 2 hours.

[d] After reaction with nitrous acid [1].

Analytical Methods

The concentration of acid (A) and basic groups (B) was determined by conductometric titration [3], and the content of hydroperoxides (HP) by iodometry in 2,2,2-trifluoroethanol [4].

The number-average molecular weight ($\overline{M}_n$) was calculated from viscosity measurements [5] from which the concentration of polymer molecules N = 1000/M_n (in mol/kg) was calculated.

RESULTS AND DISCUSSION

The free-radical chain reactions proceeding during thermooxidation of polyamides [6] are susceptible to many circumstances of physical and chemical character.

Thermooxidation of nylon 6 proceeds only in noncrystalline domains which are accessible to oxygen [7]. The polymer investigated were of the same crystallinity (about 40%), so they were identical as far as physical structure is concerned.

The chemical structure of caprolactam polymers depends on the type of polymerization mechanism. Caprolactam is one of the very few monomers which can be polymerized anionically (with strong bases), cationically (with strong acids), as well as with neutral agents like water. Regular end groups of hydrolytic polymers are carboxylic and primary amino groups. Cationic polymers are terminated by primary amine and *N*-acyllactam structures, whereas anionic polymers also contain *N*-alkylamide groups in addition to *N*-acyllactam and primary amino groups. Further structural defects arise from side reactions, *N,N'*-Disubstituted amidine groups may be present in hydrolytic and cationic polymers and a series of defect structures arising from a Claisen-type condensation of imides in anionic polymers [8]. In addition to these irregular structures incorporated into polymer chains, unextracted anionic and cationic polymers contain low-molecular-weight residues of the catalytic system, i.e., strong base or strong acid. The extent and nature of these and additional side reactions also depends on the polymerization temperature, purity of the monomer, and technological discipline. Except for the polymerization temperature, the polymers investigated were prepared under comparable conditions from the same batch of monomer.

Effect of Polymerization Mechanism

Thermooxidation of the polymers prepared by anionic, cationic, and hydrolytic polymerization proceeds very differently (Fig. 2). Moreover, extraction of anionic and cationic polymers with water changes their oxidizability significantly (Fig. 2). The strong acid present in cationic polymers initiates their thermooxidative degradation to such an extent that these polymers are actually useless. When the strong acid has been removed by extraction, the thermal oxidation of the cationic polymer is similar to that of the hydrolytic one.

On the other hand, the basic residues from the anionic catalyst have a distinct stabilizing effect. Extraction with water not only removes the stabilizing base but also produces carboxylic groups (by hydrolysis of *N*-acyllactam structures) which accelerate the thermal oxidation. The acceleration at the beginning of oxidation of extracted anionic polymers may be due to some labile defect structures which act as initiators of oxidation.

Effect of End Groups in Hydrolytic Polymers

Hydrolytic caprolactam polymers represent the most important type of nylon 6. Its yearly production of more than 10^6 tons is destined predominantly for spinning. Because most ruptures during the spinning process are caused by microgel

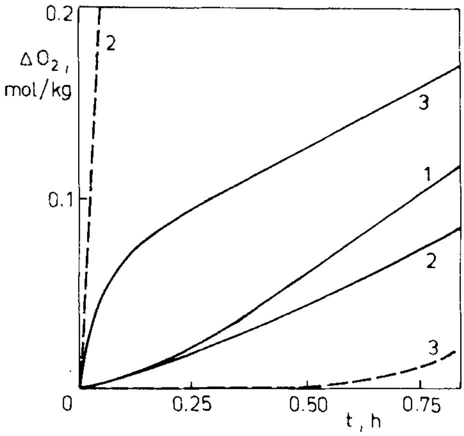


FIG. 2. Oxygen consumption (ΔO_2) during thermooxidation of nylon 6 (see Table 1 for the polymer number). Hydrolytic polymer (1), cationic polymer (2), and anionic polymer (3). The dashed curves denoted unextracted polymers.

particles formed by oxidative crosslinking, the industry requires polymers of a good stability toward thermal oxidation.

