

The Stress Cracking of Polyamides by Metal Salts. Part II. Mechanism of Cracking

P. DUNN and G. F. SANSOM,
*Australian Defence Scientific Service,
Department of Supply Defence Standards Laboratories,
Melbourne, Australia*

Synopsis

The action of metal halides on polyamide (nylon 6) and secondary amide model compounds has been investigated, using infrared and NMR techniques. Metal halides, which are active stress cracking agents for polyamides, induce characteristic changes in the spectra of both nylon 6 and the model compounds. Two types of changes were observed, depending on the metal halide involved, and on this basis the metal halides have been classified as Type I or Type II. The spectral changes appear to be due to the formation of complexes between the amide group and the metal halide, and structures for these complexes are proposed. Type I metal halides, such as zinc, cobalt_{II}, copper_{II} and manganese_{II} chlorides, form complexes in which the metal atom is coordinately bonded to the carbonyl oxygen atom of the amide group. These agents cause stress cracking by interference with the hydrogen bonding in the polyamide. Type II metal halides, such as lithium, calcium and magnesium chlorides and lithium bromide in solution form proton donating, solvated, species which act as direct solvents for nylon 6 in a manner similar to phenols and formic acid. Type II agents appear to cause simple solvent cracking.

INTRODUCTION

In Part I,¹ the action of a number of metal halides, in both aqueous and methanolic solution, on polyamides (nylons) has been described. The mechanism of rupture does not appear to be one of simple hydrolysis or of metal catalysed hydrolysis. Concentrated solutions of metal halides actively promoted stress cracking but solutions of hydrochloric acid of the same or higher hydrogen ion concentration were inactive even in the presence of lower concentrations of active metal halides. Solutions of metal acetates and sulphates did not promote cracking. The chemical action of the stress cracking agents of nylon 6 films and model compounds, has now been investigated.

EXPERIMENTAL

Film Treatments

Nylon films, as controls, were prepared for infrared studies by biaxially stretching 0.001 in. thick extruded, blown, unplasticised nylon 6 film.

Treated films were produced by immersing samples of 0.001 in. thick film in solutions of active metal salts for various periods, after which the films were removed and excess solution removed from the surface of the nylon with absorbent paper. The films were then biaxially stretched over a 1.0 in. diameter open-ended cylindrical glass support and dried.

Cast films containing metal salts were also prepared. Addition of a methanolic solution of the metal salt to a formic acid solution of nylon 6 gave a mixed solution, from which films were cast onto an ultrathin polypropylene support film.

Model Compounds

N-ethyl acetamide was purified by distillation. ϵ -Caprolactam was purified by repeated recrystallization from cyclohexane and dried over phosphorus pentoxide to give a white crystalline product of mp, 67°C. *N*-methyl-2-pyrrolidone was purified by distillation.

Preparation of Complexes

Complexes of *N*-ethyl acetamide and *N*-methyl-2-pyrrolidone with metal salts were prepared by addition of an acetone solution of the amide to a methanolic solution of the metal salt followed by evaporation under vacuum to a small volume. Repeated additions of dried petroleum ether, followed by evaporation, gave solid products with cobalt_{II} chloride but viscous liquids or glasses with zinc chloride.

Complexes of ϵ -caprolactam and cobalt_{II} chloride were prepared by dissolving the anhydrous chloride in molten ϵ -caprolactam under dry, CO₂-free nitrogen, until deep blue solutions were obtained. These solutions were then allowed to cool and solidify. No attempt was made to isolate the pure complexes from the solidified reaction mixtures, but care was taken to ensure that correct stoichiometric quantities were used.

Infrared Spectra

The infrared spectra of the treated nylon films, cast films and model compound reaction products were determined on a Beckman I.R. 8 or Perkin-Elmer 125 spectrophotometer. The spectra of the films were recorded directly, or in the case of some cast films, on an ultra-thin polypropylene support film. Spectra of the complexes were obtained on nujol mulls between NaCl plates, or in KBr disks.

NMR Spectra

The NMR spectra of the complexes were obtained in acetone solution, using a Varian HA-60-IL spectrometer.

RESULTS

Action of Metal Halides on Nylon 6 films

Immersion of nylon 6 films in reagent solutions for 30 min followed by mounting, washing and drying gave films with an opaque appearance. The

infrared spectra of these films showed no gross changes from those of untreated films.

