On the Mechanism of Polyamide Degradation in Chlorinated Water

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

Experiments were performed in an attempt to identify the reactive intermediate(s) involved in the degradation of a polyamide, *Nylon 66*, in chlorinated water. According to previous studies, *N*-chlorination is certainly one reaction that ultimately contributes to polyamide degradation. In this case, the intermediates involved could either be Cl_2 or HClO. Available information also indicates that, for many polymers, singlet molecular oxygen ($a^1\Delta_g$), chemically generated from HClO, could likewise be involved as an intermediate in a degradation reaction. Thus, tests were undertaken to specifically address this latter issue with respect to polyamide degradation. The degradation of *Nylon 66* was monitored under a variety of conditions by FT-IR spectroscopy. The rate of degradation was pH-dependent, and degradation was most pronounced at $pH < 5$. Characteristic tests for the intermediacy of singlet oxygen, however, were negative. Rather, the data strongly pointed to Cl_2 as the key intermediate in the degradation. The presence of compounds capable of being oxidized by Cl_2 arrested the degradation reaction. These results should be pertinent in an attempt to stabilize polymers exposed, *e.g.*, to water that has been chlorinated to kill bacteria (*i.e.*, drinking water).

Introduction. – The use of Cl_2 as a disinfectant to kill bacteria and thus make water potable is well-established [1]. It is also acknowledged that many polymeric materials in contact with chlorinated water degrade at rates that can adversely influence the properties and, hence, function of the polymer [2–4]. Purification membranes, pipes, and pump parts made from, *e.g.*, polyamides, polyethylene, and polypropylene routinely show the effects of exposure to chlorinated water that, in turn, often requires replacement of these items at more frequent intervals. In the present context, degradation means any change at the molecular level that alters the properties of the polymer. Low levels of degradation can influence properties such as elasticity and permeability, whereas high levels of degradation can result in loss of material and the formation of sizable cracks in molded samples.

To more accurately describe 'chlorinated water', it is necessary to specify the pH of the system and to consider the equilibrium of *Eqn. 1*.

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl \qquad (1)$$

It is then appropriate to speak of the pH-dependent concentration profiles of three species, in particular Cl_2, HClO, and ClO^-, which have been measured spectroscopically [5]. Alkaline systems are characterized by a high concentration of ClO^-, which rapidly drops to zero as the pH is lowered from *ca.* 9 to 8. As the system is further acidified, and the pH lowered through *ca.* 8, the concentration of hypochlorous acid, HClO, correspondingly increases. The latter reaches a maximum at pH *ca.* 5 and, thereafter, decreases upon further acidification. At the same time, upon acidification, and beginning at pH *ca.* 7, the concentration of Cl_2 increases slowly. At pH values less than *ca.* 5, the equilibrium of *Eqn. 1* shifts to the left, and the decrease in HClO concentration is accompanied by a further increase in the concentration of Cl_2. Thus, at a pH of *ca.* 7, 'chlorinated water' is characterized by a high concentration of HClO and a low concentration of Cl_2. At pH values less than *ca.* 4, the reverse holds, and 'chlorinated water' is characterized by a high concentration of Cl_2 and a low concentration of HClO.

It is well-established that the lowest excited electronic state of molecular oxygen, singlet oxygen ($a^1\Delta_g$), is produced in the reaction of ClO^-/HClO with H_2O_2 in aqueous solutions [6–8]. It has also been established that singlet oxygen is formed simply upon acidifying aqueous solutions of NaClO [9]. In this latter study, the yield of singlet oxygen was nicely shown to correlate with the pH-dependent concentration profile of HClO. In short, the concentration of singlet oxygen increased as the pH was lowered from a value of *ca.* 8, reaching a maximum at a pH of *ca.* 5. Thereafter, as the pH was further lowered, the singlet oxygen concentration precipitously dropped.

Singlet oxygen is a reactive intermediate capable of oxygenating organic molecules that contain sites of unsaturation [10]. By extension, singlet oxygen is also a key intermediate involved in the degradation of many polymeric materials [11][12]. The susceptibility of a given polymer to reaction with singlet oxygen often depends on the thermal history of that particular polymer sample. Specifically, for polymers that have been molded at high temperatures, thermal degradative processes can result in sites of unsaturation that, although present in low concentration, can react with singlet oxygen [12–14]. The immediate products of these reactions, a variety of hydroperoxides, can then initiate a plethora of radical chain reactions that ultimately contribute to the degradation of the material.