The hydrolytic polymerization of caprolactam initiated with water should yield polymer molecules having one amino and one carboxylic group at the ends, so that the number of polymer molecules should be equal to the number of free amino or carboxylic groups. In order to accelerate the addition of lactam molecules at amino end groups and to stabilize molecular weight at the required value, the industrial process is usually performed with the system water + carboxylic acid. The resulting nylon 6 is then composed of two types of macromolecules: $NH_2\sim\sim COOH$ and $RCO{-}NH\sim\sim COOH$. Similarly, initiation with water + amine or water + alkylammonium carboxylate systems leads to macromolecules terminated with the corresponding alkylamide groups in addition to those terminated with amino and carboxylic groups.

The choice of catalytic system or of the method of molecular weight control also affects the oxidizability of the polymer. The rate of thermooxidation of hydrolytic nylon 6 depends mainly on the ratio of carboxylic (A) and basic groups (B) (Fig. 3).

Also, the rate of thermooxidation of polymers containing almost only carboxylic groups (and no or very few amino groups) increases with the concentration of carboxylic groups (Fig. 4). In these oxidized polymers, the consumed oxygen is present as hydroperoxide and new carboxylic groups. The increase of carboxylic groups content (ΔA) is equal to the increase of the number of macromolecules (ΔN) because each chain splitting is accompanied by the formation of one carboxylic group. This finding may be inferred from our knowledge of the kinetics and mechanism of the oxidation of low-molecular-weight *N*-alkylamides. In the absence of impurities affecting radical reactions, thermooxidation of alkylamides proceeds as an autocatalytic reaction. *N*-Alkylamide hydroperoxide (HP), as the primary oxidation product, decomposes by homolytic cleavage according to Scheme 1 into an alkoxyl and hydroxyl radical [9–11]. Thus HP acts as the initiator of subsequent

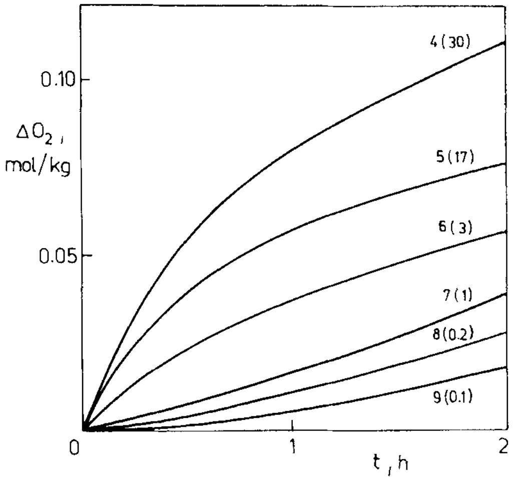


FIG. 3. Effect of the ratio of acid and basic end-group concentration ([A]/[B]) on the course of thermooxidation of hydrolytic nylon 6 at 140°C. The numbers in parentheses indicate the ratio [A]/[B].

oxidation of the amide, starting by hydrogen abstraction of the methylene group adjacent to nitrogen. The alkoxyl radical is subsequently converted into an aldehyde which reacts with hydroperoxide to yield a carboxylic group and another aldehyde molecule (Scheme 1). The carboxylic acid initiates homolysis of hydroperoxide [4, 9, 12] as well as the reaction of aldehyde with hydroperoxide [4].

The oxidation of the polymers containing predominantly amino groups proceeds in a different way. Preliminary results indicate that the hydroperoxide or the RO· radical formed by its homolysis reacts with primary amino groups under the