However, nylon 6 films treated with aqueous zinc chloride solutions or methanolic solutions of other stress cracking metal halides, and dried,

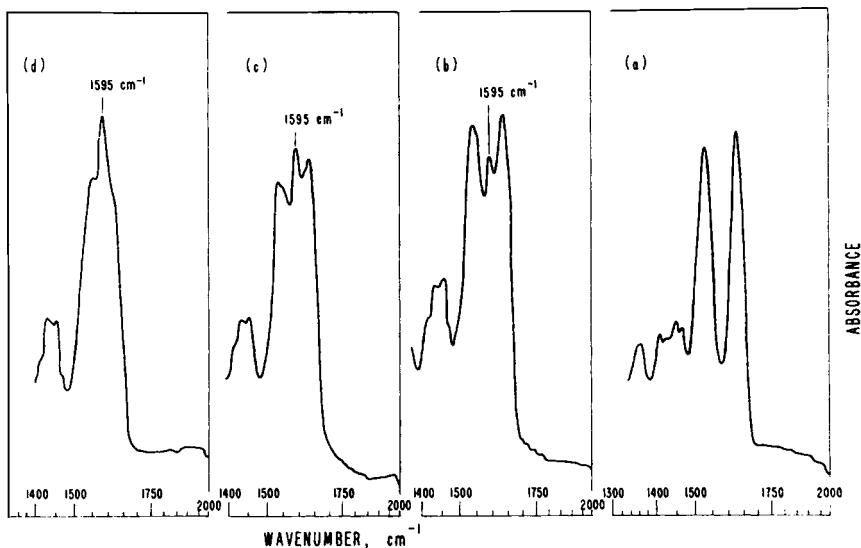


Fig. 1. Spectral changes in nylon 6 film treated with aqueous $ZnCl_2$ (80% w/v): amide I and amide II band region. (a) Untreated; (b) treated, 30 min.; (c) treated, 120 min.; (d) treated, 240 min.

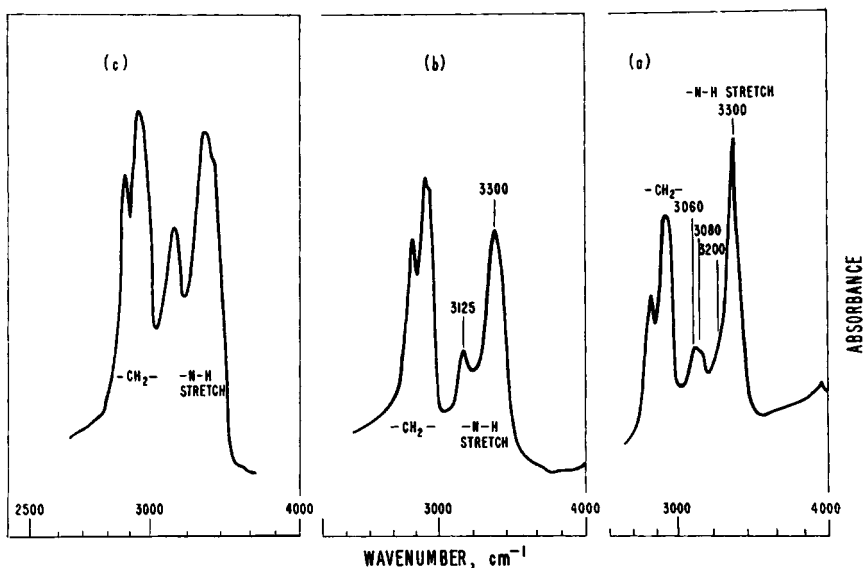


Fig. 2. Spectral changes in nylon 6 treated with Type I metal halides: N-H stretching band region. (a) untreated; (b) treated with $ZnCl_2$; (c) treated with $CuCl_2$.

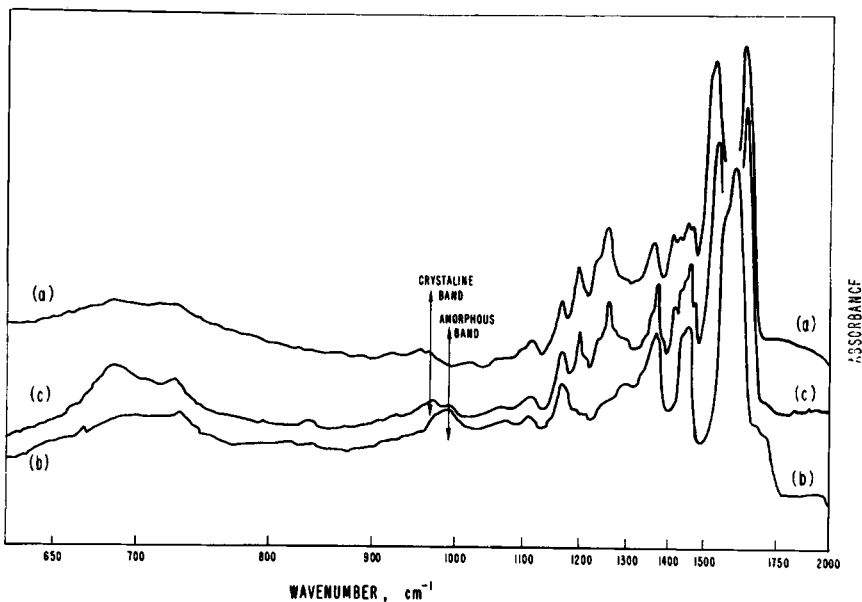


Fig. 3. Spectral changes in cast nylon 6 film containing ZnCl_2 : spectral region $600\text{--}2000\text{ cm}^{-1}$. (a) cast film, control; (b) cast film containing ZnCl_2 ; (c) cast film containing ZnCl_2 after leaching with water.