On the basis of the preceding discussion, it is thus reasonable to suggest that singlet oxygen might in fact be a reactive intermediate involved in the degradation of heat-pressed polymeric materials exposed to chlorinated water. Indeed, such speculations [4] attracted our attention to this problem early on. Of course, singlet oxygen may not be the only reactive intermediate involved, particularly in such an oxidizing environment that also contains Cl_2 and HClO. With amides and polyamides, for example, it is acknowledged that *N*-chlorination is one reaction that readily occurs in chlorinated water [2][15]. Thus, the relative importance of singlet oxygen as a reactive intermediate is expected to depend on the particular polymer under consideration. Nevertheless, if it is possible to establish that, in a given system, singlet oxygen indeed plays a role, then a specific singlet oxygen quencher could be incorporated as a stabilizer into the polymer. In this way, one could arguably extend the functional lifetime of a polymeric device exposed to chlorinated water.

In the present study, we set out to ascertain whether or not singlet oxygen was a reactive intermediate involved in the degradation of heat-pressed *Nylon 66*, a polyamide, upon exposure of the polymer to chlorinated water.

Results and Discussion. – The degradation of heat-pressed *Nylon* films was monitored under a variety of conditions by FT-IR absorption spectroscopy. To avoid complications that might arise in spectroscopic measurements of the more heavily degraded samples, where cracks in the sample could influence the spectra obtained from large sample areas, spectra were recorded with the aid of a microscope attached to the FT-IR spectrometer. In this way, data were always recorded from homogeneous domains in the sample. As outlined in the *Exper. Part*, samples of chlorinated water were prepared by acidifying 0.08M NaClO with HCl to the desired pH. The polymer samples were immersed in these solutions for a specified period of time, then removed, rinsed, and dried and the FT-IR spectra recorded.

pH Dependence of Degradation. The rate of polyamide degradation depended strongly on the pH of the chlorinated water solution (*Fig. 1*). At pH values greater than *ca.* 8, no changes in the polyamide spectrum were observed over a reaction period of several days. At a pH of 7, noticeable changes could be recorded in the FT-IR spectra within hours. At pH values less than 5, significant changes in the FT-IR spectra were observed within 1 h upon exposure to chlorinated water under our conditions. Over these same time periods, no changes in the FT-IR spectrum were observed upon exposure of the polyamide sample to water that lacked NaClO but that had merely been acidified with HCl to $pH < 3$.

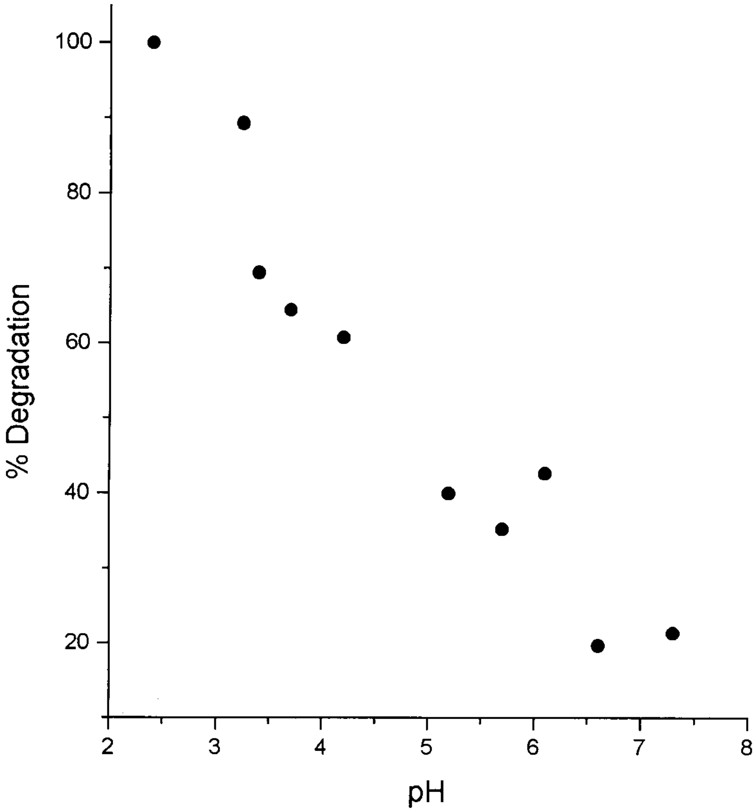

Fig. 1. *Percent polyamide degradation* vs. *the pH of the chlorinated water solution into which the polymer was immersed*. Polyamide degradation was quantified by monitoring changes in the N–H absorption band at *ca.* 3060 cm^{-1} for an immersion time in chlorinated water of 1 h. Errors on each point are *ca.* ±10%.

