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N-Chloro Nylons as Polymer Reagents

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ABSTRACT

A series of N-chlorinated nylons were prepared so that in most cases more than 90% of the N—H bonds were converted to N—Cl bonds. Suitable chlorinating reagents were t-butyl hypochlorite, chlorine monoxide in carbon tetrachloride, and aqueous hypochlorous acid. Chemical and spectroscopic evidence helped confirm the N—Cl polymeric structures. The N-chlorinated polymers were found to readily oxidize secondary and primary alcohols in the same manner as low molecular weight N-halogenated amides and imides. The N-chlorinated polymers were also found suitable for the oxidation of sulfides to sulfoxides. In most cases of the oxidation of alcohols and sulfides, the polymers formed an insoluble powder which was readily removed by filtration, facilitating the work-up of the desired product.

INTRODUCTION

Because of the unique properties associated with a polymer in comparison to a corresponding low molecular weight substance, there

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has been an effort in recent years to use polymers as reagents in chemical reactions. In order for a polymer molecule to serve as a chemical reagent it must have a large number of reactive groups along its backbone. The classic works of Cassidy [1] and Manecke [2] with redox resins exemplify the basic concept of incorporating reactive small molecules into a polymer chain.

The incorporation of the known reactivity of N-halogenated amides and imides like N-chlorosuccinimide (NCS) and N-bromosuccinimide (NBS) into a polymer system is one area that has received attention. Okawara [3], as early as 1958 and later in 1969, reported the synthesis of linear and cross-linked polyimides and their subsequent N-bromination. These polymers were not of high halogen content and were not characterized to a large extent. They were found to have some activity as both oxidation and bromination reagents; however, they were not as reactive as NBS. Yaroslavsky and co-workers [4] have also recently used this type of polymer for brominating substituted styrenes. The first report of the halogenation of some of the many linear polyamides that are readily available was made by Bamford [5] and co-workers in 1968. This work was in the main concerned with N-chlorinated nylon fibers and the grafting of other monomers to these fibers. Wayman and colleagues [6] also have chlorinated various polyamides and studied the release of chlorine. However, in all the above cases little was reported on the characterization of the halogenated polymers. In continuation of our earlier work on polymers with reactive groups a systematic study was undertaken of preparing N-chlorinated linear polyamides, fully characterizing the products, and then investigating the oxidation and other reaction capabilities of these chlorinated polymers.

PREPARATION AND CHARACTERIZATION OF POLYMERS

The chlorination of several linear polyamides (e.g., nylon 66 and nylon 3) was successfully accomplished by the use of *t*-butyl hypochlorite or chlorine monoxide in carbon tetrachloride [7]. Aqueous hypochlorous acid has also been found to serve as an easy reagent to use for these chlorinations. Both *t*-butyl hypochlorite and hypochlorous acid yielded chlorinated polymers without appreciable degradation. In nearly all cases, greater than 90% N-chlorinated polymers were obtained, i.e., 90% of the N-H bonds were converted to N-Cl bonds (Table 1).

The chlorine content was determined by iodometric titration and verified by total chlorine elemental analysis. The NMR spectrum (Fig. 1) of the N-chloro nylon 66 (NC-66) shows the methylene protons adjacent to the nitrogen shifted downfield and as a triplet as would be expected. The IR spectrum of NC-66 (Fig. 2) is in complete agreement with the propos

TABLE 1. Examples of Chlorinations of Various Polymers

Polymer	Chlorination reagent	Time (hr)	Temp ($^{\circ}$ C)	Yield (%)	Conversion (%)
Nylon 66	t-BuOCl	3	15	86	94
	Cl ₂ O	12	-20	80	93
	HOCl	40	20	95	95
Nylon 3	t-BuOCl	3	15	68	10
	HOCl	24	20	95	59
Nylon 6	t-BuOCl	3	15	80	55
	(-)-Poly-S·(-)-4-methylazetidinone-(2)				
	t-BuOCl	24	20	90	95
	HOCl	24	20	95	-

N—Cl structure. The N—H bands at 3300 and 3080 cm^{-1} have disappeared as has the amide II band at 1530 cm^{-1} . The carbonyl band is blue shifted about 35 cm^{-1} .