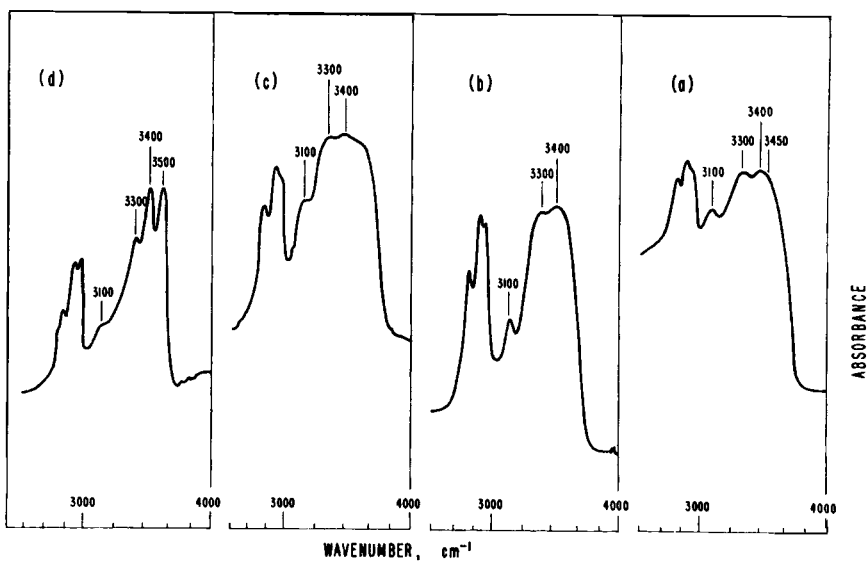


Fig. 4. Spectral changes in cast nylon 6 film containing Type II metal halides: N—H stretching band region. (a) With LiCl ; (b) with CaCl_2 ; (c) with MgCl_2 ; (d) with NiCl_2 . A spectrum of a nylon film control is shown in Figure 2a.

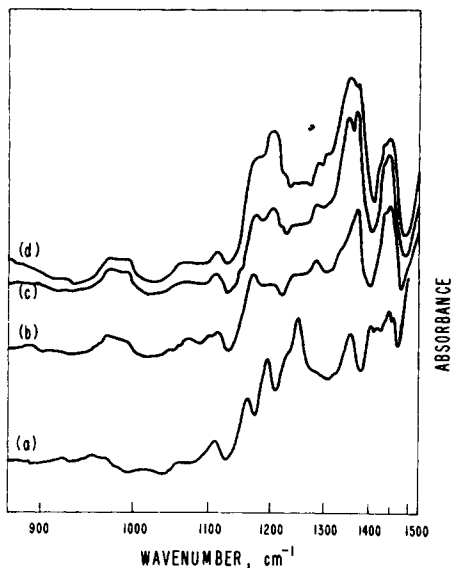


Fig. 5. Spectral changes in cast nylon 6 film containing Type II metal halides: spectral region 900-1500 cm^{-1} . (a) Untreated; (b) with LiCl; (c) with CaCl_2 ; (d) with MgCl_2 .

without washing, showed distinctive changes in their infrared spectra. In the unwashed, but dried films, clarity was unimpaired but the films were swollen and elastic rather than tough. On washing and redrying these films, a change to the normal nylon 6 spectrum occurred and the films became opaque.

Films treated for various periods (15, 30, 60, 120, 240 min) with aqueous zinc chloride solution, showed cumulative changes in their spectra. These changes, as shown in Figure 1, were not due to excess zinc chloride solution at the surface as polypropylene films, treated in the same way, showed no changes in their infrared spectra. Some reagents such as methanolic cobalt_{II} chloride required treatment at high temperatures to induce modifications to the nylon 6 spectra.

Cast films produced from mixed solutions of nylon 6 and metal halides in methanol/formic acid gave spectra of the same type as those associated with nylon films treated with solutions of the corresponding metal halides. Details of spectra, as given in Tables I and II, indicated that active metal halides could be divided into two types according to the modifications they induced in the spectra of nylon 6 films.

Type I: Zinc chloride, cobalt_{II} chloride, copper_{II} chloride, iron_{III} chloride, chromium_{III} chloride and manganese_{II} chloride

Type II: Lithium chloride, lithium bromide, magnesium chloride and calcium chloride

Cast nylon 6 films containing Type I metal halides all gave spectra with a characteristic new absorption band at about 1595 cm^{-1} which was not