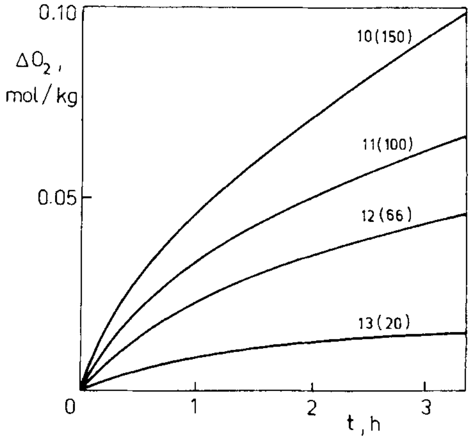
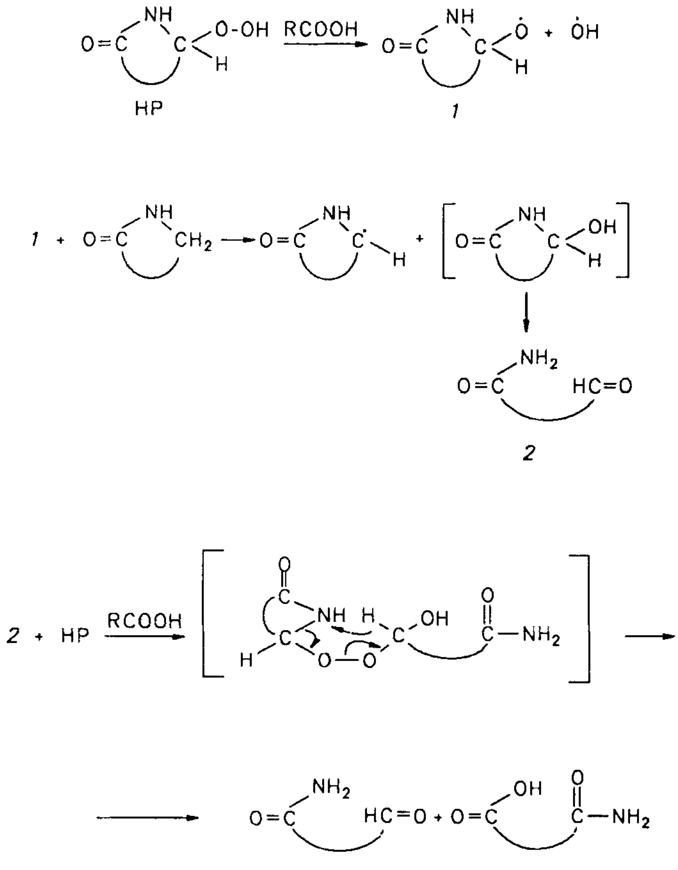


FIG. 4. Effect of the carboxylic-group concentration ([A], mmol/kg) on thermooxidation (140°C) of hydrolytic nylon 6 containing a minimum of amino groups. The numbers in parentheses indicate the concentration of carboxylic groups.



SCHEME 1.

formation of an imine group [13]. This reaction is accompanied by the combination of two macromolecules. During oxidation of such polymers (with a high B/A ratio), their molecular weight increases as long as amino groups are available [13]. The preferential reaction of amine with hydroperoxide decreases the concentration of the latter, so that the rate of its homolytic scission and, consequently, also the rates of initiation and oxidation decrease. The higher the content of amino groups, the more are the polymers resistant to thermal oxidation (Fig. 5), but the more intensive is the yellowing of oxidized polymers. On the contrary, polymers containing carboxylic groups primarily did not change their color during the investigated period of thermal oxidation.

In hydrolytic polymers containing both amino and carboxylic groups, both types of reactions proceed, i.e., homolytic scission of hydroperoxide initiated by carboxylic groups (with chain scission and formation of a carboxyl and primary amide group), as well as combination of two macromolecules [13]. For these polymers, $\Delta O_2 = HP + \Delta A - \Delta NH_2$ and $\Delta N = \Delta A + \Delta NH_2$. Figure 6 indicates that thermooxidation of these polymers is in agreement with this reaction mechanism.

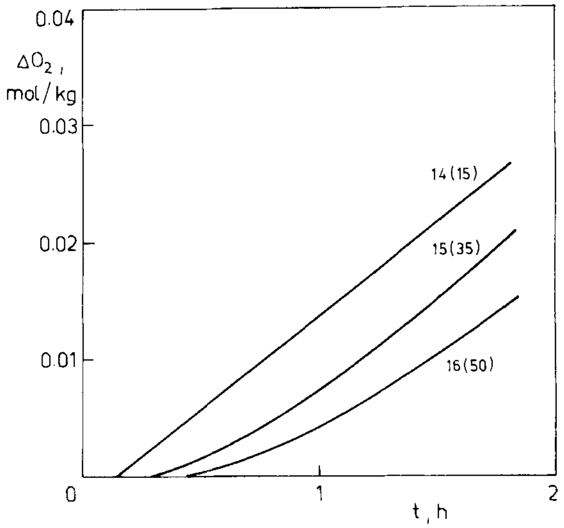


FIG. 5. Effect of amino-group concentration ([B], mmol/kg) on thermooxidation (140°C) of hydrolytic nylon 6 containing 15 mmol A/kg. The numbers in parentheses indicate the concentration of amino groups.