The modified polymer, which now has no hydrogen bonds, has remarkable solubility properties in comparison with the original nylon. The once difficult to dissolve nylon is now readily soluble in chloroform, benzene, and toluene among others. The chlorinated polymers also have been observed to undergo both thermal and photochemical rearrangements. These studies will be published at a later date.

Because of its ease of preparation and ease in handling (white powder), NC-66 was chosen for the following oxidation studies.

OXIDATIONS

NC-66 was found to be capable of oxidizing a large variety of compounds including hydroquinone, o- and p-phenylenediamine, benzidine, hydrazobenzene, ferrous sulfate, formic acid, primary and secondary alcohols, and sulfides. The oxidations of alcohols and sulfides were studied in the greatest detail because of the importance of preparative methods for these conversions.

OXIDATION OF ALCOHOLS

NC-66 was found to easily oxidize secondary alcohols to ketones under very mild conditions (35 $^{\circ}$) [8]. The general reaction, shown in Eq. (1),

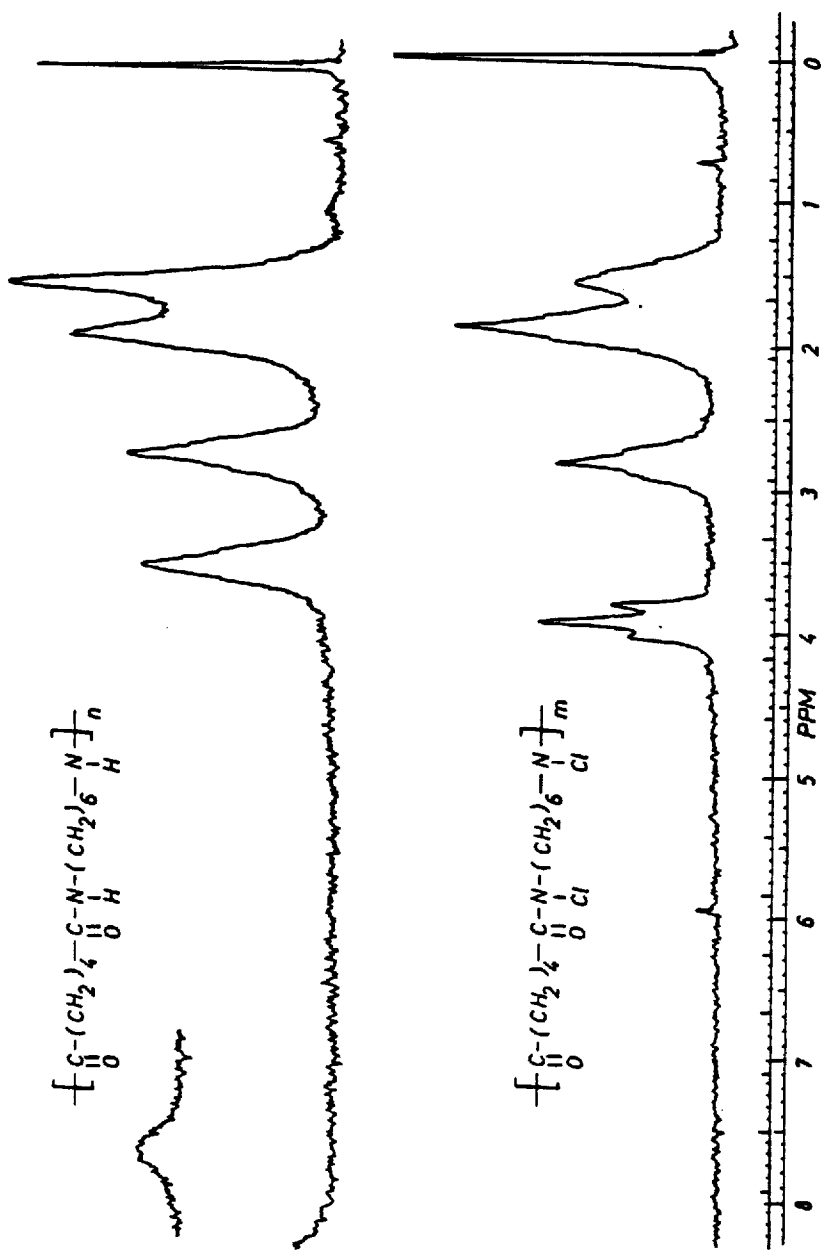


FIG. 1. NMR spectra (60 MHz) of N-Cl nylon 66 and nylon 66.

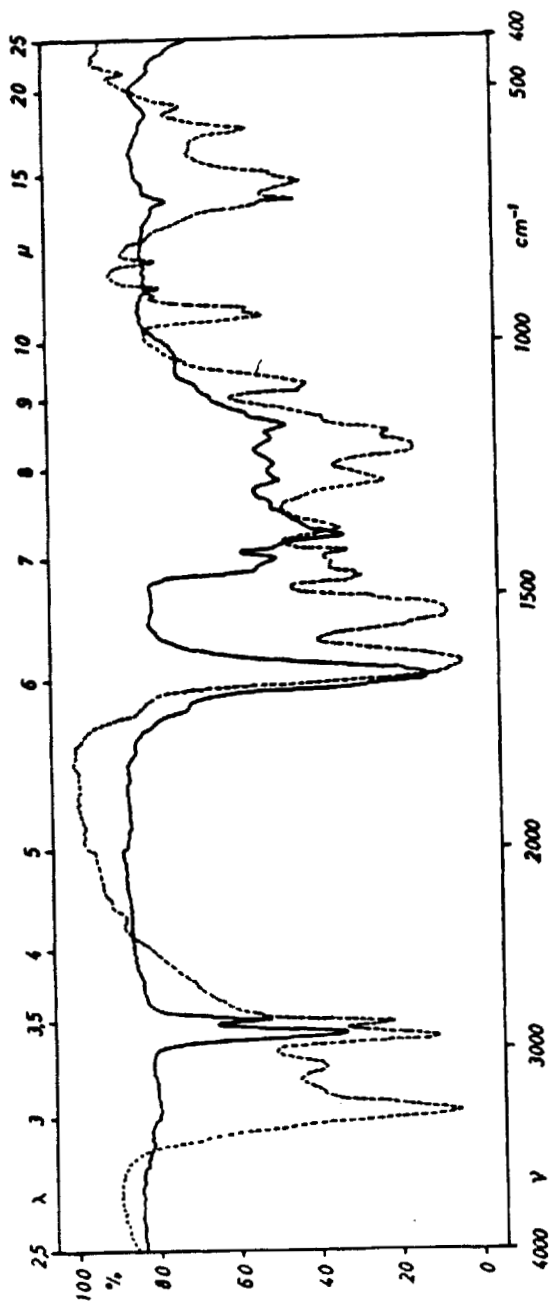
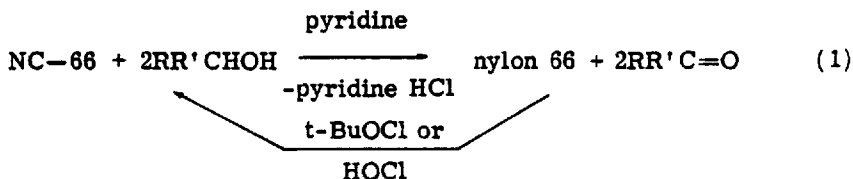