TABLE I
 Infrared Data on Nylon 6 Films Treated with Metal Halides

Treatment, time	3080 3060 cm ⁻¹ band		Spectral data, cm ⁻¹				Position of new band
	Posi- tion, Shift		Amide I band		Amide II band		
			Position,	Shift	Position,	Shift	
Nylon 6 film untreated	3060	Nil	1637	Nil	1530	Nil	—
Aqueous ZnCl ₂							
15 min	3080	+20	1625	-11	1537	+7	1595
30 min	3090	+30	1630	-7	1537	+7	1595
60 min	3090	+30	1630	-7	1537	+5	1595
120 min	3110	+50	1630	-7	1540	+10	1595
240 min	3120	+60	1625	-11	1555	+25	1595
Aqueous CoCl ₂							
1 week	3120	+60	1637	Nil	1540	+10	Nil
Methanolic CoCl ₂							
1 min at the boiling point	3080	+20	1630	-7	1540	+10	1595
HCl solutions							
1.7N, 60 min	3060	Nil	1635	-2	1535	+5	Nil
2.2N, 60 min	3060	Nil	1630	-7	1530	Nil	Nil
2.2N, 120 min	3060	Nil	1635	-2	1530	Nil	Nil
2.2N, 180 min	3060	Nil	1635	-2	1530	Nil	Nil
4.5N, 60 min	3060	Nil	1630	-7	1530	Nil	Nil
Cast films							
Nylon 6/ZnCl ₂	3125	+65	1605(?)	-32	1580	+50	1595
Nylon 6/CoCl ₂	3140	+80	1610(?)	-27	1580(?)	+50	1595
Nylon 6/HCl	3060	Nil	1635	-2	1530	Nil	Nil

present in nylon films containing Type II metal halides. Type II halides caused the formation of a broad band in treated nylon films at about 3400⁻¹, but Type I halides did not. Films treated with nickel_{II} chloride showed spectral changes similar to those caused by both Type I and Type II halides. The new absorption band at 1595 cm⁻¹ in the spectra of nylon 6 containing Type I metal halides increased in intensity with increasing time or temperature of treatment. Simultaneously the amide I and amide II bands, at 1637 cm⁻¹ and 1530 cm⁻¹ respectively, decreased in intensity and showed shifts towards each other until both bands were hidden in the new band. Major changes also occurred in the N—H stretching band at about 3300 cm⁻¹ which became broadened and showed reduction of the height of the band. Marked shifts also occurred in the small bands at 3060 cm⁻¹ and 3080 cm⁻¹ in nylon 6. These changes are shown for nylon 6 films treated with zinc chloride, in Figures 1 and 2.

Other changes were also observed in the spectra of nylon 6 films treated with Type I metal halides. Two bands, at 1460 and 1480 cm⁻¹, appeared in films treated with aqueous zinc chloride, and replaced the four C—H

TABLE II
Infrared Data on Cast Nylon 6 Films Treated with Metal Halides

Cast films	N—H stretch		3080–3060 cm ⁻¹ Band		Spectral data, cm ⁻¹				Position of new band
	Position,	Shift	Position,	Shift	Amide I band		Amide II band		
					Position,	Shift	Position,	Shift	
Untreated nylon 6	3300	—	3080/3060	—	1637	—	1530	—	—
Nylon 6/HCl	3300	Nil	3060	—	1635	-2	1530	Nil	Nil
Type I Halides									
Nylon 6/ZnCl ₂	3300	Nil	3135	+75	1605(?)	-32	1580	+50	1595
Nylon 6/Zn(OAc) ₂	3360(?)	+60	3060	Nil	1637	Nil	1530	Nil	Nil
Nylon 6/CoCl ₂	3300	Nil	3140	+80	1610(?)	-27	1580(?)	+50	1595
Nylon 6/CoSO ₄	3300	Nil	3060	Nil	1637	Nil	1530	Nil	Nil
Nylon 6/CrCl ₃	3300	Nil	3130	+70	1625	-12	—	—	1595
Nylon 6/NiCl ₂	3300	Nil	—	—	1635	-2	1575	+45	1595, 3400, 3500
Nylon 6/CuCl ₂	3300	Nil	3120	+60	1635	-2	1560	+30	1595
Nylon 6/FeCl ₃	3300	Nil	—	—	1595	-42	1530	Nil	1595
Nylon 6/MnCl ₂	—	—	—	—	—	—	—	—	1595
Type II Halides									
Nylon 6/LiCl	3250	-50	3100	+40	1635	-2	1550	+10	3400, broad
Nylon 6/MgCl ₂	—	—	—	—	1635	-2	1560	+30	3400, broad
Nylon 6/CaCl ₂	3300	Nil	3100	+40	1625	-12	1562	+32	3450, broad
Nylon 6/CdI ₂ ^a	—	—	—	—	1630	-7	1545	+15	1595, shoulder

^a Solubility limitations prevented the addition of excess CdI₂.

deformation bands at 1500, 1480, 1460 and 1420 cm^{-1} in normal nylon 6 spectra. The sharp band at 1200 cm^{-1} was eliminated and the band in the amide III region replaced by a broad absorption band at 1275 cm^{-1} . These spectral changes in the region 2000–650 cm^{-1} , for nylon 6 films treated with zinc chloride, are shown in Figure 3.