The IR spectra recorded (*Figs. 2–4*) are consistent with degradation product(s) that are independent of the pH of the chlorinated water solution. In turn, this implies that, over the entire pH range studied, there may only be one degradation process, with only one pertinent reactive intermediate. The most striking changes observed in the IR spectra are *1*) a decrease in the intensity of bands associated with the amide N–H (*e.g.*, 3300 and 1550 cm^{-1}), and *2*) a change in the intensity of bands in the region *ca.* 600–1200 cm^{-1}. The bands between *ca.* 900–1200 cm^{-1} are associated with amorphous and crystalline domains in the polymer [16–18], and the data indicate a decrease in the extent of crystallinity upon degradation.

This pH-dependent degradation was also manifested in the physical appearance of the samples. Freshly prepared samples and samples that had been exposed only to

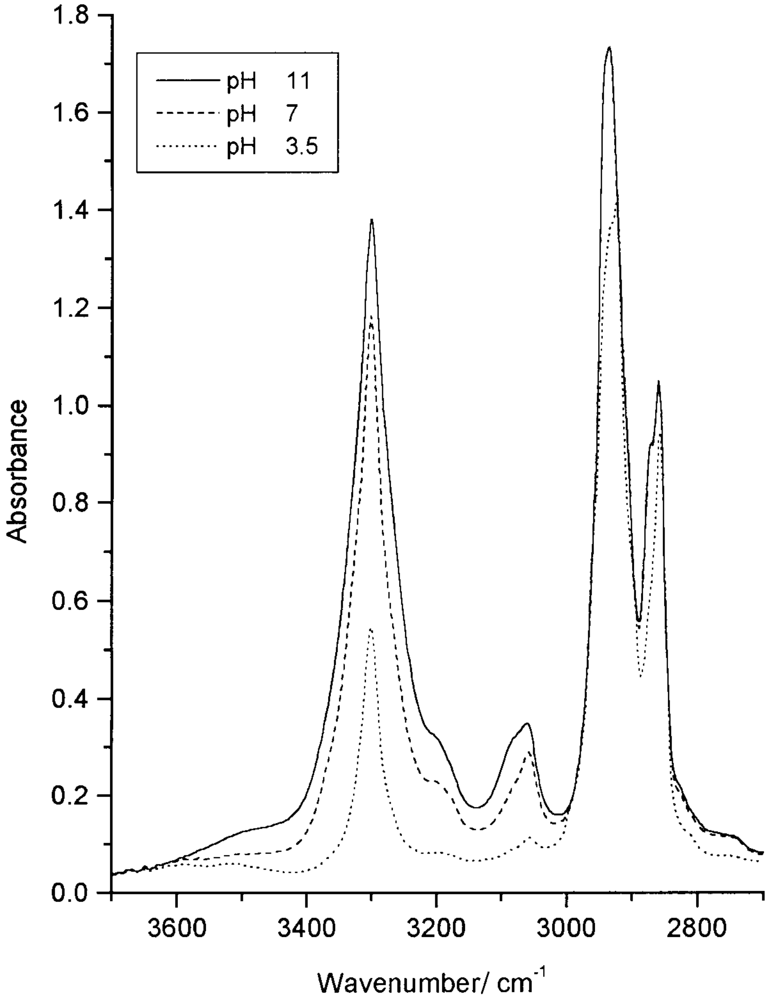

Fig. 2. *The 3700–2700 cm^{-1} portion of the FT-IR spectrum recorded from 25-μm thick polyamide samples that had been exposed to solutions of chlorinated water at pH 11, pH 7, and pH 3.5 for 3 h*