FIG. 2. IR spectra of (---) nylon 66 and (—) N-Cl nylon 66.

was done in the presence of pyridine to take up the released hydrochloric acid. As diagrammed here, the polymeric reagent can easily be regenerated. Table 2 shows the results of several oxidations with



NC-66 in comparison to the literature values of two low-molecular weight reagents, 1,3-dibromo-5,5-dimethylhydantoin (DBH) [9] and N-bromoacetamide (NBA) [10]. Yields were determined in all cases by gas chromatography and in some cases by preparation of the semi-carbazone derivative. In most cases the yields were as good as or better than those obtained with DBH and NBA. The oxidations were found to be quite dependent on the solvent. Benzene and cyclohexane were found to be the preferred solvents. With these solvents the reduced polymer was an insoluble powder, facilitating separation from the oxidation products.

Primary alcohols were also oxidized by the N-chloro nylon (Table 3 [8]). Aliphatic primary alcohols yielded, for the most part, the esters of their corresponding acids, probably by way of the hemiacetal as previously described in the chromic acid oxidation of primary alcohols [11]. The yields with the polymer are of the same order as those of other methods described in the literature.

OXIDATION OF SULFIDES

Although hydrogen peroxide has been the most widely employed reagent for the oxidation of sulfides to sulfoxides and sulfones [12] (Eq. 2), numerous other reagents have been found suitable for these conversions. Walling and Mintz [13] have reported the use of hypochlorites for these conversions. Harville and Reed [14] found N-halosuccinimides in methanol convenient reagents for these oxidations. We have found NC-66 in methanol also to be suitable for the oxidation of various sulfides to sulfoxides as shown in Table 4. In contrast to the NBS and NCS reactions which were done at 0°, slightly elevated temperatures were necessary for these reactions. The products were identified from their IR spectra (S=O 1020-1050 cm^{-1})

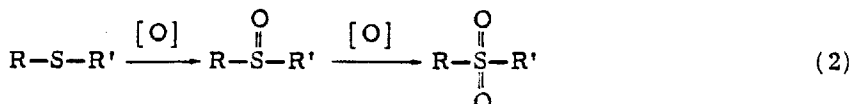


TABLE 2. Examples of Oxidations of Secondary Alcohols with NC-66 in Benzene at 35° and 24 hr

Alcohol	Yield of ketone			Recovered alcohol (%)	Literature yield, DBH-semicarbazone [9] (%)	NBA-2,4-dinitrophenylhydrazone [10] (%)
	Gas chromatography (%)	Semi-carbazone (%)				
Borneol	97	76		0	-	-
Cyclohexanol	82	-		8	-	-
PhCH ₂ CHOHCH ₃	90	62		10	51	35
Ph(CH ₂) ₂ CHOHCH ₃	95	68		0	74	-
PhCHOHCH ₃	95	80		0	61	80
(PhCH ₂) ₂ CHOH	62 ^a	-		37	-	1
PhCH ₂ CHOHCH(CH ₃) ₂	92	60		12	53	1

^aYield determined after 93 hr.

TABLE 3. Examples of Oxidation of Primary Alcohols with NC-66 at 35° and 48 hr

Alcohol	In reaction mixture		
	Ester (%)	Aldehyde (%)	Alcohol (%)
PhCH ₂ OH	0	95 ^a	0
PhCH=CHCH ₂ OH	-	10	40
CH ₃ (CH ₂) ₆ CH ₂ OH	80	5	0
CH ₃ (CH ₂) ₂ CH ₂ OH	75	5	-

^aAfter 24 hr.