Treatment of nylon 6 films with Type II metal halides gave smaller shifts in the amide I and amide II bands similar to those for Type I reagents, as shown in Table II, without the appearance of a new band at 1595 cm^{-1} . Marked spectral changes occurred in the N—H stretching region in cast films containing nickel, magnesium, calcium or lithium chloride and these are shown in Figure 4. Other changes in the 1550–900 cm^{-1} region with cast films include appearance of double absorbance at about 1460 and 1480 cm^{-1} , doubling of the band at about 1350 cm^{-1} and partial or complete elimination of the bands at 1200 cm^{-1} and 1250 cm^{-1} . These spectral changes in cast films containing lithium chloride, calcium chloride and magnesium chloride are shown in Figure 5.

Nylon 6 films treated with dilute hydrochloric acid show only very minor changes in spectra, as shown in Tables I and II.

Action of Metal Halides on Model Compounds

In order to interpret the spectral changes observed in treated nylon 6 films, the action of metal halides on secondary amide model compounds was investigated. These compounds were, *N*-ethyl acetamide, ϵ -caprolactam and *N*-methyl-2-pyrrolidone.

Spectral data for solutions of zinc chloride and hydrogen chloride in *N*-ethyl acetamide and for complexes of *N*-ethyl acetamide with zinc chloride and cobalt chloride are given in Table III. The spectra of the complexes show large shifts in the amide I and amide II bands and the appearance of a new band at 1595 cm^{-1} .

ϵ -Caprolactam and cobalt_{II} chloride gave products of different melting points depending on the mole ratio of reactants used. The products were:

Mole ratio, caprolactam: CoCl_2 , 12:1, mp., 68°C; 6:1, mp., 87–90°C; 2:1, mp., 100–103°C; 1:1, mp., 113–115°C

The products were all blue crystalline solids and they showed progressive changes from the normal spectrum of ϵ -caprolactam. The changes included a shift of the 1655 cm^{-1} band to 1525 cm^{-1} and the appearance of a new absorption band at 1595 cm^{-1} . The observed shift of -30 cm^{-1} in the amide I band and the appearance of the new absorption band at 1595 cm^{-1} were similar to the changes induced by cobalt_{II} chloride in both nylon 6 films and *N*-ethyl acetamide.

N-methyl-2-pyrrolidone formed a solid blue product of mp above 250°C, with cobalt_{II} chloride. With zinc chloride a solid derivative could not be obtained but a viscous liquid product was formed. The infrared spectra of these cobalt_{II} and zinc products showed distinctive changes from the

TABLE III
Infrared Data on Model Compounds Treated with Metal Halides

Sample	Spectral data, cm^{-1}									
	N—H stretch		3086 cm^{-1} Band		Amide I band		Amide II band		Position of new band	
	Position,	Shift	Position,	Shift	Position,	Shift	Position,	Shift	Position	of new band
N-ethyl acetamide (NEA)	3290	—	3086	—	1640	—	1537	—	—	—
NEA/ ZnCl_2^a	3300	+10	3080	-6	1640	Nil	1537	Nil	1612	1612
(dilute solution)										
NEA/ ZnCl_2^a	3300	+10	3090	+4	1630	-10	1545	+8	1600	1600
(concentrated solution)										
NEA/ ZnCl_2^a	3330	+40	3140	+54	1612	-28	1570	+33	1595	1595
complex										
NEA ₂ / CoCl_2^a	3330	+40	3130	+44	1620	-20	1565	+28	1595	1595
complex ^b										
NEA saturated with dry HCl	3250	-40	3060	-20	1640	Nil	1550	+13	Nil	Nil

^a These results are similar to those reported for the effect of ZnCl_2 and CoCl_2 on nylon 6 films (Table II).

^b Solid blue-green complex, mp. 15°C .

spectrum of *N*-methyl-2-pyrrolidone. Of these, the most important were the shifts of the carbonyl absorption band at 1665 cm^{-1} to lower frequencies. Measured shifts for zinc chloride and cobalt_{II} chloride derivatives were -35 cm^{-1} and -65 cm^{-1} respectively.

Because of solvent difficulties it was not possible to carry out high resolution NMR studies on nylon 6 in the presence of metal halides. Studies were carried out on the model compound *N*-ethyl acetamide and its metal halide derivatives.

The cobalt_{II} chloride complex of *N*-ethyl acetamide was also unsuited to NMR investigation because of the gross line broadening due to the highly paramagnetic cobalt. However with *N*-ethyl acetamide and zinc chloride (mole ratio 2:1), in acetone, the difference in chemical shift between the complex and pure *N*-ethyl acetamide was $+25\text{ cps}$ for $[\text{CO}+\text{CH}_3]$ and $+13\text{ cps}$ for $[\text{N}+\text{CH}_2]$.

DISCUSSION

Coordination of Nylon by Type I Metal Halides

The agreement between the spectra of nylon 6 treated with Type I metal halides and the spectra of the model amide derivatives suggests the formation of a coordination complex, in which the polyamide or amide acts as the ligand. Examination of the spectra of the reaction products of Type I metal halides and primary and secondary, aliphatic, aromatic and heterocyclic amines and diamines showed spectra modifications which showed the formation of a nitrogen atom-metal ion coordinate bond. Our observations agreed with those of Graddon, Heng and Watton² and Gill and Kingdon.³ The absence of similar spectral characteristics in the spectra of treated nylon 6 films and amide derivatives indicated that a coordinate bond between the metal ion and the amide group nitrogen atom was unlikely.