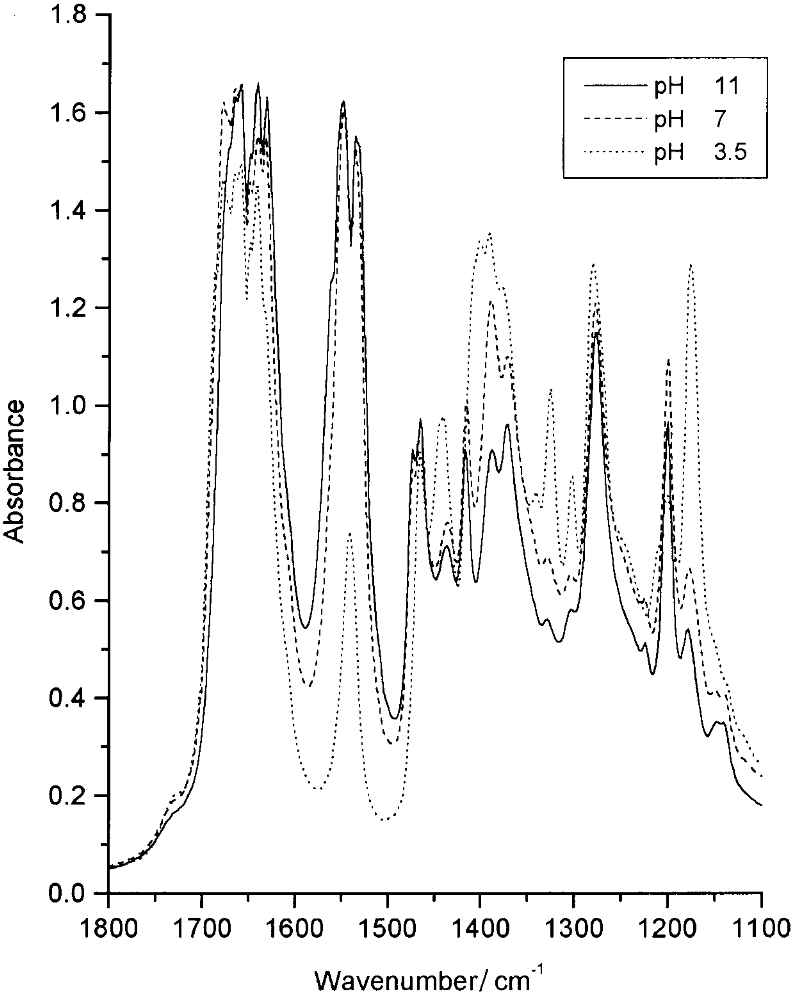

Fig. 3. *The 1800–1100 cm^{-1} portion of the FT-IR spectrum recorded from 25-μm thick polyamide samples that had been exposed to solutions of chlorinated water at pH 11, pH 7, and pH 3.5 for 3 h*

alkaline solutions of NaClO were smooth, homogeneous, and optically transparent. As the extent of degradation increased, however, cracks and blisters in the sample became more apparent. Apart from changes attributed to crack-dependent light scattering, however, no changes were observed in the UV/VIS absorption spectrum of the polyamide as a function of degradation. This latter observation contrasts with the situation observed upon photoinduced oxidative degradation of *Nylon* in which new UV/VIS chromophores are clearly produced [18].

Effect of Adding a Singlet Oxygen Quencher. In a first test to assess whether or not singlet oxygen is involved in the degradation of *Nylon 66*, aliquots of 1,4-diazabicyclo[2.2.2]octane (DABCO) were added to the solutions of chlorinated water. Among