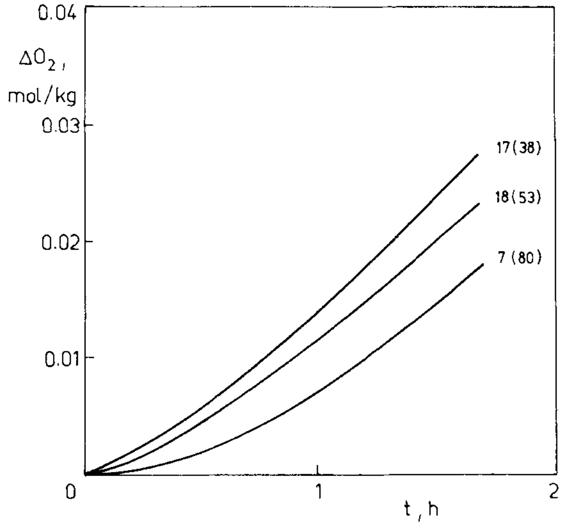


FIG. 6. Effect of end-group concentration ([A] = [B], mmol/kg) on thermooxidation (140°C) of hydrolytic nylon 6. The numbers in parentheses indicate the concentration of end groups.

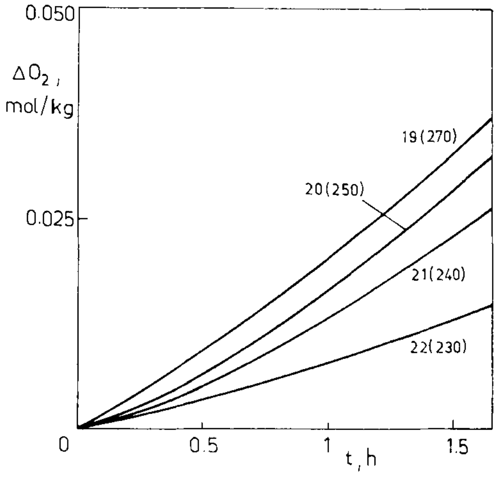


FIG. 7. Effect of polymerization temperature on thermooxidation (140°C) of hydrolytic nylon 6. The numbers in parentheses indicate the temperature of polymerization.

Effect of Temperature

In hydrolytic lactam polymers, the deficit in amino and carboxylic groups increases with increasing polymerization time and temperature (Table 1) [5]. The missing groups, mostly converted into structural defects, may be assumed to influence the oxidizability of nylon 6. The extent of side reactions leading to the loss of primary amino groups has been found to increase with increasing temperature [5], and the results shown in Fig. 7 confirm that structural defects are responsible for the increase in oxidizability with increasing polymerization temperature.

CONCLUSIONS

The nature of the catalyst largely affects the thermooxidative stability of nylon 6. Cationic caprolactam polymers are the least stable. Initiator residues (strong acids) present in the polymer are able to initiate the homolysis of the primary oxidation product (hydroperoxide) and thus accelerate the initiation reaction of oxidation. A strongly acid catalyst may also initiate reactions of other irregular structures formed by side reactions during polymerization. Consequently, extraction of cationic polymers with water significantly increases their resistance toward thermal oxidation.

In anionic caprolactam polymers, residues of catalytic systems (basic compounds) act as stabilizers of thermooxidation so that extraction with water results in a pronounced decrease in thermooxidative stability.

Thermal oxidation of hydrolytic nylon 6 depends predominantly on the content and relative ratio of carboxylic and primary amino groups. Carboxylic groups initiate homolytic decomposition of hydroperoxides. They also promote the reaction of the aldehyde (formed from the alkoxide) with another hydroperoxide, resulting in scission of the polymer molecule with the formation of one terminal carboxyl and one primary amide group. These reactions play an important role in the thermooxidation of polymers in which carboxylic groups predominate over amino groups. Thermal oxidation of such polymers is accompanied by a strong decrease in molecular weight.

Reaction of a terminal amino group with hydroperoxide leading to imine structures results in the combination of two polymer molecules. Imine groups are subject to further reactions, and polymers in which amino groups predominate over carboxylic groups turn yellow during thermal oxidation.

Some of the structural defects formed in side reactions during polymerization decrease the thermooxidative stability. The extent of these side reactions increases with polymerization temperature and, therefore, the sensitivity of nylon 6 to thermal oxidation increases accordingly.

The results presented indicate that the thermooxidative stability of nylon 6 may be affected not only by the addition of ecologically undesirable antioxidants but also by proper choice of polymerization mechanism, composition of the catalytic system, and temperature, as well as by controlling the polymerization process and purity of the monomer.

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