The strong shifts observed in the amide I and amide II bands of treated nylons and amide derivatives, however, suggest that the structure of the amide group has been modified. Bull, Madan and Willis⁴ have described oxygen-metal bonded complexes between *N,N*-dimethyl acetamide and metal halides, and have shown that marked shifts of the amide I band to lower frequencies occur. The similar shifts observed in treated nylon 6 films and amide derivatives indicate that an oxygen-metal bond is present. Carty⁵ has also described the NMR and infrared spectra of some zinc halide complexes of *N,N*-dimethyl acetamide (DMA). Shifts of the amide I band to lower frequencies and of the amide II band to higher frequencies were observed together with the appearance of new bands at 1618 cm^{-1} , 1622 cm^{-1} and 1610 cm^{-1} for the DMA complexes with zinc chloride, bromide and iodide respectively. Typical shifts for complexes with zinc chloride are shown in Table IV.

TABLE IV
 Band Shift for Amide—Zinc Chloride Complexes

	Band Shift, cm^{-1}			
	DMA ⁴	DMA ⁵	<i>N</i> -ethyl acetamide	Nylon 6
Amide I band shift	-42, -59	-60	-28	-32
Amide II band shift	—	+18	+33	+50
New band position, cm^{-1}	—	1618	1595	1595

Carty⁵ and Kuhn and McIntyre⁶ have described the NMR spectra of complexes of zinc chloride and *N,N*-dimethyl acetamide and *N,N*-dimethyl formamide respectively. Their reported chemical shifts are similar to the shifts observed for the zinc chloride-*N*-ethyl acetamide derivative in acetone solution, as shown in Table V. On this evidence, the amide

 TABLE V
 Chemical Shifts for Amide—Zinc Chloride Complexes

Compound	Chemical Shift, cps.			
	[CO—CH ₃]	[CO—H]	[N—CH ₃]	[N—CH ₂ —]
HCONMe ₂ :ZnCl ₂ (2:1) ⁶	—	+13.0	+14, +17 ^a	—
CH ₃ CONMe ₂ :ZnCl ₂ (2:1) ⁶	+18.6	—	+10.2	—
CH ₃ CONHEt:ZnCl ₂ (2:1)	+25.0	—	—	+13.0

^a *Cis* and *trans* methyl groups distinguished.

group in nylon 6 treated with Type I metal halides appears to be linked to the metal ion through the oxygen atom.

Structure of Type I Metal Halide—Amide Complexes

According to Bellamy⁷ the N—H stretching frequency of amides in *cis*-form is about 100 cm^{-1} lower than that of *trans*-form, and that an appreciably higher N—H deformation frequency would be expected. In the *cis*-form the amide II band would be expected to approach very close to the amide I band and may coincide with it. Cyclic lactams, such as caprolactam and 2-pyrrolidone, which are only present in the *cis*-form show only one band. The shifts of the amide I and amide II bands, together and the appearance of a new band at 1595 cm^{-1} , in nylon 6 treated with Type I metal halides, and in *N*-ethyl acetamide derivatives (Tables I and II) may be explained by a *trans*- to *cis*-transformation in addition to the shift of the carbonyl stretching frequency to a lower value due to the formation of a carbonyl-metal coordinate link.

Shifts to a higher frequency were noted for the absorption bands at 3086 cm^{-1} in *N*-ethyl acetamide and at 3060 and 3080 cm^{-1} in nylon 6 when treated with Type I metal halides, together with corresponding shifts in the amide II band. The observed shifts bring these bands to a fre-

quency very close to that observed in the spectrum of 2-pyrrolidone and other lactams in which the amide exists in the *cis*-form only and confirms that these bands are in fact overtones of the amide II band.

The broadening and reduction in band height of the N—H stretching frequency in nylon 6 films treated with Type I metal halides is typical and can be seen in Figure 2 for nylon 6 films treated with copper^{II} chloride and zinc chloride. Higher resolution spectra are shown in Figure 6.