TABLE 4. Examples of Sulfide to Sulfoxide Oxidation

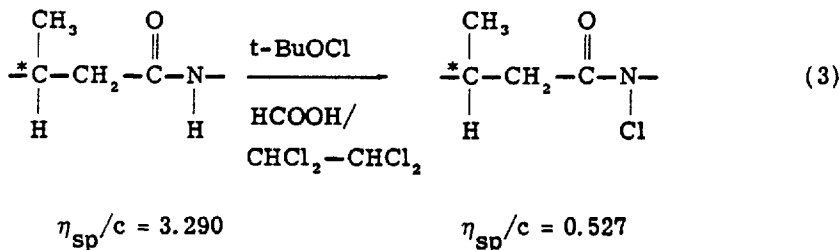
Substrate	Temp (°C)	Time (hr)	Crude mp (Pure mp)	Yield after purification (%)
PhCH ₂ SCH ₂ Ph	60	1.5	110-115 (134-135)	-
"	60	3	oil	-
"	50	1.25	95-100	-
"	40	4	115-120	-
"	20	24	100-108	-
PhCH ₂ SPh	60	1	105-115 (123)	-
"	40	4.5	115-117	70
"	50 ^a	1.5	115-118	70
PhSPh	50	1.5	Oily solid (70.5)	65

^aWith N-chloro(-)-poly-S(-)-4-methylazetidinone-(2).

and where possibly by recrystallization to pure compounds with correct melting points.

In all cases the crude yield was nearly quantitative since the reduced polymer reagent was easily separated by filtration, a definite advantage of the nylon. It was difficult to obtain a pure product because of incomplete conversion. The incomplete conversion was attributed to the side reaction of methanol oxidation and thermal rearrangement. The absence of side reactions of the sulfides was indicated by an NMR spectrum of the crude reaction product from the oxidation of dibenzylsulfide at 40°. The spectrum showed a 78/22 mixture of sulfoxide to sulfide and no other products. Thin-layer chromatography corroborated that only starting material and sulfoxide were present.

Since sulfoxides which have two different R groups can be chiral, we thought it worthwhile to explore the use of an optically active N-Cl nylon to attempt the asymmetric oxidation of a sulfide to a sulfoxide. (-)-Poly·S·(-)-4-methylazetidione-(2) [15] was N-chlorinated to 95% of the theoretical amount (Eq. 3). Unfortunately considerable chain degradation occurred, as shown by the viscosity comparison, under the somewhat more rigorous conditions. The oxidation of phenyl



benzyl sulfide to its sulfoxide proceeded smoothly; however, the resulting sulfoxide was optically inactive.

COLUMN OXIDATIONS

Application of the oxidative capabilities of the N-chloro nylons to columns has been found feasible. Columns have been prepared utilizing nylon particles or nylon-coated inert substances such as glass beads. Several oxidations have been carried out. The results of these experiments will be presented at a later date.

EXPERIMENTAL

Preparation of Polymers

The preparation of N-chloro polyamides by t-BuOCl and Cl₂O has been previously described [7]. The aqueous HOCl solution was prepared by the method of D'Ans and Freud [16] from 10-12% sodium hypochlorite solution. From the iodometric titration of the HOCl the concentration was 0.1 to 0.7 m. An example of the chlorination procedure using the HOCl solution is as follows: In a 500-ml Erlenmeyer flask 2.55 g of nylon 66 particles, of 0-0.3 mm diameter, were covered with 220 ml of 0.11 m HOCl solution and stirred in the dark. After 40 hr the nylon was filtered and washed with water several times. The polymer was then purified to a powder by dissolving in benzene (50°) and precipitating into ether. Iodometric titration showed a 95% conversion of N-H to N-Cl.

Oxidation of Alcohols

The experimental procedures followed for the alcohol oxidations have been previously described [8].

Oxidation of Sulfides

General Procedure

To a mixture of sulfide (5.0×10^{-3} mole) and 30 ml of reagent grade methanol, NC-66 (5.0×10^{-3} equivalents) was added and the heterogeneous mixture was stirred for the duration of the reaction time. The polymer was removed by filtration and the resulting filtrate evaporated carefully on a rotary evaporator. Recrystallization was done in the appropriate solvent.

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