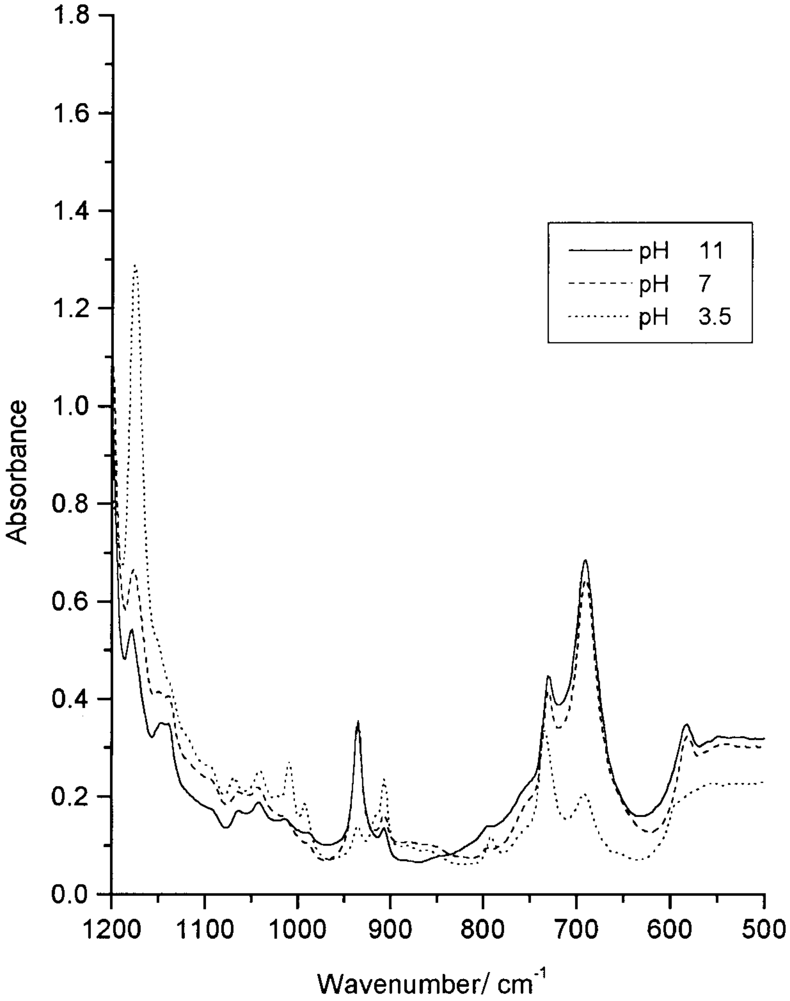

Fig. 4. *The 1200–500 cm^{-1} portion of the FT-IR spectrum recorded from 25-μm thick polyamide samples that had been exposed to solutions of chlorinated water at pH 11, pH 7, and pH 3.5 for 3 h*

other things, DABCO is an acknowledged quencher of singlet oxygen [19] and has a bimolecular rate constant for singlet-oxygen removal of *ca.* $3 \cdot 10^8$ s^{-1} M^{-1} [20]. Indeed, upon the addition of DABCO to the solutions of chlorinated water ([DABCO] > [NaOCl]), changes in the FT-IR spectrum of the polyamide could not be detected, implying that the degradation reaction was arrested entirely.

Effect of Solvent Deuteration. To further test the possible intermediacy of singlet oxygen in the degradation of this heat-pressed *Nylon*, the polymer samples were exposed to solutions of chlorinated D_2O as opposed to chlorinated H_2O. It is acknowledged that the lifetime of singlet oxygen in D_2O is *ca.* 15 times longer than that in H_2O [19] [20]. Thus, if singlet oxygen was indeed involved as an intermediate in these reactions, the rate of sample degradation should be significantly accelerated in D_2O. This change in degradation rate would be due simply to the fact that the reaction between the polymer and singlet oxygen would now compete more effectively against the process of solvent-induced singlet-oxygen deactivation.

The FT-IR spectra clearly revealed that, upon exposure of the polyamide films to D_2O solutions, there was a rapid and facile H/D exchange at the amide moiety. Specifically, the N–H bond evolved into an N–D bond, even in solutions lacking hypochlorite. This exchange was reversed upon immersing the samples, previously exposed to D_2O, into H_2O solutions. Because the effects of the degradation induced by chlorinated water are most pronounced in the N–H bond, it was deemed most appropriate to first monitor the degradation in D_2O with other absorption bands in the FT-IR spectrum (*e.g.*, bands at 900–1200 cm^{-1}, *vide supra*). Nevertheless, according to the following procedure, it was also possible to use changes in the N–H absorbance to monitor the degradation in D_2O. The N–H absorbance in a given sample was first recorded prior to immersion in D_2O. After exposure to the chlorinated D_2O solution, the reaction was stopped with a fresh, hypochlorite-free H_2O wash. The sample was then equilibrated with H_2O to regenerate the N–H bond, and the FT-IR spectrum re-recorded to measure the percent change in N–H absorbance due to the degradation reaction. Results obtained by both of these methods were identical.

The FT-IR spectra recorded from *Nylon* samples exposed to solutions of chlorinated water indicated no effect of solvent deuteration on the rate of polymer degradation. Thus, this test implies that something other than quenching of singlet oxygen may be occurring upon the addition of DABCO to the system.

Exposure to Singlet Oxygen Produced in a Photosensitized Reaction. In yet another test to assess whether or not singlet oxygen is involved in the degradation of a heat-pressed polyamide exposed to chlorinated water, and to potentially clarify the results of the DABCO and D_2O experiments, the polymer samples were exposed to singlet oxygen independently generated in a photosensitized reaction. In these experiments, FT-IR spectra of the polyamides were recorded as a function of the elapsed irradiation time of a singlet-oxygen sensitizer dissolved in the solvent surrounding the polymer.