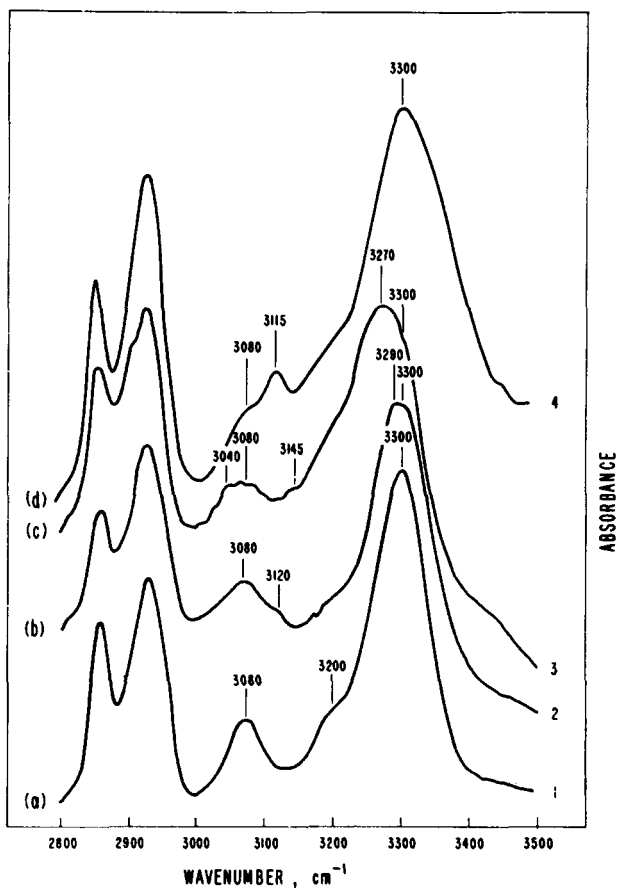


Fig. 6. Spectral changes in nylon 6 film treated with aqueous ZnCl_2 (80%): N—H stretching band region—high resolution spectra. (a), untreated; (b), treated, 50 min.; (c), treated 120 min.; (d), treated, 10 min. at 100°C .

We believe that the N—H stretching band in nylon 6 at about 3300 cm^{-1} is a composite band consisting of a higher frequency *trans*-form contribution and a lower frequency *cis*-form contribution. The nonsymmetry of the band with a low frequency shoulder and the subsequent changes on treatment with metal halides can be explained by increasing change of structure from the *trans*- to the *cis*-form. On this basis we have proposed

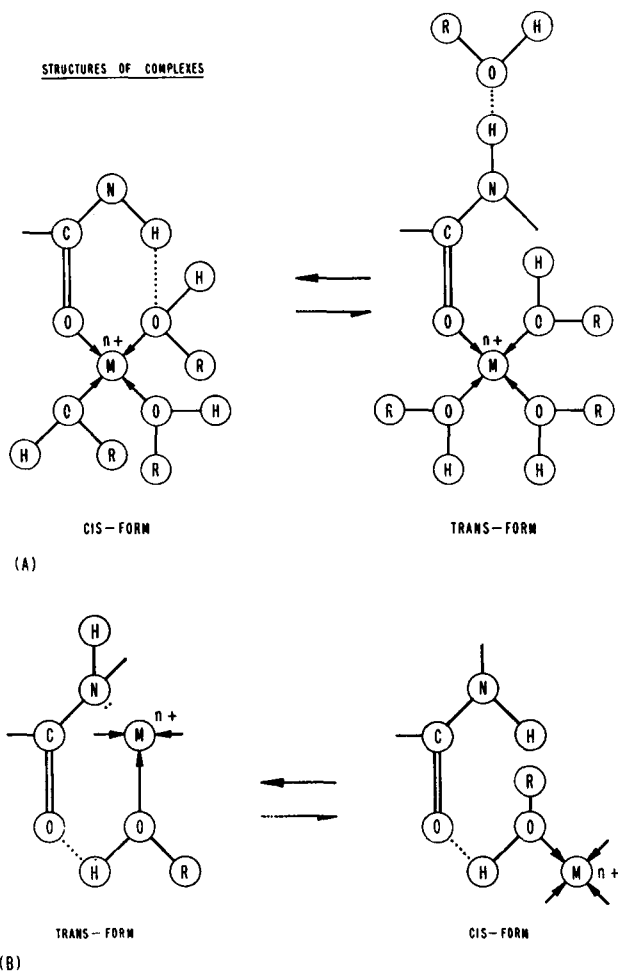


Fig. 7. Proposed structures for complexes with polyamides: *a*, with Type I metal halides; *b*, with Type II metal halides.

a cyclic *cis*-form complex, as shown in Figure 7*a*, for nylon 6 and amide products with Type I metal halides.

The Amorphous Nature of Nylon 6 Treated with Metal Halides

The changes observed in the spectra of nylon 6 treated with metal halides, of both Types I and II, in the region $1500\text{--}650\text{ cm}^{-1}$ have been described and are shown in Figures 3 and 5. The changes are such that spectral features similar to those in the spectra of amorphous, steric hindered 1,1-dimethyl substituted nylon 66 as reported by Cannon⁸ are visible. This result is ascribed to a change in the nylon from the crystalline form to a more amorphous form, when it is complexed with the metal halide.

The Action of Type II Metal Halides

In Part I,¹ calcium, lithium and magnesium chlorides were shown to be inactive as stress cracking agents in aqueous solution but active in methanolic solution. Nylon films treated with these agents gave different spectral changes as compared to films treated with Type I metal halides and a different action is proposed. The absence of the new band at 1595 cm^{-1} and only minor shifts in the amide I and amide II bands (see Tables I and II) indicate that coordination between the oxygen of the amide group and the metal ion is unlikely.