In the first experiment, a water-soluble sulfonated derivative of tetraphenylporphine was irradiated at wavelengths greater than 475 nm with the output of a Xe lamp for periods of up to 5 h. Although singlet oxygen was clearly generated in this system, as documented by the observation of the $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ phosphorescence at 1270 nm, no changes were observed in the FT-IR spectra of the polymer. In a second experiment, the polymer was immersed in a benzene solution containing the singlet-oxygen sensitizer acridine. In this solvent, where the lifetime of singlet oxygen is *ca.* 8 times longer than in H_2O [20], no changes in the FT-IR spectrum of the polymer were likewise observed upon irradiation of acridine at wavelengths greater than 335 nm.

The results of these independent photosensitized experiments are thus consistent with the results of the H_2O/D_2O study. Specifically, the data indicate that singlet oxygen is not a reactive intermediate involved in the degradation of heat-pressed polyamide samples.

The Pertinent Reactive Intermediate. The data presented thus far indicate that singlet oxygen does not play a role in the degradation of heat-pressed polyamides. The question thus remains as to the identity of the reactive intermediate(s) principally responsible for the polymer degradation. We have already mentioned that amides and polyamides readily undergo *N*-chlorination in chlorinated water [2] [15], and the FT-IR data reported herein are certainly consistent with a process of *N*-chlorination. Other points to be considered include the observation that, under our conditions, the degradation reaction converges on the same product, independent of pH. Moreover, there is no degradation at pH values > 8, but the rate of degradation increases as the pH is lowered (*Fig. 1*). Clearly, at pH values less than *ca.* 8, one must consider the equilibrium of *Eqn. 1*, where both Cl_2 and HClO can be the active chlorinating agents. However, because the pH-dependent profile of polyamide degradation (*Fig. 1*) matches the pH-dependent profile of Cl_2 concentration and not the pH-dependent profile of HClO concentration [5] [9], it appears most likely that Cl_2 is the principal intermediate in this reaction. Moreover, in addition of these changes in the degradation rate that correlate with the *concentration* of Cl_2, data from other amide *N*-chlorination studies [21] [22] suggest that the *rate constant* for the reaction of *Nylon* with Cl_2 will be greater than that for the reaction of *Nylon* with HClO.

Recall that in the first test to assess the possible intermediacy of singlet oxygen, the amine DABCO was added to the aqueous solution, and the degradation reaction was arrested. More specifically, changes in the FT-IR spectrum now attributed to *N*-chlorination were arrested. In a related study, attempts were made at one point to examine *Nylon* degradation in a buffered solution of hypochlorous acid. The buffer used for this particular study, *Tris* ($(HOCH_2)_3CNH_2$), was chosen to maintain a pH of *ca.* 7 in the solution of chlorinated water. As in the case where DABCO was added to the solution, addition of this particular amine likewise completely arrested the degradation reaction. These observations are entirely consistent with the perspective that a chlorination reaction is responsible for polyamide degradation. In short, aliphatic amines, including tertiary amines such as DABCO, are readily chlorinated under these reaction conditions [15] [23]. Thus, the added amine simply competes with the polyamide for the available chlorinating species and, as a consequence of being chlorinated itself, minimizes or ultimately precludes the chlorination of the polyamide.

Nakagawara et al. [5] have established that the bactericidal activity of chlorinated water correlates with the pH-dependent concentration profile of HClO. Thus, the maximum bactericidal effect of chlorinated water is observed at a pH of *ca.* 5. Unfortunately, even at pH values of *ca.* 6–7, where some bactericidal activity is still observed, there is a sufficient amount of Cl_2 still present in the system, and polyamide degradation is still appreciable (*Fig. 1*). Thus, polymer 'stabilizers' or Cl_2 trapping devices must be incorporated into systems in which materials made from polyamide come in contact with chlorinated water.

Conclusions. – Experiments were performed to identify the reactive intermediate(s) involved in the degradation of a heat-pressed polyamide (*Nylon 66*) in chlorinated water. Previous studies indicated that *N*-chlorination was one reaction that contributed to the degradation of polyamides, and that either Cl_2 and/or HClO were the pertinent reactive intermediates. Available information also indicated that singlet molecular oxygen ($a^1\Delta_g$), chemically generated from HClO, could likewise be involved as a reactive intermediate. The data now recorded, however, clearly indicate that singlet oxygen is not involved as an intermediate in this degradation reaction. FT-

IR Spectra recorded from the polyamide samples are consistent with *N*-chlorination as the initial step in the degradation of the polymer. A correlation between the pH-dependence of the degradation rate and the pH-dependent Cl_2 concentration profile implicate Cl_2 as the principal reactive intermediate in this process. An amine added to the system effectively competes with the amide moiety for the chlorinating agent and, as a consequence, arrests the degradation of the polyamide.

Experimental Part

Polymer-Sample Preparation. Additive-free *Nylon 66* (*Aldrich*, product No. 42,917-1) was received as pellets. *Nylon* films were prepared by hot-pressing the pellets in a press (*F. S. Carver Inc.*, model *C*) that was equipped with a film-pressing tool (*Specac Inc.*). The latter consisted of heated platens, two polished stainless-steel pressing plates, disposable aluminium-foil wafers between which the polymer pellets were placed, and calibrated spacer rings to control the film thickness. In a typical preparation, the polymer pellets were first heated to melting (275°) and held at this temp. for *ca.* 5 min to *a*) remove dissolved water, and *b*) render the polymer melt homogeneous. The polymer was then pressed at 275° and 1.5 tons for 3 min with a 25 µm spacer ring. Upon releasing the pressure, the steel plates containing the sample were cooled to 25° by a water-cooled heat sink (*Specac Inc.*). The polymer film was then removed from the pressing plates and the aluminium-foil wafers peeled away and discarded. Films thus prepared were optically transparent and did not have visible heterogeneities (*i.e.*, cracks and blisters). Polymer films thinner than 25 µm were extremely fragile and thus difficult to handle.

Chlorinated Water Baths. The hot-pressed *Nylon* films were immersed in baths of chlorinated water contained in a light-tight jar. Solns. of chlorinated water were prepared by first adding *ca.* 8 ml of a 10% NaClO soln. (*Aldrich*, product No. 42,504-4) to *ca.* 80 ml of distilled water. The absorption spectrum of this soln. was recorded (actually a diluted aliquot of this soln.) and, with a value of $350\ cm^{-1}\ M^{-1}$ for the hypochlorite absorption coefficient at 290 nm [24], the amount of water and hypochlorite were adjusted to yield a starting NaClO concentration of 0.08M for the degradation studies. Solns. of different pH were then prepared by adding aliquots of HCl to this stock soln., monitoring the process with a pH meter (*Radiometer*, A/S; electrode model No. pHC2401-7). After being immersed in a solution of chlorinated water for a prescribed period of time, the *Nylon* film was removed, rinsed with Cl_2-free H_2O, and dried and the FT-IR spectrum recorded. For a given experiment where data from one polymer sample were compared to those from a different polymer sample, the same NaClO stock soln. was always employed.

Spectroscopic Measurements. FT-IR Spectra were recorded with a modified *Bruker IFS-66v/S* step-scan spectrometer that was operated in the continuous scan mode. Polymer samples were mounted on the stage of a microscope (*Bruker IRscopeII*) attached to the FT-IR spectrometer, and the spectra were recorded from only a small spatial domain to avoid artifacts from heterogeneities (*e.g.*, cracks, blisters) that appeared during the course of the degradation reaction. A complete description of our FT-IR spectrometer and attached microscope is provided elsewhere [25][26]. For quantitative studies of the change in IR absorbance (*e.g.*, *Fig. 1*), bands with an initial absorbance of < 1.0 were always used. As mentioned above, it was difficult to handle polyamide films thinner than 25 µm, thus the absorbance of several bands > 1.0 (see *Figs. 2–4*).

Other Compounds. Deuterated water (*Deutero GmbH*, 99.9%), 1,4-diazabicyclo[2.2.2]octane (*Aldrich*), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine-*p,p′,p″,p‴*-tetrasulfonic acid tetrasodium salt dodecahydrate (=4,4′,4′,4″-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[benzenesulfonic acid] tetrasodium salt dodecahydrate; *Aldrich*), *Tris* (=*tris(hydroxymethyl)aminomethane* = *2-amino-2-(hydroxymethyl)propane-1,3-diol; Aldrich*), and acridine (*Aldrich*) were used as received.

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