The broad absorbance above 3300 cm^{-1} noted in nylon 6 films treated with Type II metal halides is similar to the observations reported by Sarda and Peacock⁹ for nylon 6 and 66 films treated with lithium or magnesium perchlorates or lithium bromide. Spectral details are shown in Figure 4.

In the spectrum of nylon 6 film, the N—H stretching frequency at about 3300 cm^{-1} is about 100 cm^{-1} lower than the normal free N—H stretching frequency of amides in dilute solution. According to Rao¹⁰ this could indicate the presence of hydrogen bonding. The new broad absorbances observed in films treated with Type II metal halides (LiCl, LiBr, CaCl₂, MgCl₂ etc.) can then be interpreted as free N—H stretching absorptions resulting from elimination of hydrogen bonding.

Methanolic solutions of Type II metal halides act as proton donating agents in a manner similar to phenol and formic acid. These preferentially hydrogen bond with the amide carbonyl oxygen and cause solution of the nylon. The proposed structure of the Type II metal halide-nylon 6 product is shown in Figure 7b.

We believe the different behaviour of the Type II metal halides in various solvents, especially in water and in methanol, is dependent on the degree of solvation of the halide. For hydrogen bonding between the reagent and the carbonyl oxygen atom to occur, the charge distribution over the protons of the solvated metal salt must be highly localised. For example, calcium chloride in aqueous solution is hydrated with at least 6 molecules of water in the coordination sphere of the calcium ion, and the charge density on each proton is $+2e/12$. However calcium chloride in methanolic solution exists as the alcoholate, $\text{CaCl}_2 \cdot (\text{CH}_3\text{OH})_4$ ¹¹ and in this case the charge density on each proton is much greater, $+2e/4$, making it a stronger proton donor.

Nickel_{II} chloride represents a singular case, presenting features of both Type I and Type II metal halides. Like Type I agents, with nylon 6, it gives large shifts of the amide I and amide II bands and a new absorption band at about 1595 cm^{-1} . Like Type II agents it gives absorption bands above 3300 cm^{-1} in which two distinct bands at 3400 and 3500 cm^{-1} are observed. Details are given in Table II and Figure 4.

The absorption bands at 3400 and 3500 cm^{-1} respectively are believed to be due to two free N—H stretching frequencies. The lower frequency

band resulting from a normal free N—H absorption and the higher frequency band from an acidic proton N—H stretching absorption. The acidic proton is believed to result from some delocalization of the lone pair of electrons on the nitrogen atom as a result of the proximity of the metal ion in the cyclic structure proposed (Fig. 7b).

Mechanism of Stress-cracking

The stress-cracking of nylon 6 by metal halides appears to be due to two distinct mechanisms.

With Type I metal halides, physical effects such as surface wetting and localised notch stresses may contribute to crack initiation. However, the major effects are migration of the metal halide into the nylon where it is attracted to the dipolar amide groups. As a result, hydrogen bonding between polymer chains is weakened, and the amide N—H protons form bonds with the conditioning agent (normally water) or with hydrated metal halide molecules. This effectively sheathes the nylon chains with solvent molecules and causes local plasticisation and swelling of the nylon, increasing the internal stresses. Also formation of a complex between the amide group of the nylon and the solvated metal halide occurs, and this destroys interchain hydrogen bonding, replacing it with intra-chain hydrogen bonding as shown in Figure 7a.

The complexed nylon with changed structure becomes more amorphous and as a result increased absorption of water or solvent can occur. This increases plasticization, lowers the yield stress of the nylon and rupture occurs.

The complex between nylon and Type I metal halides is rapidly destroyed by excess water or other oxygen containing solvents. This accounts for the "reversion" of the spectrum of treated nylon 6 films, on washing.

Higher temperatures promote cracking by allowing more rapid migration of the metal halide to occur. As the level of conditioning agent in the nylon is increased the initial yield stress is reduced and a more effective pathway for migration of the metal halide into the nylon is provided. In dry nylon migration cannot occur.

Type II metal halides are essentially true solvent cracking agents in that solution of the nylon by the proton donating system occurs, as with phenol and formic acid, and this results in rupture of stressed specimens.

The action of metal thiocyanates on nylon 6 films has been studied and the results confirm our proposed mechanism. These studies are described in Part III.

References

1. P. Dunn and G. F. Sansom, *J. Appl. Polymer Sci.*, **13**, No. 8 (1969).
2. D. P. Graddon, K. B. Heng, and E. C. Watton, *Aust. J. Chem.*, **19**, 1801 (1966).
3. N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, **19**, 2197 (1966).
4. W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).
5. A. J. Carty, *Can. J. Chem.*, **44**, 1881 (1966).

6. S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).
7. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methven and Co. Ltd., 1958, p. 217, London.
8. G. C. Cannon, *Spectrochim Acta*, **16**, 302 (1960).
9. G. Sarda and N. Peacock, *Nature*, **200**, 67 (1963).
10. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, 1963, London.
11. E. H. Rodd, *Chemistry of Carbon Compounds*, Volume 1A, Elsevier, 1951, p. 298, London.

Received January 31, 1969